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Activation energies derived from the pre-glass transition annealing peaks

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Dedicated to Professor Wolfgang Hemminger on the occasion of his 65th anniversary.

Abstract

The paper explores the use of the DSC annealing peaks for estimating the activation energies of the β-relaxation in low and high molecular glassy systems. For the four studied systems that include D-glucose (dextrose), maltitol, poly(methyl methacrylate) and poly(ethylene terephthalate) the estimated values of the activation energy are 59 ± 10, 71 ± 6, 73 ± 12 and 75 ± 7 kJ mol^{-1}. These values together with the activation energies determined earlier from the annealing peaks of polystyrene (PS), PS–clay nanocomposite, indomethacin, ursodeoxycholic acid and poly(vinylpyrrolidone) have been compared against the literature values of the activation energies of the β-relaxation. It is concluded that the DSC estimates typically do not deviate for more than 20% from the reference values obtained by the standard dielectric and mechanical methods.

Keywords: Activation energy; β-Relaxation; DSC; Kinetics; Pharmaceuticals; Polymer

1. Introduction

It was originally reported by Illers [1] that reheating of polyvinyl chloride annealed significantly below the glass transition temperature, T_g, results in detecting a small endothermic DSC peak that may occur before the glass transition step. A similar effect was later reported for several metallic glasses by Chen [2,3] and for several polymers by Bershtein et al. [4,5]. Chen explained this effect as the partial enthalpy relaxation (during annealing) and recovery (during reheating) that occur at the expense of the faster part of a broad relaxation spectrum of the glassy state. On the other hand, Bershtein et al. [4,5] linked this effect specifically to the β-relaxation process that is normally detected by dynamic mechanical [6] and dielectric techniques [7]. Chen as well as Bershtein et al. suggested using the shift in the annealing peak temperature, T_p, with the heating rate, q, to determine the effective activation energy, E, of the underlying process as follows:

$$E = -R\frac{\mathrm{d}\,\ln q}{\mathrm{d}T_p^{-1}} \tag{1}$$

where R is the gas constant. The resulting E values were consistently found [2–5] being several times smaller than the respective activation energies of the main glass transition (i.e., α-relaxation) event, i.e., as it is typically reported [6,7] for the respective β- and α-relaxations in polymers. Conversely, Hodge and Berens [8] showed that one can simulate the annealing peaks by substituting the activation energy of the α-relaxation in the Tool–Narayanaswamy–Moynihan (TNM) model and then varying other parameters of the model. Note that this result does not actually prove that the activation energy of the process that causes the annealing peak is similar to that of the α-relaxation for several reasons. Firstly, accurate applications of the TNM model are limited “to systems in which viscosity obeys an Arrhenius dependence within and above the glass transition range” [9] or, in other words, to so-called “strong” [10] glass forming systems. However, most liquids show a “fragile” behavior, which is characterized by the VTF/WLF temperature dependence [9,11] and, therefore, by a temperature dependence of the activation energy that is especially profound in the most fragile liquids such as polymers [12]. Secondly, the TNM model is known [13,14] being incapable of predicting annealing in the temperature region significantly below T_g. However, regardless of the limitations and a physical meaning, the four parameter TNM model has enough computational flexibility to fit simultaneously the glass transition event and an annealing peak. Thirdly,

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according to the substantial array of experimental data [15], the process of annealing at temperatures far below T_g has an activation energy that is several times smaller than that of the α-relaxation. In addition, as the temperature falls below T_g, the cooperative α-process fades away very quickly giving way to the local β-process that becomes the major contributor to the relaxation that occurs on annealing glasses well below T_g, i.e., during the so-called physical aging [15–17]. In this circumstance, it does not seem unreasonable that a fair approximation to the activation energy of the β-relaxation, E_β, can be obtained as an activation energy estimated from the annealing peaks produced well below T_g, as was originally found by Bershtein et al. [4,5] for several polymers. This has also been the case of our previous work on polystyrene (PS) and PS–clay nanocomposite [18], indomethacin (IM) [19], ursodeoxycholic acid (UDA) and poly(vinylpyrrolidone) (PVP) [20]. In the present paper we explore this issue further by combining our previous results with a study of the four new systems that include two polymers (poly(methyl methacrylate) (PMMA) and poly(ethylene terephthalate) (PET)) and two low molecular compounds (glucose (Gl) and maltitol (Mt)). For all four systems, the activation energies of the β-relaxation have been determined by using either dielectric or mechanical spectroscopy and reported in the literature that affords a straightforward comparison with values derived from the annealing peaks. In addition to testing the obtained values against the literature data, we also test them against the empirical correlation, $E_\beta = (24 \pm 3)RT_g$ reported by Kudlik et al. [21].

