Glass transition relaxation and fragility in the molecular glass forming \( m \)-toluidine: A study by thermally stimulated depolarization currents

Natália T. Correia, Cristina Alvarez, and Joaquim J. Moura Ramos\(^{a,b} \)
Centro de Química-Física Molecular, Complexo I, IST, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

Marc Descamps\(^{a,c} \)
Laboratoire de Dynamique et Structure des Matériaux Moléculaires, UFR Physique, Bâtiment P5, 59655 Villeneuve d’Ascq Cedex, France

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The glass transition relaxation in \( m \)-toluidine was studied by thermally stimulated depolarization currents (TSDC). The departure from the zero entropy prediction, also called compensation behavior, was analyzed and the fragility index of the glass-former \( m \)-toluidine was calculated from the TSDC data according to a recently proposed procedure. The obtained result was compared with literature values. A particular attention was focused on the physical aging process of the nonequilibrium glass, which was followed easily because of its slow evolution. The influence of the aging temperature on the aging rate was analyzed. The significance of the so-called compensation point was discussed on the basis of the results obtained in this study of structural aging. © 2000 American Institute of Physics. [S0021-9606(00)50532-7]

INTRODUCTION

The nature of the glassy state and of the liquid-to-glass transition still remains an unsolved problem.\(^1,2\) This is an interdisciplinary subject, whose importance for different areas of science and technology has been underlined in recent phenomenological reviews.\(^3,4\) One of the most important features of the behavior of glass-forming liquids is probably the departure from the Arrhenius behavior, which is particularly pronounced for the so-called fragile glass formers.\(^3\)\(^-\)\(^7\) This behavior is expected to come partly from a complex topology of the surface of the Gibbs energy landscape. The most fragile glass-formers are those which show, above \( T_g \), the most important temperature changing of their structural configuration, and thus exhibit the higher structural weakness.

In a recent work,\(^8\) we used the technique of thermally stimulated depolarization currents (TSDC) in order to study the relaxation mechanisms present in some fragile glass-formers, namely salol, glycerol, and maltitol. We were able to analyze in detail the glass transition relaxation in these materials as well as the \( \beta \)-relaxation of maltitol. The results obtained seem to show, without any ambiguity, that the TSDC technique is very capable of providing new and complementary information about the molecular dynamics in such materials in the approach of their glass transition temperature. In the present work we report results obtained on another fragile glass-former: \( m \)-toluidine. A complete analysis of the glass transition relaxation will be presented, as well as an extensive study of the aging processes occurring in the glass transformation range. \( m \)-toluidine appears as an excellent glass-former because of high tendency for easy undercooling. The crystallization conditions have been carefully determined,\(^9\) showing that the metastable liquid can be studied during long periods of time without interference of recrystallization effects. This is indeed an important practical advantage to our TSDC investigation since the nonspherical nature of the experimental technique requires performing temperature scans in wide temperature ranges.

EXPERIMENT

\( m \)-toluidine was a Fluka product, catalogue no. 89620, purity >99% and was used without further purification. Some experiments carried out on a purified sample (by distillation and drying) lead to results similar to those obtained on the nonpurified sample. It is liquid at room temperature (with a melting temperature of \(-31.5 \, ^o \)C)\(^10\) and has a calorimetric glass transition temperature reported in the literature as \( T_g = -87 \, ^o \)C.\(^9\) The differential scanning calorimetry thermogram we obtained gave an onset temperature of \(-85 \, ^o \)C at a heating rate of 4 \( ^o \)C min \(^{-1}\).

Thermally stimulated depolarization current (TSDC) experiments were carried out with a TSC/RMA spectrometer (TherMold, Stamford, CT, USA) covering the range 170 to +400 \( ^o \)C. In order to analyze specific regions of the TSDC spectrum, different methods of polarizing the sample were used, namely the so-called TSDC global experiment and the thermal sampling (TS) experiment (often called thermal windowing or cleaning). The TS method, where the polarizing field is applied in a narrow temperature interval, allows the polarization of specific segments of a complex global relaxation or, otherwise stated, it allows to resolve a global peak into its individual relaxation modes. Performing different TS experiments in the global peak’s temperature region allows the selective activation of the different fractions or segments of the global peak, i.e., the separation of a broad distribution of relaxations into its narrowly distributed components. This

\(^{a}\)Authors to whom correspondence should be addressed.

