

Local motions in L-identol glass: Identifying different types of secondary relaxations

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Abstract

The sub- T_g relaxations in amorphous L-identol have been studied by thermally stimulated depolarisation currents (TSDC). The effect of aging on these motional processes was analysed during annealing at 253 and at 243 K, temperatures respectively 19 and 29 K below its calorimetric glass transition temperature $T_g = 272$ K. The features of different motional components of the secondary relaxation have been monitored as a function of time as the glass structurally relaxes on aging. It was concluded that the faster components of the secondary relaxation are negligibly dependent on aging and may be ascribed to intramolecular modes of motion, while the slower motional modes show a significant dependence on aging and correspond to the genuine Johari–Goldstein β -relaxation. The dielectric strength of the JG relaxation was found to decrease with increasing aging time, and there is no evidence for any modification with aging of the kinetic features of the local mobility.

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1. Introduction

It is now generally accepted that different kinds of slow motions, all of them designated under the common name of secondary relaxations, can occur in the amorphous solid state, at temperatures well below the glass transition temperature, T_g [1]. A common feature of such motions is that they are local, and have low amplitude and low activation energy, i.e. they possess much weaker temperature dependence of the relaxation time compared with the α -relaxation. Furthermore, they display an Arrhenius behaviour below the glass transition temperature. Some of those motions have an intramolecular origin and consist of internal rotations, i.e. of rotations about sigma covalent bonds, of a part of a molecule relative to the other part. However, other secondary relaxations seem to have an intermolecular origin, given that they are observed in systems composed by rigid molecules where internal rotations cannot take place [2,3]. These are called β or Johari–Goldstein (JG) relaxations. The JG relaxation must thus

involve motions of the molecules as a whole, probably rotational jump-motions in their cage [3], and it is often considered as a universal feature of the glassy state that precedes the α -relaxation in time. The JG relaxation is the slower mobility among the secondary relaxations, and is believed to play an important role in the crystallisation from the amorphous solid state.

One of the most widely used experimental techniques to analyse the slow molecular mobility in the amorphous solid and viscous liquid state is dielectric relaxation spectroscopy (DRS). A drawback of the DRS technique in this context is that the β -relaxation is most often not resolved from the main or glass transition relaxation (the so-called α -relaxation): it appears as a shoulder in the high frequency flank of the α -peak, or sometimes even more submerged in the form of the so-called excess wing [4]. With aging or with applied pressure the disguised β -process becomes more prominent, in opposition to the other secondary relaxations, with intramolecular nature called γ , δ , ... that are negligibly dependent on pressure and on aging [5]. It was recently shown that the separation between the α and β -processes also increases by dissolving the molecule in a non-polar viscous solvent [6].

The technique of thermally stimulated depolarisation currents (TSDC) is a dielectric-related technique, which has been

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frequently used to study slow molecular mobility in the glassy state [7–9]. One advantage of the TSDC technique is its low equivalent frequency [10], which leads to an enhanced resolution of the different relaxation processes. As a consequence of this feature, the slow β -relaxation appears most often in the TSDC spectra as a very broad peak, well separated from the main relaxation. Another important advantage of TSDC is the possibility of using the experimental procedure of thermal sampling or partial polarisation, which enables (see experimental part) to resolve a global distributed peak into its individual relaxation modes. This is indeed a very important feature of the TSDC technique, since it permits the experimental deconvolution of a broad heterogeneous distribution into its narrowly distributed components. Furthermore, the temperature dependent relaxation time associated with a given mode of motion can be calculated from TSDC data, and this possibility constitutes a basic quantitative advantage of the technique. Let us note that dielectric relaxation spectroscopy is not able to determine the temperature dependent relaxation time of a single (or narrowly distributed) relaxation mode. Instead, the result of the analysis of the data provided by this technique is a mean relaxation time of the whole distribution (the same occurs with other techniques as, for example, temperature modulated differential scanning calorimetry (TMDSC)). Finally, since the secondary relaxations appear in the TSDC spectrum at temperatures much lower than the glass transition temperature, T_g , the TSDC experimental technique appears as very useful to the study of such relaxations given that there is no interference between the experiment itself and the aging treatments.