2. Experimental

Gl (dextrose), Mt, PMMA (Mw ∼ 75,000) and PET (Mw ∼ 18,000) were, respectively, purchased from Fisher, MP Biomedicals, Polymer Scientific Products and Aldrich and used without further purification. In order to produce amorphous (glassy) samples, 10–20 mg of a sample was placed in 40 μL closed Al pans and heated to ∼10 °C above their respective melting points, 161 °C (Gl), 149 °C (Mt), 280 °C (PET) or ∼70 °C above its T_g (PMMA). Shortly after heating the samples were quenched into liquid nitrogen. The glass transition temperatures of the amorphous samples were estimated as midpoint temperatures of the DSC glass transition steps measured at 10 °C min^{-1}. The resulting values were 36 °C (Gl), 48 °C (Mt), 75 °C (PET) and 105 °C (PMMA). For annealing measurements, freshly quenched samples were quickly placed into the DSC cell (Mettler-Toledo DSC 822^e) that was maintained at −40 °C. The temperature and heat flow calibration of DSC were performed by using an Indium standard. From −40 °C the samples were heated to an annealing temperature, T_a, and held at it for 30 min. The annealing temperatures were −30, −25, −20 and −10 °C for Gl, −20, −10 and 0 °C for Mt, 20, 30 and 40 °C for PET, and 10, 15, 20, 30 and 40 °C for PMMA. After completion of the annealing segment, the samples were cooled down to −40 °C and immediately heated above T_g. The heating rates were 15, 20, 25 and 30 °C min^{-1}. The resulting endothermic peaks observed on heating were used to determine the peak temperature, T_p, by using the standard DSC software that subtracts an extrapolated baseline and finds the peak position.

3. Results and discussion

The annealing peaks are easily produced by annealing a glassy material at $T_a \sim 0.8T_g$. Recall that the dielectric and mechanical loss peaks for β-relaxation in polymers are commonly found at temperatures around $0.75T_g$ [22]. The glass annealed in this region relaxes lowering its enthalpy. The lost enthalpy is recovered on reheating producing a small endothermic effect that is observed in DSC as a very broad and shallow "annealing peak", which starts to evolve above the annealing temperature. While broad and shallow, the peaks are readily noticeable when comparing DSC traces for annealed samples with those for not annealed samples which demonstrate a monotonic behavior before the glass transition step (cf. Figs. 1–4). Increasing annealing temperature increases the size of the peak and shifts it to higher temperatures (Fig. 1). As a result, the peak may appear not only before the glass transition step, but also during and after the step, ultimately emerging as the large enthalpy overshoot that is typically observed in the glasses aged not far below T_g [18,19]. At any given annealing temperature the peak increases in size and shifts to higher temperatures with increasing the heating rate (Figs. 2–4) that is used for estimating the effective activation energy by Eq. (1). As discussed earlier [19], the use of the lowest feasible T_a gives rise to better estimates for the activation energy of the β-relaxation.

3.1. Gl sample

Fig. 1 shows the effect of the annealing temperature on the annealing peak. For Gl, T_g is 36 °C so that $0.8T_g$ is around −25 °C. It is seen that annealing at −30 °C barely produces any

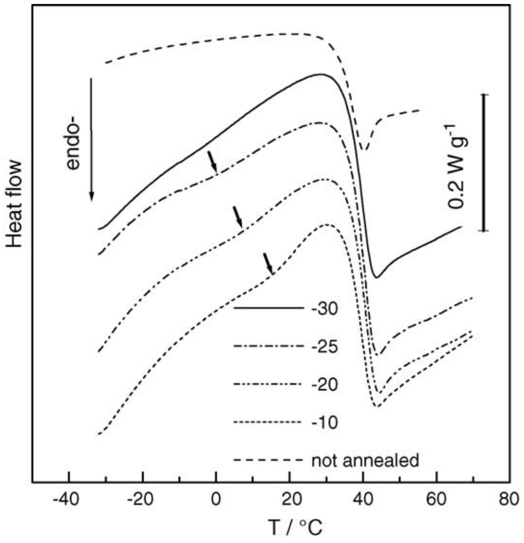

Fig. 1. DSC curves obtained on heating of Gl at 20 °C min^{-1} after annealing for 30 min at different T_a. The values of T_a (°C) are shown by respective line types. "Not annealed" denotes a curve produced without annealing at 10 °C min^{-1}. Arrows show the location of the annealing effect.