\(^{b}\)Electronic mail: pcmramos@alfa.ist.ulis.pt

\(^{c}\)Electronic mail: Marc.Descamps@univ-lille1.fr
as in polymeric materials. The fact that the TS peaks become steeper as time increases. Figure 1 also shows that the intensity of the TS peaks strongly increases as temperature increases. This behavior is a general feature of the glass transition relaxation as studied by TSDC, and is observed in low molecular weight compounds as well as in polymeric materials. The fact that the TS peaks become steeper as temperature increases indicates, as will be seen later, that the activation energy of the corresponding polarized segments also increases. Figure 1 also shows that the intensity (and the area) of the TS peaks in the glass transformation range strongly increases with temperature. The peak with maximum intensity has a location in the temperature axis at \( T_m = T_M = -81.7 \, ^\circ C \). The dotted peaks in Fig. 1 correspond to the higher temperature components, whose intensity decreases as temperature increases. For polarization temperatures far below \( T_g \), only the lower activation energy modes had enough time to be activated (small and broad TS peaks). As the polarization temperature increases approaching \( T_g \), the electric field is allowed (in the same polarization time \( t_p \)), equal for all experiments in Fig. 1) to activate barriers with increasing amplitude (the TS peaks show higher intensity and steepness). When the polarization temperature, \( T_p \), exceeds a given temperature in the vicinity of \( T_g \), a large part of the modes are depolarized during the no-field cooling (dotted TS peaks in Fig. 1, showing a decrease of intensity). The peak with higher intensity in Fig. 1 (with \( T_m = T_M = -81.7 \, ^\circ C \)) thus corresponds to a situation where a higher extent of polarization was allowed to be “frozen-in.” Otherwise stated, at the polarization temperature of the TS peak with higher intensity in the glass transition region, the electric field was allowed (in the polarization time \( t_p \)) to explore all the available energy barriers (including the higher ones). On the other hand, the higher temperature TS peaks (dotted peaks in Fig. 1) have intensities which decreases as \( T_p \) increases because the “frozen-in” of the polarization is increasingly difficult, indicating the transformation to the equilibrium (ergodic) metastable supercooled liquid state. The temperature, \( T_M \), of the TS peak with higher intensity in the glass transition region thus probably represents the lower temperature limit of the transformation range, defining a time scale of the system when nearly all the activation barriers were activated (a time scale of the system very near the equilibrium). This problem will be discussed again on the basis of the aging results presented later.

**RESULTS AND DISCUSSION**

**Thermal sampling analysis of the glass transition relaxation**

This relaxation has been studied using the procedure of thermal sampling. Some of the TS peaks obtained, which are representative of the evolution in the glass transformation range, are shown in Fig. 1 and the experimental procedure is schematically presented as an insert. The glass transition relaxation of \( m \)-toluidine appears in the TSDC spectrum with a maximum at \(-82 \, ^\circ C \). It can also be observed from Fig. 1 that the lower temperature components are broader and that the TS peaks become narrower and steeper as the polarization temperature, \( T_p \), increases. This behavior is a general feature of the glass transition relaxation as studied by TSDC, and is observed in low molecular weight compounds as well as in polymeric materials. The fact that the TS peaks become steeper as \( T_p \) increases indicates, as will be seen later, that the activation energy of the corresponding polarized segments also increases. Figure 1 also shows that the intensity of the TS peaks in the glass transformation range strongly increases with \( T_p \). The peak with maximum intensity has a location in the temperature axis at \( T_m = T_M = -81.7 \, ^\circ C \). The dotted peaks in Fig. 1 correspond to the higher temperature components, whose intensity decreases as \( T_p \) increases. For polarization temperatures far below \( T_g \), only the lower activation energy modes had enough time to be activated (small and broad TS peaks). As the polarization temperature increases approaching \( T_g \), the electric field is allowed (in the same polarization time, \( t_p \)), equal for all experiments in Fig. 1) to activate barriers with increasing amplitude (the TS peaks show higher intensity and steepness). When the polarization temperature, \( T_p \), exceeds a given temperature in the vicinity of \( T_g \), a large part of the modes are depolarized during the no-field cooling (dotted TS peaks in Fig. 1, showing a decrease of intensity). The peak with higher intensity in Fig. 1 (with \( T_m = T_M = -81.7 \, ^\circ C \)) thus corresponds to a situation where a higher extent of polarization was allowed to be “frozen-in.” Otherwise stated, at the polarization temperature of the TS peak with higher intensity in the glass transition region, the electric field was allowed (in the polarization time, \( t_p \)) to explore all the available energy barriers (including the higher ones). On the other hand, the higher temperature TS peaks (dotted peaks in Fig. 1) have intensities which decreases as \( T_p \) increases because the “frozen-in” of the polarization is increasingly difficult, indicating the transformation to the equilibrium (ergodic) metastable supercooled liquid state. The temperature, \( T_M \), of the TS peak with higher intensity in the glass transition region thus probably represents the lower temperature limit of the transformation range, defining a time scale of the system when nearly all the activation barriers were activated (a time scale of the system very near the equilibrium). This problem will be discussed again on the basis of the aging results presented later.