In recent works, we used TSDC to study the aging influence on the α and β -relaxations of D-sorbitol [11], and on the secondary relaxations of trehalose [12]. The obtained results allowed an interesting discussion about the nature of the secondary relaxation at the molecular level. In the present work we will also explore the advantages of TSDC to study the secondary relaxations in L-idoitol, a diastereoisomer of sorbitol. As will be shown, the obtained results throw some light on the origin intra- or inter- molecular of the secondary relaxations.

2. Experimental

L-idoitol ($C_6H_{14}O_6$, CAS number 488-45-9) is a diastereoisomer of hexane-1,2,3,4,5,6-hexol. It was purchased from Acros (mass fraction > 0.99) and, prior to the experiments, the sample was heated up to 378 K (105 °C) and degassed under vacuum during 1 h. The melting point is reported to be at 353 K (80 °C), and the calorimetric glass transition temperature at $T_g = 271.8 \text{ K} = -1.3 \text{ °C}$ [13]. The DSC measurements we performed on our samples confirm this value of the glass transition temperature (see Fig. 1). The manufacturer was not able to provide us the sample in the crystalline form, despite the fact that the melting point is well above room temperature. Our samples were thus received as supercooled liquid, and they showed an enormous resistance to crystallisation.

Thermally stimulated depolarisation current (TSDC) experiments were carried out with a TSC/RMA spectrometer (TherMold, Stamford, CT, USA) covering the range from 103 to

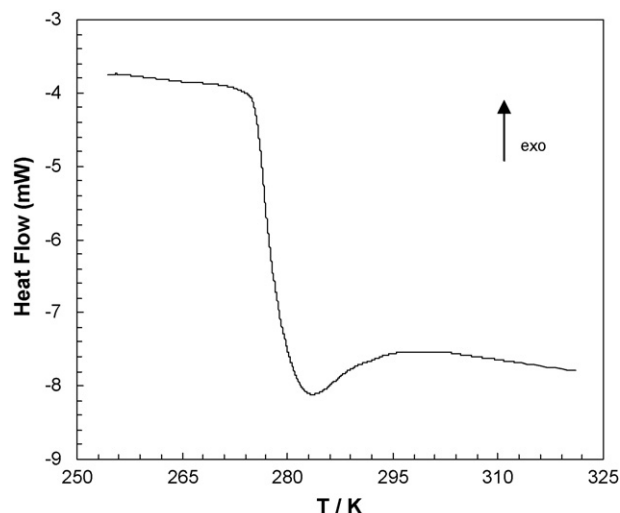


Fig. 1. Differential scanning calorimetry results obtained for amorphous L-idoitol at a heating rate of 10 K min^{-1} . The onset of the glass transition signal is at $T_{on} = 275.1 \text{ K}$.

673 K. For TSDC measurements the sample was placed between the electrodes of a parallel plane capacitor with effective area of $\sim 38 \text{ mm}^2$ (thickness of $\sim 0.5 \text{ mm}$). The sample is immersed in an atmosphere of high purity helium (1.1 bar). The fact that the relaxation time of the motional processes is temperature dependent and becomes longer as temperature decreases, enables to immobilize them by cooling. This is the basis of the TSDC technique, which is particularly adequate to probe slow molecular motions. In order to analyse specific regions of the TSDC spectrum, different methods of polarising the sample can be used, namely the so-called TSDC global polarisation experiment and the partial polarisation (PP) experiment. In the global polarisation experiment the polarising electric field scans a wide temperature interval so that the polarisation of the sample is constituted by a wide distribution of relaxation modes. Oppositely, the PP method, where the polarising field is applied in a narrow temperature interval, enables to resolve a global peak into its individual relaxation modes, i.e. to retain (or to freeze) a polarisation that arises from a narrow variety of dipolar motions. A more complete explanation of the electric and thermal treatments most often used in the TSDC studies can be found elsewhere [14,15]. The temperature/time scheme of a partial polarization experiment is shown in insert of Fig. 2.