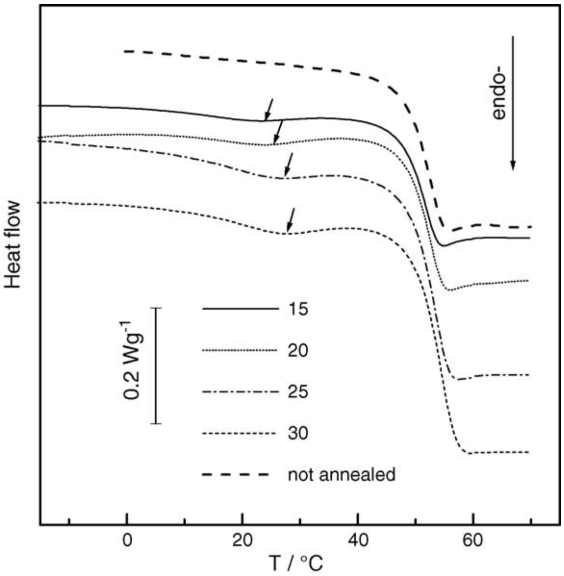

Fig. 2. DSC curves obtained on heating of Mt at different heating rates 15–30 °C min^{-1} after annealing for 30 min at 0 °C. The values of the heating rate (°C min^{-1}) are shown by respective line types. "Not annealed" curve obtained by heating a sample immediately after quenching. Arrows show the location of the annealing effect.

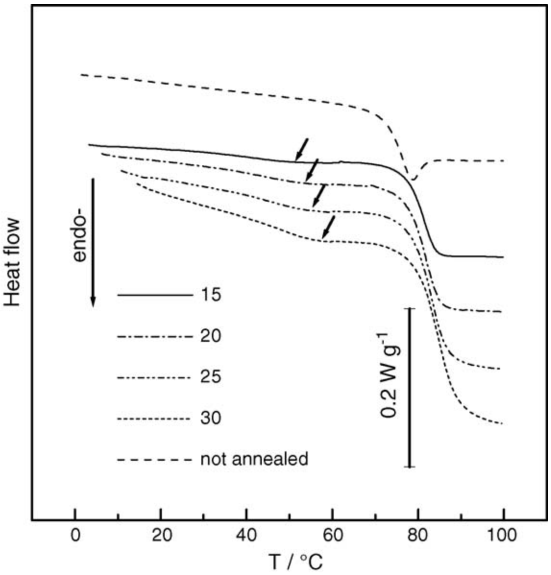

Fig. 4. DSC curves obtained on heating of PET at different heating rates after annealing for 30 min at 20 °C. The values of the heating rate (°C min^{-1}) are shown by respective line types. "Not annealed" denotes a curve produced without annealing at 10 °C min^{-1}. Arrows show the location of the annealing effect.

detectable effect. The annealing effect starts to become visible at $T_a = -25\,°C$. It becomes even more obvious at the annealing temperatures −20 and −10 °C. The Gl samples annealed at each of the three annealing temperatures (i.e., −25, −20 and −10 °C) have been reheated at four heating rates and the peak temperatures have been determined. Plots of the natural logarithm of the heating rate against the reciprocal peak temperature are shown in Fig. 5. The slope of the plots yields an effective value of the activation energy by Eq. (1). The values of E typically increase with the annealing temperature that reflects an increasing contribution of the cooperative relaxation modes (i.e., α-relaxation) that are associated with markedly larger activation energies than those of the non-cooperative β-process. Therefore, the value of E obtained at the lowest $T_a = -25\,°C$ yields our estimate for the activation energy of the β-relaxation, E_β. This value is 59 ± 10 kJ mol^{-1}. The literature reports the following values of E_β: 42 kJ mol^{-1} [23], 52 kJ mol^{-1} [24], 57 and 61 kJ mol^{-1} (∼1% water content) [25] and 62 kJ mol^{-1} [26]. All these values have been obtained by using dielectric analysis. Our estimate obviously falls within the region of the reported values.

