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Study of the relaxation behaviour of a tri-epoxy compound in the supercooled and glassy state by broadband dielectric spectroscopy

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Abstract

The dynamics of the glass-forming tri-epoxy triphenylmethane triglycidyl ether (TPMTGE) was investigated in the supercooled and glassy state by broadband dielectric spectroscopy. Measurements were performed in a frequency range between 10^{-2} Hz and 10^{10} Hz for temperatures in the range between 120 and 350 K. The dielectric response revealed the existence of two relaxation processes: the lower frequency one (α -relaxation) slows down very rapidly on cooling the system and leaves the experimental window on approaching the glass transition temperature T_g ; the higher frequency one (β -relaxation) is observable both above and below T_g . The β -relaxation is comparatively quite fast, thus a large separation between the main and the secondary peaks is observed, and no complete merging of the α - and the β -process is found within the experimental window even at the highest temperatures. Besides, a third relaxation (β'), very weak indeed, was observed in the glassy state. The detailed analysis performed on the experimental data indicated that a single Vogel–Fulcher–Tamman equation well describes the change of the α -relaxation time in the entire temperature interval. In the same temperature range, the conductivity and the α -relaxation time are related to each other by a fractional Debye–Stokes–Einstein law. Moreover, our results confirmed the proportionality between the β -activation energy and the glass-transition temperature, which was found in other systems. As observed in previous experiments, both the shape parameters and the relaxation strength of β -relaxation are strongly affected by the transition from liquid to glassy state.

1. Introduction

Understanding the microscopic mechanism which rules the glass transition, and in particular the strong super-Arrhenius character of different dynamic observables (such as viscosity, structural dielectric relaxation time, conductivity) near the glass transition temperature T_g , is still an unsolved problem in condensed matter physics [1–4]. In the liquid state, above the melting

point, the temperature-activated dynamics gives usually raise to a mono-exponential relaxation response and to an Arrhenius-like (ARR) [5] temperature dependence of the characteristic time:

$$\tau(T) = \tau_{01} \exp[\Delta E/RT] \quad (1)$$

where ΔE and τ_{01} are the activation energy of the process and the relaxation time at very high temperatures, respectively.

When temperature is reduced, the mobility of the molecules constituting the liquid drastically decreases and the relaxation behaviour loses the mono-exponential character [6]. The temperature dependence of the main-relaxation time is usually well described by a Vogel–Fulcher–Tamman law (VFT) [7–9]:

$$\tau(T) = \tau_{02} \exp[DT_0/(T - T_0)] \quad (2)$$

where D is referred to as strength parameter and T_0 is the temperature at which equation (2) predicts the divergence of the relaxation time.

In many liquids, not only the main (α -) relaxation but also a secondary (β -) relaxation is observable [10–16]. The secondary relaxation is usually considered to be related to a local motion which seems to remain thermally activated even below the glass-transition, as for example the arrangement of an internal molecular degree of freedom or a Johari–Goldstein process, the second meaning a more fundamental process which should be intrinsic to the glassy state [17–19].

Experiments [13–15, 20–22] demonstrated that in the supercooled state additional effects can occur in the proximity of a temperature, T_B , well above the glass transition temperature, T_g :

- a crossover between two different dynamic regimes of the α -relaxation;
- the splitting between the main and the secondary relaxation;
- the breakdown of the Debye–Stokes–Einstein relation, connecting the conductivity and the α -relaxation characteristic time.

As concerns specifically the secondary process, the shape parameters of the relaxation function and the slope of the strength against the reciprocal temperature change noticeably when T_g is crossed.

Several approaches have been worked out in order to interpret this complex scenario, including models employing the free volume concept [23–25], thermodynamic theories [26–28] and the mode coupling theory [29], recently proposed to give a detailed description of the microscopic dynamics of supercooled systems. However, at the present no theory is able to offer a completely satisfactory explanation of the whole glass-transition phenomenology: hence the importance of additional experimental results for testing the theoretical predictions. For this purpose, one needs very wide band and accurate spectroscopic techniques, such as dielectric spectroscopy, which is very suitable for studying the supercooled and glassy phase.