3. Results

First let us note that our attempts to study the α -relaxation of L-idoitol by TSDC were not successful, because of a prominent spontaneous current peak with a maximum near $\sim 268 \text{ K}$ (-5 °C), independent of the presence of the electric field, that is always present in the TSDC spectra. In fact, line 1 in Fig. 2 is a baseline, i.e. the result of an experiment carried out on the depolarised sample. This signal is not thus induced by the polarising electric field, and so it does not correspond to dipolar relaxations but rather to the collective orientational motions

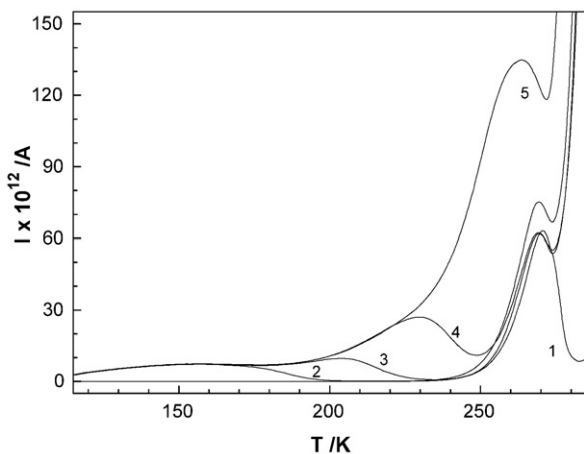


Fig. 2. TSDC thermograms obtained from different global experiments. The relevant experimental parameters are: strength of the polarising electric field, $E = 400 \text{ V mm}^{-1}$, polarisation time, $t_p = 5 \text{ min}$, freezing temperature, $T_0 = 108 \text{ K}$, heating rate, $r = 8 \text{ K min}^{-1}$. The polarisation temperatures were: curve 2, $T_p = 173 \text{ K}$; curve 3, $T_p = 198 \text{ K}$; curve 4, $T_p = 223 \text{ K}$; curve 5, $T_p = 243 \text{ K}$. The thin curve 1, flat on the left and showing a peak at $\sim 270 \text{ K}$, is a baseline (obtained by heating the non-polarised sample).

that are associated to the recover of mobility that occurs on heating in the glass transformation range. Given its relatively high intensity, this occurrence (which is not physically relevant for the study of molecular reorientations) prevents the study of the slow molecular mobility in the glass transition temperature region. These difficulties are augmented by the presence of a conductivity tail, which sharply increases in intensity as temperature increases above 273 K (see the extreme right-hand side of Fig. 2). That is the reason why this work is only concerned with the secondary relaxations of L-Iditol.

3.1. Secondary relaxations in amorphous L-Iditol

The TSDC global spectrum of L-Iditol is displayed in Fig. 2 (curves 2–5 which are the result of four different experiments).

Curves 2–4 in Fig. 2 correspond to distributions of motional modes of the secondary relaxation, while curve 5 (obtained with a polarisation temperature $T_p = -30^\circ\text{C}$) contains, in the higher temperature side, the contribution of the lower temperature modes of the glass transition relaxation. We can conclude from Fig. 2 that the secondary relaxation of iditol is very broad, extending from -165°C (the lower temperature limit of our equipment) up to $\sim -20^\circ\text{C}$.

The partial polarisation (PP) procedure was used in order to analyse the distribution of relaxation times (activation energies and pre-exponential factors, or activation enthalpies and entropies), which characterises this slow mobility. Fig. 3 shows a series of PP components of the secondary relaxations of iditol.

The peaks in Fig. 3 correspond to motional components of the secondary relaxation, i.e. are individual modes of the broad and distributed peaks shown in curves 2–5 of Fig. 2. As discussed later, a convenient analysis of these partial polarisation peaks allows the calculation of the kinetic parameters of the corresponding mobility.