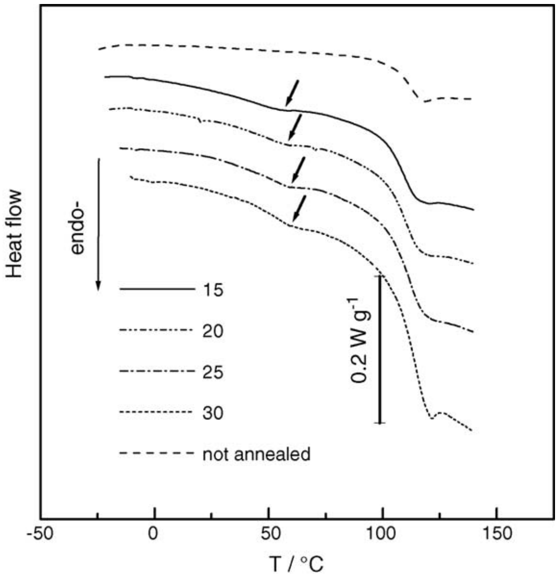

Fig. 3. DSC curves obtained on heating of PMMA at different heating rates after annealing for 30 min at 30 °C. The values of the heating rate (°C min^{-1}) are shown by respective line types. "Not annealed" denotes a curve produced without annealing at 10 °C min^{-1}. Arrows show the location of the annealing effect.

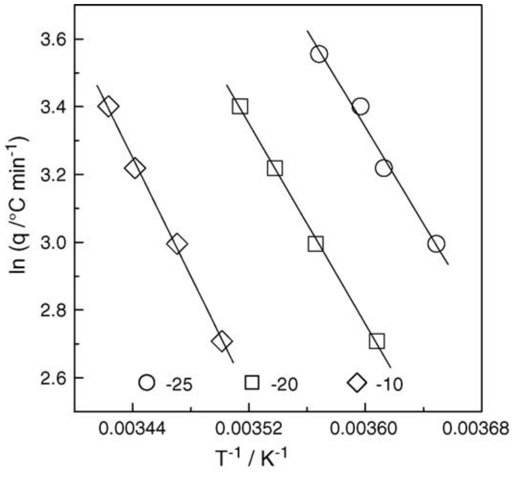

Fig. 5. Evaluating effective activation energies from annealing peaks of Gl annealed at different temperatures (values in °C are shown by respective symbols).

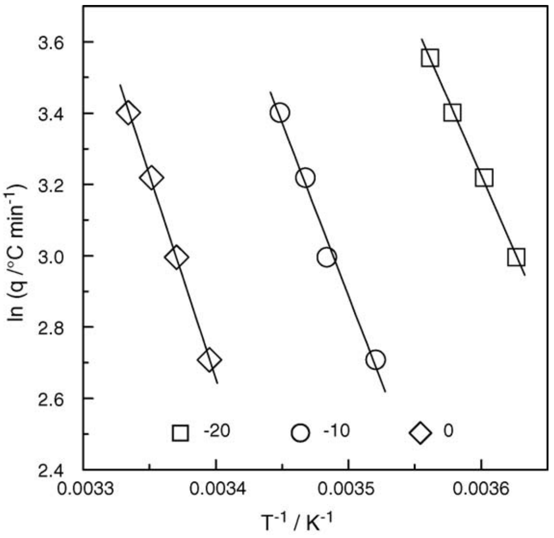

Fig. 6. Evaluating effective activation energies from annealing peaks of Mt annealed at different temperatures (values in °C are shown by respective symbols).

3.2. Mt sample

For maltitol, $0.8T_g$ is around −20 °C, and good annealing peaks have been obtained at T_a = −20, −10 and 0 °C. As seen in Fig. 2, at a constant annealing temperature, the peak temperature increases with increasing the heating rate that has been used to estimate the effective activation energies by Eq. (1). The resulting $\ln q$ versus T_p^{-1} plots are displayed in Fig. 6. It is seen that the slopes of the plots increase with increasing the annealing temperature. The respective increase in the effective value of E with T_a is as follows: 71, 77 and 95 kJ mol^{-1}. Therefore, the best estimate of E_β should be 71 ± 6 kJ mol^{-1}.

There are several E_β values reported in the literature. The values 62 and 61 kJ mol^{-1} have been, respectively, obtained by mechanical and dielectric spectroscopy [27]. Dielectric measurements have also yielded the value 57 kJ mol^{-1} [28]. An increase in the activation energy from 45 to 65 kJ mol^{-1} with increasing temperature from −120 to −30 °C has been reported in a study [29], using the method of thermally stimulated depolarization current. Our estimate is somewhat larger than the literature values.