**The relaxation time of a thermal sampling peak**

The relaxation time of the processes activated in a TS experiment, i.e., the relaxation time associated to a given TS peak, can be obtained from the experimental depolarization current. Figure 2 shows the log \( \tau \) vs. \( 1/T \) lines of the peaks shown in Fig. 1. Since the TSDC technique is not a very familiar one, we believe that it is helpful to give some explanations about the procedure used to calculate the relaxation time and to comment on its significance.

The depolarization current, which is the experimental output of the TS experiment, is given by

\[
i(T) = -\frac{dP(t)}{dt} = -r \frac{dP(T)}{dT}
\]
where \( r \) is the heating rate of the TS experiment and \( P(T) \) is the remaining polarization at temperature \( T \) (or at time \( t \)) of the constant rate heating ramp (depolarization step). This polarization at temperature \( T \) is given by

\[
P(T) = \frac{1}{r} \int_{T}^{T_f} i(T')dT' = \frac{1}{r} \int_{T}^{T_f} i(T')dT',
\]

where \( T_f \) is a temperature well above the temperature of the maximum of the TS peak, at which the sample is already completely depolarized. Assuming that the depolarization process in the TS depolarization step follows a Debye-type decay with a temperature dependent relaxation time, \( \tau(T) \), it comes out that

\[
\tau(T) = \frac{P(T)}{i(T)} = \frac{1}{r} \int_{T}^{T_f} \frac{i(T')dT}{i(T)}.
\]

Equation (3) is used to calculate \( \tau(T) \) for each TS peak, a procedure which is often called the Bucci method.\(^{15} \)

A TSDC peak is thus considered as a consequence of a continuous depolarization process, induced by the constant rate heating process, governed by the Debye exponential relation, and \( \tau(T) \) is a temperature dependent relaxation time. It is assumed that the reorientation processes which give rise to a TSDC peak are only those which are sufficiently temperature dependent to give rise to a "frozen-in" of the polarization. These are thermally activated processes, characterized by a "thermal relaxation time,"\(^{16} \) describing the adjustment of the polarization during the depolarization process (constant rate heating step). We want also to underline that the temperature dependent relaxation time which is obtained from a TS peak is characteristic of a depolarization process occurring in the nonergodic glassy state. This relaxation time is not thus to be identified with any relaxation time obtained from experimental measurements on the supercooled liquid (ergodic) state.

It can be observed from Fig. 2 that the log \( \tau(T) \) vs. \( 1/T \) lines corresponding to the lower temperature components of the glass transition relaxation are straight, while those corresponding to the higher temperature components show a significant curvature. The log \( \tau(T) \) vs. \( 1/T \) line obtained for a given TS peak often follows the Arrhenius law. This is the case, for example, for the so-called secondary relaxations. Nevertheless, for systems presenting a glass transition relaxation, and particularly for those presenting a sharp glass transition, the Arrhenius representation of the \( \tau(T) \) lines of the TS peaks show an appreciable curvature. The origin of this curvature is a controversial subject and this problem was discussed in some detail elsewhere.\(^{8} \) It is experimentally found that the observed curvature is independent of the width of the polarization window.\(^{17} \) We also found from systematic experiments in \( m \)-toluidine and other glass-formers (results not presented in the present work) that the curvature of the log \( \tau(T) \) vs. \( 1/T \) lines do not change even if heating rates as low as \( 1 \degree C \min^{-1} \) are used in the TS depolarization step. Since the curvature of the log \( \tau(T) \) vs. \( 1/T \) line is not suppressed even if very low heating rates are used in the TSDC scan, i.e., in situations where the polarization is in thermal equilibrium at each temperature, we believe that it arises from the fact that the electric field polarizes a variety of modes of motion with a distribution of activation energies. As the depolarization process proceeds, the polarized modes are depolarized on heating in the order of increasing activation energy. The nonlinearity of the log \( \tau(T) \) vs. \( 1/T \) lines of the TS peaks in the glass transition region has been observed in several molecular glass-formers,\(^{8} \) as well as in polymeric systems,\(^{18} \) and it can be considered as a general feature of fragile systems.