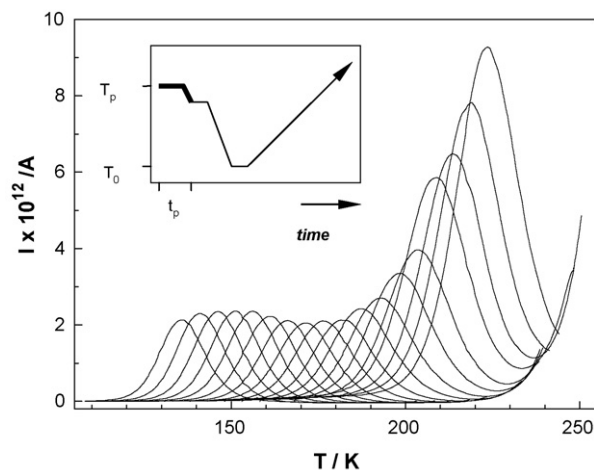


Fig. 3. Partial polarisation components of the sub- T_g molecular mobility of iditol. The polarisation temperatures, T_p , were from 133 to 218 K , with intervals of 5 K . The other experimental conditions were: strength of the polarising electric field, $E = 450 \text{ V mm}^{-1}$; polarisation time, $t_p = 5 \text{ min}$; width of the polarisation window, $\Delta T = 2 \text{ K}$; heating rate, $r = 4 \text{ K min}^{-1}$. The insert is a schematic representation of the experimental procedure and the thicker line segments correspond to the polarizing steps where the electric field is applied.

3.2. Aging effect on the secondary relaxations in amorphous L-Iditol

In order to study the effect of aging on different motional components of the complex secondary relaxation of iditol we chose different PP windows (with different temperature locations in the TSDC spectrum) as probes to monitor the evolution with aging of the different mobilities. From a large set of experimental results obtained at different aging temperatures, T_a , we chose the results at $T_a = 253 \text{ K}$ (-20°C), 19° below the calorimetric glass transition, to report in the present work. Prior to each probe experiment, the sample was annealed at the aging temperature, T_a , during different periods of aging time, t_a (normally $t_a = 0, 2, 5, 15, 30, 60, 120$ and 180 min). The chosen probe experiments were the partial polarisation windows with $T_p = 143, 173, 188, 198$ and 213 K . Let us emphasize that all these probing peaks correspond indeed to mobility components of the secondary relaxation of iditol: first of all because the higher polarisation temperature of those probing experiments (213 K) is much lower in comparison with the glass transition temperature of iditol which is $T_g = 272 \text{ K}$; secondly because from the observation of Fig. 2 (line 4 for example) it becomes clear that the secondary relaxation extends at least to temperatures up to $\sim 243 \text{ K}$. Fig. 4 shows results on the effect of the aging time on the probe experiments.

From the observation of Fig. 4 we can conclude that the five probing peaks show two sharply different kinds of behaviour. The higher temperature ones, peaks 3, 4 and 5 with $T_p = 188, 198$ and 213 K , display a significant influence of aging, with intensities (and areas) that decrease with increasing aging time. The lower temperature probing peaks 1 and 2 show, oppositely, a negligible dependence on aging. Let us draw attention to the higher temperature side of the peaks 4 and 5 that show an aging dependent increasing tail. This tail is the same as that shown in

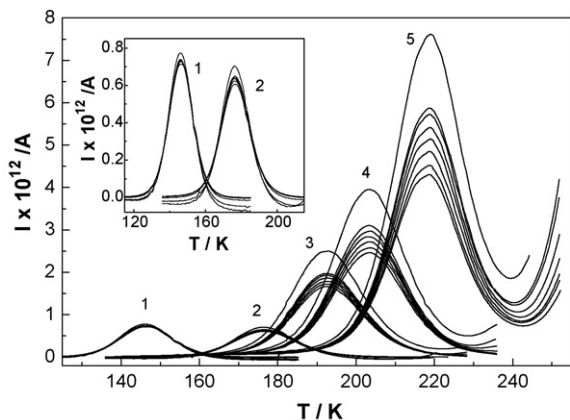


Fig. 4. Effect of aging on different motional components of the secondary relaxations of L-iditol (partial polarisation probes at $T_p = 143, 173, 188, 198$ and 213 K, numbered from 1 to 5 in the order of increasing T_p). The polarisation time was $t_p = 5$ min, the width of the polarisation window was $\Delta T = 2$ K, and the heating rate $r = 4$ K min^{-1} . The aging temperature was $T_a = 253$ K, and the aging times were, in order of decreasing intensity, $t_a = 0, 2, 5, 15, 30, 60, 120$ and 180 min. The insert is an enlargement of the two lower temperature probing peaks.

the right-hand side of Fig. 3, above ~ 220 K and, as commented before, it corresponds to a spontaneous current peak that appears independently of the presence of the electric field. Taking into account its temperature location, this feature on the higher temperature side of these probing peaks is not expected to have any influence in the evolution with aging time of the intensity of the peak's maxima.