3.3. PMMA sample

The value of $0.8T_g$ for PMMA is ∼30 °C. However, the annealing peaks have remained detectable down to T_a = 10 °C. Fig. 3 displays a shift of the annealing peak of PMMA with the heating rate. Overall, five annealing temperatures have been used. At each of these temperatures four heating rates have been employed to evaluate the peak temperatures. The resulting plots of $\ln q$ versus T_p^{-1} are shown in Fig. 7. It is seen that the slope of these plots decreases with decreasing the value of T_a reflecting a decrease in the effective activation energy. Again, the E value related to the lowest feasible value of T_a has been taken as an estimate for E_β. Note that the use of T_a = 10 and 15 °C has yielded practically identical E values. However, the value estimated for T_a = 10 °C has almost two times larger error bars. Therefore, we consider the E value obtained for T_a = 15 °C as a better estimate. The value is 73 ± 12 kJ mol^{-1}.

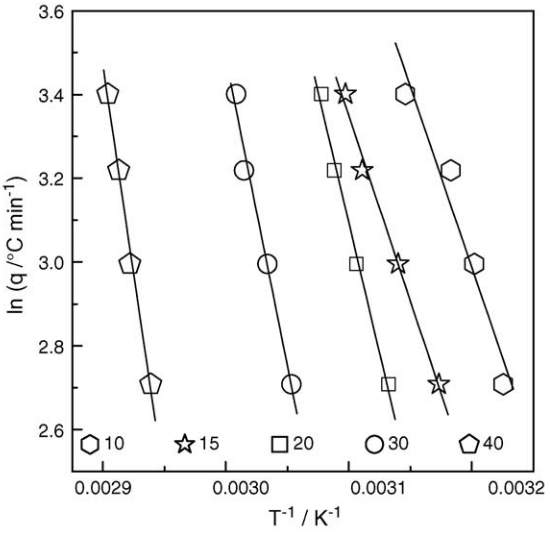

Fig. 7. Evaluating effective activation energies from annealing peaks of PMMA annealed at different temperatures (values in °C are shown by respective symbols).

There are a number of literature reports on the E_β values for PMMA. The values obtained by the mechanical method are 71 and 75 kJ mol^{-1} [6], and 78 kJ mol^{-1} [30]. The use of the dielectric techniques has given rise to the values 84 kJ mol^{-1} [7] and 80 kJ mol^{-1} [31]. The values 75 kJ mol^{-1} [32] and 82 kJ mol^{-1} [33] have been reported when using the method of thermally stimulated current. Clearly, our estimate fits in the range of the reported values. A somewhat larger value (90 ± 8 kJ mol^{-1}) has been reported by Bershtein and Yegorov [5], who also used DSC annealing peaks.

3.4. PET sample

For PET $0.8T_g$ is ∼5 °C. Nevertheless, no annealing peaks could be produced at this temperature as well as at 10 °C. The peaks have become detectable starting from T_a = 20 °C. The effect of the heating rate on the annealing peaks produced at this temperature is shown in Fig. 4. Two more annealing temperatures have been used to demonstrate the general trend in the $\ln q$ versus T_p^{-1} plots. The T_p values have been determined for different heating rates for each of the three annealing temperatures. The resulting plots are shown in Fig. 8. As for the two previous samples, we can see a decrease in slope of the plot with decreasing the annealing temperature and, therefore, in the value of the effective activation energy. An estimate of the E_β taken as the effective activation energy obtained at the lowest temperature is 75 ± 7 kJ mol^{-1}.

The E_β values for PET seem to be well documented. The values estimated by using mechanical analysis are as follows: 71 kJ mol^{-1} [6], 71–75 kJ mol^{-1} [34] and 70 kJ mol^{-1} [35]. Dielectric methods give rise to a larger span: 54 kJ mol^{-1} [7], 56 kJ mol^{-1} [35], 58 kJ mol^{-1} [36], 71 kJ mol^{-1} [37] and 51–81 kJ mol^{-1} [38]. It should be noted that it has been

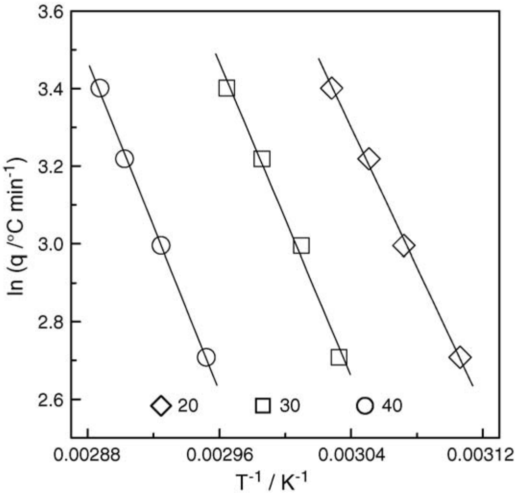

Fig. 8. Evaluating effective activation energies from annealing peaks of PET annealed at different temperatures (values in °C are shown by respective symbols).

demonstrated in some publications [37,38] that the β-relaxation in PET has several components of different activation energies, which increase with increasing the temperature. Since we are approaching the β-relaxation from the high temperature side, the higher temperature (i.e., larger) E_β values are more relevant to our study. At any rate, our estimate falls well within the range of the reported values.