The activation parameters associated with each TS peak can be obtained by fitting the corresponding log \( \tau(T) \) vs. \( 1/T \) line with an appropriate equation.\(^{19} \) In particular, the apparent activation enthalpy at the maximum of the TS peak was calculated from the slope at \( T_m \) considering that:

\[
\left[ \frac{d \log \tau(T)}{d(1/T)} \right]_{T_m} = \frac{1}{2.303} \left[ \frac{\Delta H(T_m)}{R} + T_m \right].
\]

Figure 3 shows the activation enthalpy of the TS peaks in the glass transition region obtained at the temperature of maximum intensity, as a function of their location, \( T_p \), in the temperature axis. It can be observed from Fig. 3 that the activation enthalpy of the TS peaks shows a sharp increase as the glass transition temperature is approached on heating. This behavior, which is often called compensation behavior or departure from the zero entropy prediction,\(^{20} \) has been shown to be a feature of the glass transition relaxation as studied by TSDC\(^{21} \) and will be discussed in the following.

The zero entropy line and fragility

For noncooperative relaxations, which are often considered as arising from local segmental motions uninfluenced by neighbors, the activation entropy is negligible. On the
FIG. 3. Activation enthalpy of the TS components of the glass transition relaxation of \textit{m}-toluidine as a function of the peak’s location, \(T_m\). The dotted line corresponds to the zero entropy prediction.

other hand, the log \(\pi(T)\) vs. \(1/T\) line of a TS peak is expected to be linear since these relaxations are characterized by very narrow energy distributions. The experience confirms this expectation. In this situation, it can be shown\(^{11}\) that

\[
\frac{kT_m^2}{r(\Delta H_0^* + kT_m)} = \frac{\hbar}{kT_m} \exp\left(\frac{\Delta H_0^*}{kT_m}\right), \tag{5}
\]

where \(\Delta H_0^*\) is the activation enthalpy for a relaxation process obeying the zero entropy approximation, \(T_m\) the temperature of maximum intensity of the corresponding TS peak, and \(r\) the heating rate of the TS experiment. Equation (5) thus gives the activation enthalpy of the TS peaks as a function of the peak’s location, \(T_m\), for a given heating rate, \(r\), for local noncooperative relaxations, i.e., for relaxations involving the motion of small groups of atoms with weak interaction with other portions of the molecule or neighboring molecules. Equation (5) describes the so-called zero entropy approximation,\(^{11}\) which corresponds to a simple reference behavior, characteristic of relaxations involving small submolecular fragments moving independently of one another. It was Starkweather who pointed out first the importance of the zero entropy prediction as a reference behavior to interpret the TSDC data.\(^{22,23}\) It can be easily shown that, for these relaxations, the preexponential factor is such that \(\tau_0 T\) equals \(h/(k e)\) or \(f_0/T = 1/(2\pi\tau_0 T)\) equals \(k e/(2\pi h)\), where \(e\) is the number of Néper. We have thus \(\tau_0 T = 1.8 \times 10^{-11}\) K s \((\tau_0 = 0.6 \times 10^{-13}\) s at 300 K) and \(f_0/T = 9 \times 10^9\) s\(^{-1}\) K\(^{-1}\) \((f_0 = 2.7 \times 10^{12}\) Hz at \(T = 300\) K).