Finally, a second conclusion we can draw from Fig. 4 is that the temperature location, T_m (temperature of maximum intensity), of all the probing peaks of the secondary relaxation appears as essentially independent of the aging time.

4. Discussion

First of all we need to elucidate the nature of the mobility corresponding to the peaks shown in Figs. 2 and 3. It is well known, and we noted it before, that a convenient analysis of the partial polarisation peaks as those of Fig. 3, allows the calculation of the temperature dependent relaxation time, $\tau(T)$, of the corresponding motional modes. Furthermore, from the fitting of the $\tau(T)$ curve with an adequate equation (Arrhenius, Eyring, Vogel, etc. . .), the respective kinetic parameters can be obtained. In Fig. 5 are presented the activation enthalpies of the TSDC-PP peaks shown in Fig. 3 plotted against their location in the temperature axis, T_m .

The representation confirms that this mobility is such that it obeys to the zero entropy law, i.e. that it has negligible activation entropy (or pre-exponential factors of the order of the Debye time 10^{-13} s). The secondary relaxation of iditol is thus broad and distributed, composed by a complex mixture of motional modes, all of them local, low amplitude, non-cooperative, given that no appreciable deviation from the zero entropy line is observed. These deductions are important in the present context since they strengthen our previous statement that the probing peaks chosen to monitor the aging effect (shown in Fig. 4), including the higher

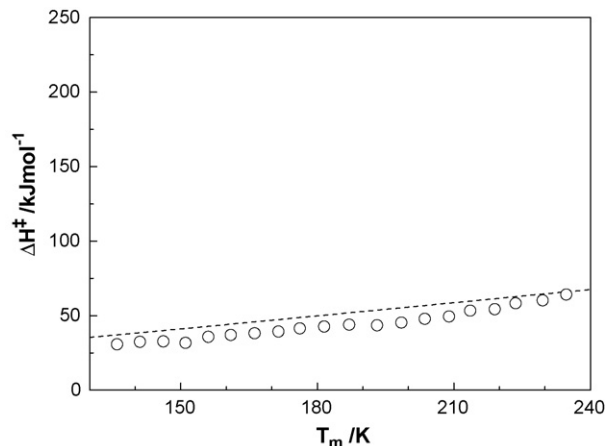


Fig. 5. Activation enthalpy, ΔH^\ddagger , of the partial polarisation components of the secondary relaxations of L-iditol as a function of the peak's location, T_m . The uncertainty in the enthalpy values is less than 2%. The dashed line corresponds to the zero entropy prediction.

temperature one with $T_p = 213$ K, correspond indeed to motional modes of the secondary relaxations.

Let us now focus on the influence of aging on the secondary relaxations of iditol. As shown in Fig. 4, the intensity of the maximum of those relaxations, I_m , as well as their dielectric strength (the permittivity due to polarisation orientation, $\Delta\epsilon = \epsilon_s - \epsilon_\infty$, proportional to the area under the peaks) increases with increasing temperature. Just to give an idea of the polarisation associated with the studied processes, let us note that the dielectric strength of the unaged probing peaks 1, 3 and 5 are of the order of 0.7, 3.0 and 8.5 respectively, and that dielectric strength of the probing peak 5 decreases with aging time from 8.5 for the unaged sample down to 5 for an aging time of $t_a = 180$ min.

As underlined before, two sharply distinct kinds of behaviour are explicit in Fig. 4, and are also clearly shown in Fig. 6(a) were the evolution of the intensity of the different partial polarisation probes, $I_m(t_a)$, normalized relative to the intensity of the non-aged peak, $I_m(0)$ (always at the same aging temperature, T_a), is represented as a function of the aging time, t_a .