3.5. *Combined results*

In this section, we combine the results of the present study with our previous results for PS and PS–clay nanocomposite [18], IM [19], UDA and PVP [20]. For some of these compounds, the values of E_β have been reported in the literature. Therefore, we perform a systematic comparison of our estimates against the literature values that we have found.

For PS and PS–clay nanocomposite we have, respectively, obtained 92 ± 12 and $94 \pm 11\,\mathrm{kJ\,mol^{-1}}$ [18]. The earlier mechanical analysis literature reports the E_β value to be $145\,\mathrm{kJ\,mol^{-1}}$ [6] that maybe somewhat extreme in the view of more recent data, $71\,\mathrm{kJ\,mol^{-1}}$ [39] and $80\,\mathrm{kJ\,mol^{-1}}$ [40,41]. Dielectric analysis produces the value $120\,\mathrm{kJ\,mol^{-1}}$ [7], whereas thermally stimulated current measurements yield $77\,\mathrm{kJ\,mol^{-1}}$ [32]. Our estimate does not seem to fall out of this literature data set, which, however, is quite scattered. It also agrees well with the values 96 and $110 \pm 10\,\mathrm{kJ\,mol^{-1}}$ determined by using the annealing peaks [5].

A few more E_β estimates have been obtained by us from annealing peaks of pharmaceutically relevant glasses (PVP, IM and UDA). For PVP, our estimate is $68 \pm 8\,\mathrm{kJ\,mol^{-1}}$ [20] that is consistent with thermally stimulated current measurements ($63\,\mathrm{kJ\,mol^{-1}}$ [42]) as well as with dynamic mechanical data ($76 \pm 10\,\mathrm{kJ\,mol^{-1}}$ [20]). For IM, we have obtained an estimate $56 \pm 12\,\mathrm{kJ\,mol^{-1}}$ [19] that is in good agreement with the value $66\,\mathrm{kJ\,mol^{-1}}$ obtained in thermally stimulated current experiments [43] as well as with $56\,\mathrm{kJ\,mol^{-1}}$ determined by dielectric spectroscopy [44]. No literature data have been found to compare with our estimate for the activation energy of the β-relaxation in UDA, $67 \pm 12\,\mathrm{kJ\,mol^{-1}}$.

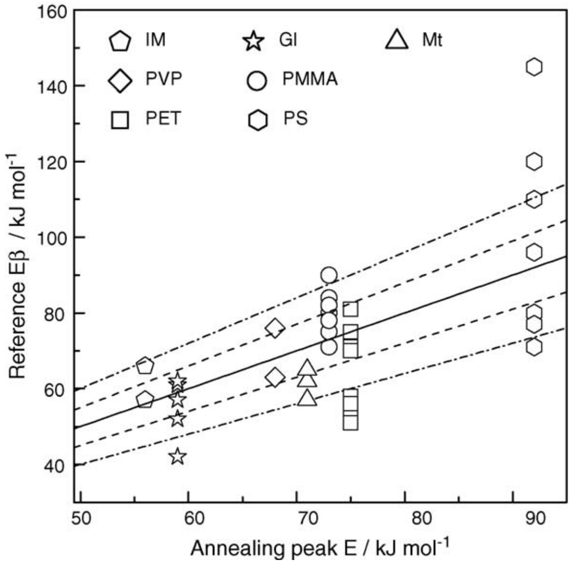

Fig. 9. Correlation of the E_β estimates from the annealing peaks with the literature values. Solid line represents exact equality; dash and dash dot lines represent 10 and 20% deviations, respectively.

Fig. 9 provides a graphic comparison of the E_β estimates against the reference values from the literature. The solid line represents exact equality. The reference values above and below this line, respectively, represent larger and smaller values. Our estimates are typically determined with a confidence interval of ∼10–20% of the value. The 10 and 20% deviations are also shown in Fig. 9. It is seen that for the most part our estimates deviate for less than 20% from the literature values except a few extreme values, the relevance of which might be questionable.