Other relaxations, often called complex relaxations, have very large activation entropies and are believed to involve a spectrum of related or cooperative motions, with extensive intra- and intermolecular interactions. The glass transition relaxation is an example of this type of complex relaxations. The TS peaks of these relaxations have activation enthalpies much higher than those predicted by Eq. (5), and they are said to deviate or to depart from the zero entropy prediction. The dotted line in Fig. 3 corresponds to the zero entropy behavior, so that the points shown in the same figure indicate a strong departure from this line. The amplitude of this deviation contributes to the definition of the fragility index. For compounds having the same \(T_g\), the more fragile is that which gives rise to the largest deviation. Comparison with glycerol, which has roughly the same \(T_g\), indicates that \textit{m}-toluidine is more fragile. The relationship between the amplitude of the deviation from the zero entropy prediction and the topology of the surface of energy barriers (or fragility) will be discussed later. As underlined before, an important feature of the glass transition relaxation as studied by the TSDC technique is the strong departure of the activation energy from the zero entropy prediction. We will quantify this amplitude, which will be designated by \(\Delta\), in the following way: \(\Delta\) is the difference between the activation enthalpy calculated at \(T_m\) of the TS peak of maximum intensity in the glass transition region, \(T_M\), and the activation enthalpy, calculated at the same \(T_M\) and for the same heating rate, on the basis of the zero entropy approximation [Eq. (5)]

\[
\Delta = \Delta H^*(T_M) - \Delta H_0^*(T_M). \tag{6}
\]

The choice of the TS peak of maximum intensity in the glass transition region seems to be a natural one, but it deserves a brief comment. Despite that this peak is not, in general, that showing the higher activation energy, it is, on the other hand, very easy to identify, and it is a well resolved peak, not usually affected by the proximity of conductivity tails or higher temperature relaxations. In fact, the TS peak of maximum intensity in the glass transition region generally appears as a very well defined peak, allowing an easy determination of its location, \(T_M\), and a confident application of the Bucci method [Eq. (3)] in order to obtain the corresponding \(\pi(T)\) line. Moreover, as pointed out before in the discussion of the significance of the results presented in Fig. 1, \(T_M\) is a characteristic temperature defining the crossing of the time scale of the heating rate of the TS experiment with the time scale of the system. It is, as noted, a time scale of the equilibrated system, when the polarization field is able to activate all the barriers. That is why \(T_M\), the temperature of the maximum of the TS peak of maximum intensity in the glass transition region (which nearly coincides with the temperature of the maximum of the global TSDC peak of the \(\alpha\)-relaxation) is often considered as the glass transition temperature provided by the TSDC technique. In this context, the choice of \(T_M\) appears as an operational choice since it is a reference temperature defining an identical time scale on heating for all samples and an identical polarization condition. It obviously depends on the heating rate, as is the case for the calorimetric glass transition temperature. \(T_M\) thus appears as a good reference temperature to be used to quantify the deviation from the zero entropy prediction [Eq. (6)] in a very wide variety of materials.

According to the definition of Eq. (6), we obtain \(\Delta = 252\) kJ mol\(^{-1}\) from our TS data obtained at an heating rate of 4 °C min\(^{-1}\) on unaged \textit{m}-toluidine samples. The physical significance of the amplitude, \(\Delta\), of the departure from the zero entropy prediction in the glass transition region is not yet completely elucidated. It corresponds to the activation energy of that part of the distribution barriers involved in the relaxation process which had not enough time to be cleaned.
during the cooling process (the freezing step of the TS experiment, without field). In a recent TSDC work on low molecular weight organic glasses we showed that this amplitude strongly varies from material to material.8 The fragility index, \(m\), of a substance was defined as the slope of the log \(\tau(T)\) vs. \(T_g/T\) line at \(T=T_g\),

\[
m = \frac{d \log_{10} \tau(T)}{d(T_g/T)} \bigg|_{T=T_g},
\]

(7)

where \(\tau\) is the structural relaxation time which slows down to 100 s at \(T_g\). Since fragility is connected to the topology of the potential energy surface,25 we tried to set up a link between the parameter \(\Delta\) and fragility. Let us note that an equation similar to Eq. (7) could be written to allow the calculation of fragility from TSDC data. In fact, if we consider the TS peak with highest intensity in the glass transition region (located at \(T_M\)), we can write

\[
m_1 = \frac{d \log_{10} \tau(T)}{d(T_M/T)} \bigg|_{T=T_M},
\]

(8)

which is formally similar to the Angell’s definition [Eq. (7)], and where the derivative is taken on the \(\tau(T)\) curve of the \(i(T)\) peak with higher intensity in the glass transition region. Taking Eq. (4) into account, Eq. (8) can be rewritten as

\[
m_1 = \frac{1}{2.303} \left[ 1 + \frac{\Delta H^0(T_M)}{RT_M} \right].
\]