Another important issue is choosing a proper molecular system for which both the main and the secondary relaxation have large strengths and well separated characteristic time scales, resulting well distinguishable in the dielectric spectra. Among molecular systems having these features, epoxy compounds were revealed to be particularly suitable for dielectric spectroscopy [13–16], because the dipole arising from epoxy rings ($\cong 2.2$ Debye) gives them a large dielectric susceptibility so permitting reliable impedance measurements. Moreover, they often possess also a large optic susceptibility and so proved to be excellent candidates in order to compare results obtained by different experimental techniques [30, 31]. Indeed, they get a weak frequency-independent conductivity from the presence of ionic impurities, allowing one to study the coupling between translational and rotational diffusion [13–15].

2. Experiment

In this study we investigated the dynamics of the commercial tri-epoxy compound, triphenylolmethane triglycidyl ether (TPMTGE obtained from Aldrich), having a molecular weight, 460.5 g mol^{-1} , and melting point of about 321 K. The molecular structure of TPMTGE is shown in figure 1. This system was chosen also because the corresponding mono-, di- and poly-epoxy are commercially available, so that it will be possible to study the influence of the molecular complexity on dielectric behaviour.

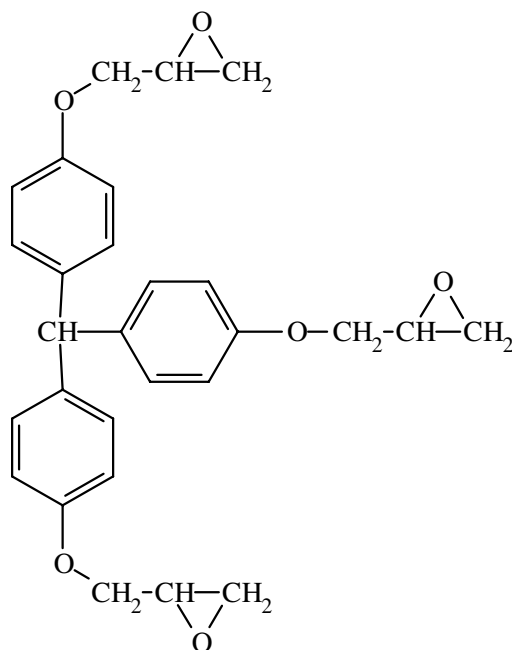


Figure 1. The molecular structure of tri-epoxy TPMTGE.

In order to assure a wide spectral overlap among the data acquired in contiguous frequency intervals, the dielectric measurements were carried out in the frequency domain by using four different pieces of apparatus: the HP4194A (Hewlett-Packard) impedance analyser was employed in the range $10^2 \text{ Hz}-4 \times 10^7 \text{ Hz}$ with a cylindrical capacitor cell of empty-cell capacity $C_0 \cong 2.3 \text{ pF}$; the Alpha frequency response analyser (Novocontrol) with a parallel plate cell ($C_0 \cong 90 \text{ pF}$) was employed in the interval $10^{-2} \text{ Hz}-10^7 \text{ Hz}$; the network analysers HP4291B with $C_0 \cong 3.5 \text{ pF}$ and HP8722D with $C_0 \cong 0.15 \text{ pF}$ were employed in the frequency ranges $5 \times 10^4 \text{ Hz}-1.8 \times 10^9 \text{ Hz}$ and $5 \times 10^7 \text{ Hz}-10^{10} \text{ Hz}$, respectively. In the latter case the sample was placed at the end of a truncated coaxial cable. Details on these experimental pieces of apparatus can be found elsewhere [13, 14, 32–34]. The measurements covered the frequency interval between 10^{-2} Hz and 10 GHz, and were carried out at temperatures between 120 K and 350 K. The highest temperature was low enough to exclude any appreciable chemical reaction, which could change the properties of the sample. For all the measurements, the sample temperature was controlled by means of a conditioned flow of dry nitrogen with an accuracy of $\pm 0.1 \text{ K}$.