Fig. 10 pulls together all our E_β estimates obtained so far. The estimates are shown against their respective glass transition temperatures. This plot allows us to check the consistency of

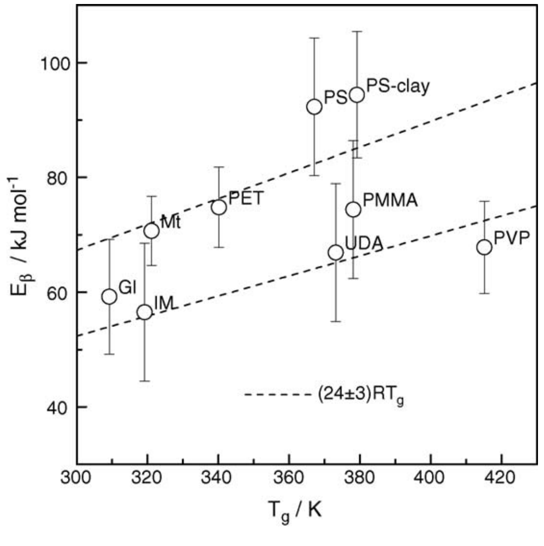

Fig. 10. The E_β estimates from the annealing peaks plotted against the respective glass transition temperatures. Dash lines represent the limits of the correlation $E_\beta = (24 \pm 3)RT_g$.

our estimates with the empirical relationship, $E_\beta = (24 \pm 3)RT_g$, established by Kudlik et al. [21]. This relationship has been found [45] to hold quite well for a great number of the E_β values determined by regular dynamic and dielectric methods for both high and low molecular compounds. Fig. 10 demonstrates that with regard of their respective confidence intervals all our estimates follow the aforementioned empirical correlation.

4. Conclusions

Annealing peaks have been produced in Gl, Mt, PMMA and PET at several annealing temperatures. The shift in the peak temperature with the heating rate has been used to determine the effective activation energies as follows: $59 \pm 10\,\mathrm{kJ\,mol^{-1}}$ (Gl), $71 \pm 6\,\mathrm{kJ\,mol^{-1}}$ (Mt), $73 \pm 12\,\mathrm{kJ\,mol^{-1}}$ (PMMA) and $75 \pm 7\,\mathrm{kJ\,mol^{-1}}$ (PET). These values as well as the values obtained earlier by the same technique prove to correlate well with the activation energies for the β-relaxation in the respective systems.

While fascinated with the observed correlation, we do realize that linking the observed sub-T_g events to the β-relaxation is not without a controversy. This has become especially clear from the comments of the referees who suggested that the observed sub-T_g effects might be related to the processes other than the β-relaxation or even that it might be coincidental. Since the reader may have similar concerns, we have decided to conclude our paper by briefly addressing them. Firstly, what is the probability of the correlation being coincidental? Assuming that the acceptable deviation of E derived from the annealing peaks from E_β is no more than 20%, and that unacceptable deviation is from 20 to 100%, the probability of accidentally obtaining a single acceptable deviation is 1/5. Then, the probability of accidentally obtaining seven acceptable deviations in a row (cf. Fig. 9) is $(1/5)^7 = 0.0000128$. This probability is similar to the probability of flipping a coin and getting tails 16 times in a row. One can easily run such experiment to get a feel of how feasible this probability is.

More realistic concerns lie with the actual nature of the process behind the annealing peak. Partially these concerns arise from the fact that there is no single accepted view of what the β-process is. Naturally, we exercise a calorimetric (i.e., simplistic) view [18–20] of the β-process as some unspecified local non-cooperative mobility occurring in the sub-T_g temperature region. This view originates from the non-specific nature of calorimetric measurements. However, dielectric, mechanical and NMR spectroscopy are capable of providing more specific information about sub-T_g processes and, therefore, of identifying various types local non-cooperative mobility. In a view of the spectroscopic measurements, one may reasonably argue that the temperatures of the β-relaxation are typically lower than the respective values T_a or T_p reported in this paper. Indeed, these values tend to be larger than the values of the loss peak temperature for β-relaxation measured by dielectric and/or mechanical spectroscopy. For instance, for PMMA the loss peak is observed [6] at ∼20 °C (mechanical spectroscopy at 1 Hz) or at ∼35 °C (dielectric spectroscopy at 20 Hz). For PET, it appears [6] at approximately −50 °C (mechanical and dielectric spectroscopy at 100 Hz). Of course, because of the frequency dependence of the peak temperatures in the dynamic measurements, they should not be directly compared with the temperatures of the DSC runs. However, it is important to mention that the β-peaks observed in mechanical and dielectric spectroscopy are usually very broad and stretch to the temperatures significantly above the loss peak temperature. For PMMA, significant absorption due to the β-process is observed around 80 °C and for PET around 20 °C so that the lowest values of T_a and the corresponding values of T_p tend to be in higher temperature region of the β-relaxation. One may also argue that the effects can be associated with the non-equilibrium mode of the α-relaxation that manifests itself as a breakpoint in the respective VTF dependence that occurs at T_g and gives rise to a smaller slope and, thus, lower activation energy (Fig. 11). For instance, such α-mode has been reported [27] for maltitol. However, the slope of the respective Arrhenius line has been significantly larger than the one found for