(9)

where \(\Delta H^0(T_M)\) is the activation enthalpy at \(T_M\) of the peak of maximum intensity in the glass transition region. The value of the fragility of unaged \(m\)-toluidine calculated from our TSDC data, obtained at a heating rate of \(4 \, ^\circ C \, \text{min}^{-1}\), using Eq. (9) is \(m_1 = 83\), which is in good agreement with the value \(m = 79\) published in the literature.5 Equations (8) and (9), as well as Eq. (7), are definition of fragility based on the activation energy at the glass transition temperature.26 As underlined before, the important feature of the glass transition relaxation as studied by TSDC is the departure of the energy (or of the enthalpy) from the zero entropy approximation, and not the activation energy at \(T_g\) itself. By analogy to Eq. (8), we could thus define fragility as

\[
m_2 = \left[ \frac{d \log_{10} \tau(T)}{d(T_M/T)} - \frac{d \log_{10} \tau'(T)}{d(T_M/T)} \right]_{\Delta S = 0} \bigg|_{T=T_M},
\]

(10)

where the second factor in the right-hand side is the slope at \(T = T_M\) of the line of \(\log_{10} \tau'(T)\) vs. \(T_M/T\) for the zero entropy prediction. Since this factor, which will be represented by \(m_0\), can be calculated as

\[
m_0 = \left[ \frac{d \log_{10} \tau'(T)}{d(T_M/T)} \right]_{T = T_M} = \frac{1}{2.303} \left[ 1 + \frac{\Delta H^0(T_M)}{RT_M} \right],
\]

(11)

where \(\Delta H^0(T_M)\) is the activation enthalpy for the zero entropy prediction obtained from Eq. (5), Eq. (10) can be rewritten as

\[
m_2 = \frac{\Delta}{2.303RT_M} = m_1 - m_0,
\]

(12)

where \(T_M\) is, as before, the temperature of the maximum of the higher intensity TS peak of the glass transition relaxation. It is to be recalled that the \(\Delta\) values were calculated at \(T_M\) (which depends of course on the heating rate as is the case for the calorimetric glass transition temperature).

The difference between the fragility \(m_1\) and \(m_2\) arises from the fact that, in Eq. (12), the main concept is the amplitude, \(\Delta\), of the departure from the zero entropy approximation [defined according to Eq. (6)] while Eq. (9) is just based on the activation energy at \(T_g\). Calculating \(m_0\) from Eq. (11) for \(m\)-toluidine (\(T_M = -81.7 \, ^\circ C\)) we obtain \(m_0 = 15\) which leads to \(m_2 = m_1 - m_0 = 68\). We will briefly comment on this difference between \(m_2\) and \(m_1\). It is well known that the Angell’s scale of fragility is such that the limit of \(m\) for infinitely strong glasses is \(m \approx 16\).24 This is also the case for \(m_1\) since we showed that the scale \(m_1\) is equivalent to the Angell’s scale. This limit arises from the fact that, for thermally activated processes, the Arrhenius preexponential factor is typically such that \(\log \tau_0 = -14\), and from the fact that the relaxation time at the glass transition temperature has a characteristic value of \(\tau(T_g) \approx 100\) sec. On the other hand, the value of \(m_0\) calculated by Eq. (11) shows a very slight dependence on \(T_M\), such that its values are 15.1, 15.3, 15.4, and 15.5, respectively, for \(T_M\) equal to \(-50, 0, 50\), and \(100 \, ^\circ C\). The fragility index for the zero entropy prediction, \(m_0\), thus represents the limit of fragility for infinitely strong glasses, according to the Angell’s scale. As a consequence, if Eq. (12) is used to define fragility, the limit of \(m_2\) for infinitely strong glasses will be \(m_2 = 0\), so that this scale of fragility appears as an absolute scale. This arises from the fact that, for fragile systems, the true feature of the glass transition relaxation as studied by TSDC is the departure from the zero entropy and not the activation energy at \(T_M\) itself.

Finally, the fact that the fragility index obtained from TSDC from experiments below \(T_g\) coincides with that obtained by isothermal techniques above \(T_g\) (Angell’s scale), indicates that the slope of the log \(\tau\) vs. \(1/T\) lines at \(T_g\) is the same, independently of looking to \(T_g\) from higher or from lower temperatures. The previous discussion seems to show that both analysis of the glass transition relaxation, that which approaches \(T_g\) on cooling from the supercooled liquid, and that which makes it on heating from the glassy state, seem to converge, i.e., seem to lead to results that are physically compatible. The technique of TSDC appears in this context as a valuable technique to study the glass transition relaxation and to determine the fragility index of glass formers.