Some motional modes (probes 1 and 2), the faster ones because they appear at lower temperatures, are not affected by aging. Since density increases on structural relaxation, it is reasonable to consider that those motional modes have an intramolecular origin given that they are independent of the molar volume and thus of intermolecular distances. Those local motions thus consist of internal rotations of one part of a molecule relative to the other part, which occur without significant interference of the neighbouring molecules. Other motional modes shown in Fig. 4 (probes 3, 4 and 5), the slower ones since they appear at higher temperatures, are affected by aging in such a way that the intensity (the dielectric strength) of the respective probing peaks decreases with increasing aging time. It seems reasonable to consider that those motional modes that are influenced by aging have an intermolecular origin. The former (intramolecular) modes are often called γ -, δ -... relaxations, while the later (intermolecular) modes correspond to the genuine β -relaxation or Johari–Goldstein relaxation, which is considered

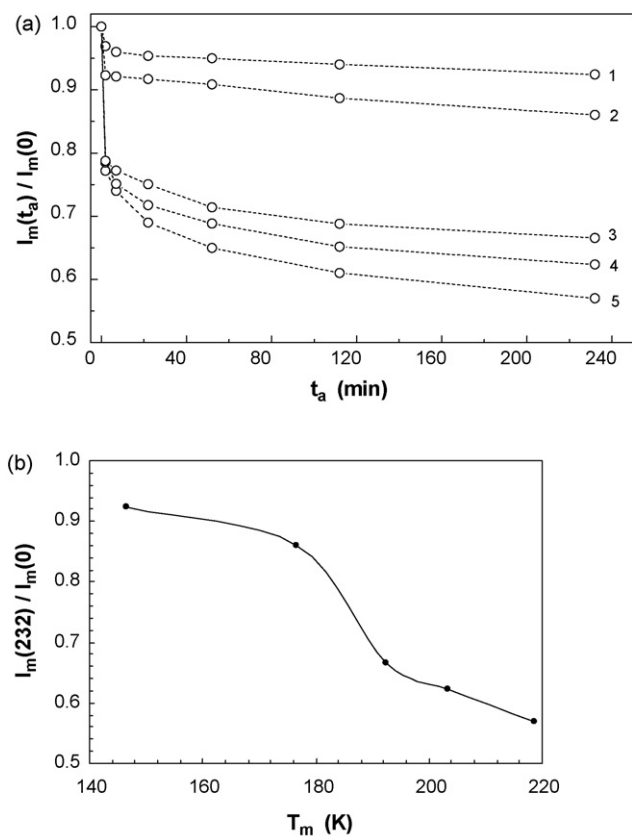


Fig. 6. (a) Evolution of the maximum intensity of the different PP probing peaks, $I_m(t_a)$, as a function of the aging time, t_a , for the aging temperature $T_a = 253$ K. The ordinate axis represents the ratio between the maximum intensity of a given peak, $I_m(t_a)$, and the maximum intensity of the peak without aging, $I_m(0)$. The correspondence between the numbered curves and the probing peaks is as in Fig. 4: $T_p = 143$ K: number 1; $T_p = 173$ K: number 2; $T_p = 188$ K: number 3; $T_p = 198$ K: number 4; and $T_p = 213$ K: number 5. The lines are just guides to the eyes. (b) Representation of the ratio $I_m(180)/I_m(0)$ between the intensity of the probing peak after an aging time of 180 min, $I_m(180)$, and the intensity of the non-aged probing peak, $I_m(0)$, as a function of the temperature location of the probing peak, T_m . The line is also just a guide to the eyes.