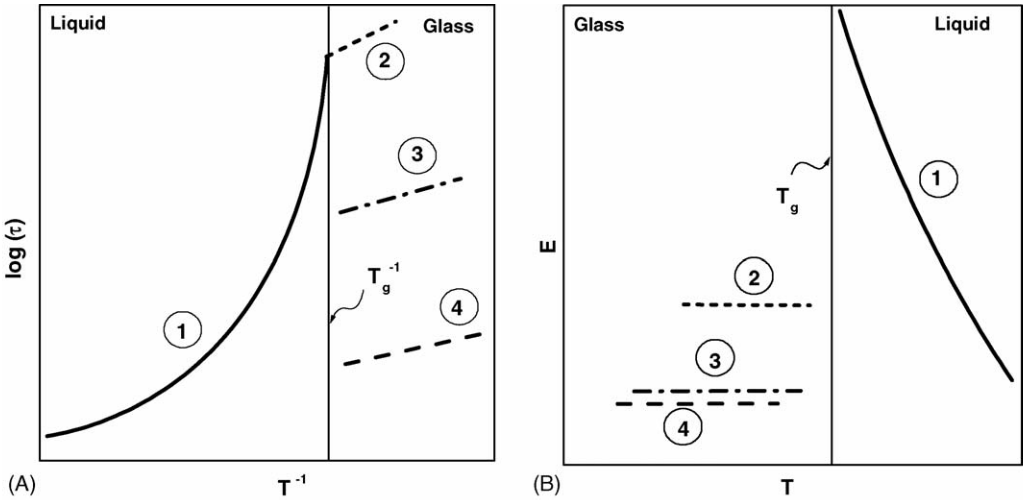

Fig. 11. Schematic presentation of the relaxation map (A) and the respective energy landscapes (B). (A) Curve 1 represents a typical VTF dependence of the α-relaxation. Straight lines 2–4 represent various processes occurring in the glassy state: (2) non-equilibrium mode of the α-relaxation; (3) α′-process; (4) β-process. (B) Sub-T_g processes 2–4 have significantly lower activation energy than the α-process.

the β-relaxation, which yielded 62 kJ mol^{-1}. Unfortunately, no information on this effect has been found in the other cited paper on maltitol [28] as well as in the cited papers on indomethacin [44], PMMA [31] and PET [37], all of which report VTF dependencies for the α-process. On the other hand, some poly(*n*-butyl methacrylate) relaxation data [46] seem to indicate that slope of the Arrhenius line for the non-equilibrium α-mode may be quite similar to that for the β-process. However, this does not seem to be the case for poly(ethyl methacrylate) [46]. Yet, another argument to be considered is the role of so-called α′-relaxation process that is observed in both metallic [47] and polymeric [48] glasses below T_g, but at a temperature notably higher than that of the dielectric or mechanical loss peak temperatures for the β-relaxation. This process is claimed [47] to be associated with the "frozen-in relaxation sites" and found to exhibit a very broad distribution of the relaxation times and a small activation energy (Fig. 11). Needless to say that the two latter features make it quite similar to the regular β-relaxation.

All in all, one must be careful not to overinterpret the observed correlation. Nevertheless, it appears safe to state that DSC allows for detecting certain sub-T_g relaxations in the upper temperature range of the β-relaxation, i.e., significantly below T_g. Unlike typical α-relaxation, the respective relaxation process has a low activation energy indicating its non-cooperative character. Although these are the features characteristic of the β-process, it remains to be understood whether this is the same process as the one detected by mechanical and dielectric spectroscopy or some other β-like process.

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