**The effect of aging**

The TS experiments whose results are shown in Fig. 1, and which have been discussed before, were made on the glassy sample prepared by cooling down from the melt (cooling rate \(4 \, ^\circ C \, \text{min}^{-1}\)) to \(-100 \, ^\circ C\), well below \(T_g\). During the TS experiments the temperature varied between \(-110 \, ^\circ C\) and \(-70 \, ^\circ C\). In order to look at the equilibration process of the glass, i.e., to the evolution from the as quenched glassy state to the equilibrated glass, we carried out series of identical TS experiments where each experi-
ment was preceded by an aging step at the polarization temperature during the time $t_a$ (see insert in Fig. 4). Figure 4 shows the results of a series of such experiments where the aging time varied from 0 to 180 min.

The most apparent conclusions we can draw from Fig. 4 are as follows: (i) The intensity (and the area) of the TS peaks decreases when the aging time increases, indicating that, as the glass equilibrates, the total polarization created by the electric field, during the same polarization time, $t_p = 5$ min, decreases. (ii) The temperature of maximum intensity of the peaks, $T_m$, slightly increases as the aging time increases. This behavior may be due to the kinetics of the recovery of the metastable supercooled liquid state, which occurs at the higher temperatures of the depolarization process (in the vicinity of $T_m$). This recovery gives rise to an overshoot in $C_p$ (in DSC experiments), and it is known that the maximum of this overshoot occurs at a temperature which increases with the aging time. It is thus reasonable to expect that the kinetics of this overshoot exchange with the apparent kinetics of the depolarization in this late stage, giving rise to the observed behavior. On the other hand, since the aged glass is more compact (higher density) than the unaged one, it is possible that the response of the system to the depolarization is retarded in the aged glass, thus contributing to the displacement of $T_m$ to higher temperatures.

Moreover, aging has a significant influence on the shape of the log $\pi(T)$ vs. $1/T$ lines associated with each TS peak (see Fig. 5). In fact, from Fig. 5 it can be concluded that (i) with increasing aging time, the slope of those lines decreases, indicating that the modes of motion polarized by the electric field (in the same polarization time, $t_p$) evolve to lower activation energy as aging proceeds. (ii) The curvature of the log $\pi(T)$ vs. $1/T$ lines decreases as the aging time increases, suggesting that the modes of motion polarized by the electric field (in the same polarization time) are more sharply distributed.

Different series of experiments have been carried out for different aging temperatures, in order to have information about the influence of temperature on the kinetics of aging. Figure 6 shows the evolution of the intensity of the TS peaks, $I_m(t_a)$, as a function of the aging time, $t_a$, for differ-

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**FIG. 4.** Effect of aging on the TS component at $T_p = -93^\circ$C of the glass transition relaxation of m-toluidine. The aging times were, in the order of decreasing intensity, $t_a = 0, 1, 10, 20, 30, 60, 100,$ and 180 min. The polarization time was $t_p = 5$ min. The other experimental conditions were similar to those of experiments in Fig. 1. The insert is a schematic representation of the experimental procedure and the thicker line segment corresponds to the polarizing step where the electric field is applied.

**FIG. 5.** Influence of the aging time on the shape of the log $\pi(T)$ vs. $1/T$ lines. Both lines correspond to the TS peak obtained with $T_p = -93^\circ$C. The continuous line was obtained on the unaged sample, while the dotted line was obtained after an aging time of 180 min. The temperature range of the lines corresponds to the lower activation energy part of the distribution in the transformation range.

**FIG. 6.** Evolution of the intensity of the TS peaks, $I_m(t_a)$, as a function of the aging time, $t_a$, for different aging temperatures, $T_a = T_p$. The ordinate axis represents the ratio between the intensity of a given peak, $I_m(t_a)$, and the intensity of the peak without ageing, $I_m(0)$. The correspondence between the symbols and the aging temperatures is as follows: $-87^\circ$C: $\bullet$; $-88^\circ$C: $\nabla$; $-89^\circ$C: $\diamond$; $-90^\circ$C: $\Delta$; $-91^\circ$C: $\circ$; $-93^\circ$C: $-94^\circ$C, and $-95^\circ$C: $\square$. The experimental conditions of these experiments were similar to those of the experiments shown in Fig. 4.
be considered as the glass transition temperature of the ma-
to different components of the glass transition relaxation oc-
a
\[ I \sim (T_m - T_c)^2 \]

served that the obtained characteristic time, \( t_\alpha \), of the different TS components of the glass transition relaxation of the equilibrated glass tend to be the same (points in the right-hand side of the figure).