as an universal feature of the amorphous solid state. On the other hand, Fig. 6(b) represents the ratio $I_m(180)/I_m(0)$ between the intensity of the probing peak after an aging time of 180 min, $I_m(180)$, and the intensity of the non-aged probing peak, $I_m(0)$, as a function of the temperature location of the probing peak, T_m . It is clear from this representation that there is a sharp boundary in the TSDC spectra at ~ -100 °C between the intramolecular modes of motion and the JG relaxation. In this context, we can go back to the TSDC global spectrum of L-iditol displayed in Fig. 2 to conclude that line 2 mainly corresponds to a distribution of local intramolecular motions, while lines 3 and 4 include additional contributions from JG modes. Furthermore, since all the probing peaks, from 1 to 5 in Fig. 4, correspond to local modes of motion, the fact that the dielectric strength of the probing peaks 3, 4 and 5 decreases with increasing aging time seems to be compatible with both of the following interpretations— 1: the number of molecules involved in this mobility decreases with increasing aging time, which is compatible with the idea of the collapse on structural relaxation of the local regions where molecules

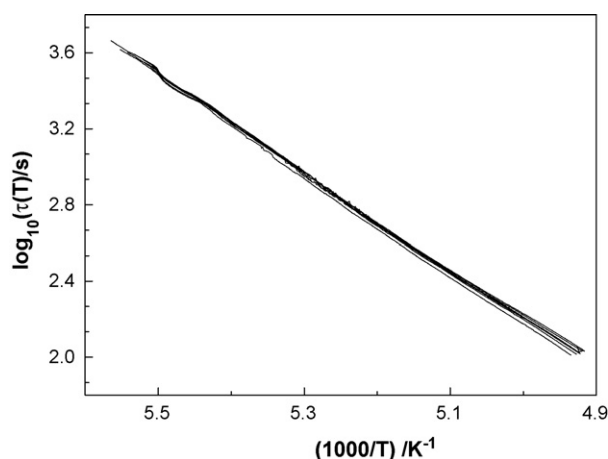


Fig. 7. Effect of the physical aging on the $\log \tau(T)$ versus $1/T$ lines of the probing PP peaks numbered 5 in Fig. 4. The fact that the lines are nearly superposed indicates that the kinetics of the corresponding mobility is not significantly affected by aging.

are capable of reorienting (disappearance of the “islands” of mobility) [16]; 2: the body angle for the rotational jump motions (the amplitude of the rotational jumps) decreases with increasing aging time, i.e. the metastable islands where, according to the Tanaka’s scenario [4], cooperativity emerges become tighter with aging.

Finally, let us focus on the influence of aging on the kinetics of the mobility. As noted before, the convenient analysis of a partial polarisation peak provides the temperature dependent relaxation time, $\tau(T)$, which characterises the corresponding mobility. Fitting the $\log \tau(T)$ versus $1/T$ lines with an appropriate equation allows the determination of the kinetic features of the mobility. Fig. 7 shows the $\log \tau(T)$ versus $1/T$ lines of the probing peaks numbered 5 in Fig. 4 (motional component with $T_p = 213$ K).

The obvious conclusion we can draw from Fig. 7 is that the temperature dependence of the relaxation time is nearly independent of aging. Exactly the same behaviour is observed for the other probing peaks in Fig. 4, so that we can firmly conclude that the activation parameters of the mobility of the secondary relaxations, intermolecular and intramolecular, are not significantly affected by aging. As a consequence, the relaxation time, $\tau(T_m)$, characteristic of the motional components of the secondary relaxations of iditol does not change with aging, in agreement with very recent reports [17]. This behaviour was also found in our recent TSDC study of sorbitol [11], and do not fully agree with the interpretation of results obtained by dielectric relaxation spectroscopy reporting that τ_{JG} of the Johari–Goldstein relaxation mimics the increase of τ_α with aging [18].

5. Conclusions

In this TSDC study of the local molecular mobility in L-iditol it was found that the secondary relaxation is broad and complex, composed of different motional modes that behave differently on aging. As structural relaxation of the glass occurs isothermally, the slower modes show a significant decrease of the dielectric strength, and are ascribed to the intermolecular Johari–Goldstein

relaxation. Oppositely, the faster modes behave independently of aging, and probably correspond to intramolecular modes of motion. The TSDC results cannot detect any clear influence of aging neither on the relaxation time nor on the activation energy of all the motional modes (intra- or inter-molecular) of the secondary relaxation.

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