ent series of experiments with different aging temperatures. The data presented in Fig. 6 was expressed as
\[ I(t_a) = I(\infty) - \frac{I(0)}{1/[T_a] - I(\infty)} \]

The results reported in Fig. 7 also show that the way the activation enthalpy increases with \( T_m \) in the glass transition region strongly depends on the degree of stabilization of the glass. This is an interesting point to notice with regard to the general discussion of the occurrence or not of the compensation point. The strong departure from the zero entropy prediction is at the origin of the so-called compensation behavior which, for some authors, is characterized by a compensation point of coordinates \( T_c \) and \( T_g \), point of intersection of the log \( \pi(T) \) vs. \( 1/T \) lines of the TS components of the glass transition relaxation. Since the so-called compensation point is determined by the increase of \( \Delta H^* \) with \( T_m \), we believe that our results provide experimental evidence for the idea that the compensation point is not an intrinsic or fundamental property of the material. It seems reasonable to conclude from Fig. 7 that the so-called compensation temperature, \( T_c \), coincides with the glass transition temperature obtained by TSDC for the equilibrated glass, and that the eventual difference between \( T_c \) and \( T_g \) arises from degree of structural aging of the nonequilibrated glass.

**CONCLUSIONS**

The glass transition relaxation in the glass former \( m \)-toluidine was studied in detail by TSDC. A departure from the zero entropy prediction was observed for this relaxation, and the amplitude of this departure was used to calculate the fragility index of this glass-former. A good agreement with the value reported in the literature was observed. The kinetics of aging of the nonequilibrium glass was followed at temperatures below \( T_g \). It was found that the TS peaks of the glass transition region show a decreasing intensity as the aging time increases, which was attributed to the decreasing of the total polarization created by the field, in the same polarization time. On the other hand, the activation enthalpy decreases as the aging time increases. This behavior can be interpreted considering that the polarized modes of motion evolve to lower activation energy as aging proceeds. Simul-

**FIG. 7.** Activation enthalpies of the TS components of the glass transition relaxation of \( m \)-toluidine as a function of the peak’s location, \( T_m \), for the glass in different aged states. The dotted line corresponds to the zero entropy approximation. The black circles correspond to the unaged sample (experiments with \( T_p \) between \(-115^\circ C \) and \(-85^\circ C \), points in Fig. 3). The correspondence between the symbols and the aging temperatures of the TS peaks is as follows: \( \bigcirc: -95^\circ C \); \( \blacklozenge: -93^\circ C \); \( \square: -91^\circ C \); \( \bigtriangleup: -89^\circ C \). It is to be noted that the temperatures of maximum intensity, \( T_m \), of the different TS components of the glass transition relaxation of the equilibrated glass tend to the same (points in the right-hand side of the figure).
taneously, the location of the peaks moves to higher temperatures probably due to the influence of the recovery of the supercooled liquid state at the later stages of the depolarization process and to the retardation of the depolarization arising from the higher density of the aged glass.

It was suggested that the results on aging obtained in the present work provide experimental evidence for the idea that the compensation point is not an intrinsic or fundamental property of the material.

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12 J. van Turnhout, Thermally Stimulated Discharge of Polymer Electrets (Elsevier, Amsterdam, 1975).
17 It is to be recalled that, in a TSDC global experiment, where the electric field is applied in a large temperature interval, the polarization includes a very wide variety of modes of motion. In a thermal sampling (TS) experiment, on the other hand, the field is applied in a narrow temperature interval, so that the polarization includes a narrow distribution of modes of motion. The width of the distribution of polarized modes decreases as the width of the polarization window decreases.
19 The equation to be used for fitting the data must have sufficient parameters to have the flexibility which is necessary to ensure a good fitting. In the present work a Vogel-type equation was used.
26 Recall that $T_M$ is the glass transition temperature (dependent on the heating rate) provided by the TSDC technique. It is found that the relaxation time at $T_M \cdot T(\tau)$, obtained by TSDC is of the order of 15–30 seconds, which can be compared with the value of $\tau(T_g) = 100$ seconds used for scaling the temperature in the Angell’s definition of the fragility index [Eq. (7)].