3. Results and discussion

Some representative spectra of the real $\varepsilon'(\omega)$ and the imaginary $\varepsilon''(\omega)$ parts of the dielectric constant for some temperatures above and below the glass transition temperature T_g are shown in figures 2 and 3, respectively. The value of ε' at high frequency approaches a value of about 2.4, which is characteristic of the completely unrelaxed dielectric constant in epoxy systems; accordingly, the presence of an appreciable dielectric relaxation process localized at higher frequencies can be excluded [13, 14, 16].

The spectra of ε'' clearly show the existence of three relaxation processes: (1) a main (or α -) relaxation, whose peak enters the experimental window at about 290 K and moves towards high frequencies with the increasing of temperature; (2) a secondary (or β -) process, active both in the glassy and in the liquid phase, which, due to its weaker temperature dependence, approaches more and more the α -relaxation as the temperature increases, but a merging is not observed up to the highest investigated temperature; (3) a third (or β' -) loss-peak well visible for temperatures between 174 K and 237 K, which is localized at frequencies intermediate between those of the α - and the β -relaxation peaks. Moreover, the contribution of dc conductivity is observable in the low frequency part of the spectra for temperatures above 298 K.

The dielectric spectra were analysed by a fitting procedure employing the Havriliak–Negami relaxation function (HN), which proved to be quite suitable for representing the dielectric response both in polymers and in low molar mass glass-forming liquids [13, 14, 16, 35]:

$$\varepsilon(\omega) = \frac{\Delta\varepsilon_i}{[1 + (i\omega\tau_i)^{1-\alpha_i}]^{\beta_i}} \quad (3)$$

where $\Delta\varepsilon_i$ is the relaxation strength, τ_i is the characteristic relaxation time and α_i and β_i are the shape parameters of the relaxation process labelled by the index, i .

In this study we used a linear superposition of HN functions to fit the overall relaxation spectrum. In recent years a raising debate was developed about the best way to combine the two relaxation functions $\Phi_\alpha(t)$ and $\Phi_\beta(t)$, which describe the α - and the β -relaxation, respectively, for representing the overall relaxation process. Beyond the usual linear superposition (i.e. $\Phi(t) = \Phi_\alpha(t) + \Phi_\beta(t)$), which implies a complete de-coupling between the two relaxations, another approach was proposed (Williams' *ansatz*), which uses the following function:

$$\Phi(t) = S(T)\Phi_\alpha(t) + [1 - S(T)]\Phi_\beta(t) \quad (4)$$

where $S(T)$ is the weight, assumed to be temperature dependent, of the α -process with respect to the whole relaxation [36]. Actually, it was demonstrated that results determined from the two fitting approaches appreciably differ only if the component peaks are less than two decades from each other (see [36] and references therein). In our case, the minimum spectral separation between α - and the β -peaks is more than two decades, consequently the superposition seems to be a physically very reasonable choice. Anyway, the issue is very open and need more precise checks.

The fitting procedure was performed simultaneously on the real and imaginary part data and the contribution of d.c. conductivity σ was taken in account by adding to the fitting function the term $-i\sigma/\omega\varepsilon_v$, ε_v being the vacuum dielectric constant.

For all temperatures no more than two relaxation processes are visible in the spectra: in fact, for $T < 240$ K only the β - and the β' -loss-peaks are observable inside the experimental window; for higher temperatures the contribution of the β' -relaxation is completely negligible with respect to the α - and the β -relaxations. Consequently, at any temperature the fitting function here used was a superposition of two HN functions plus, where necessary, the conductivity term.

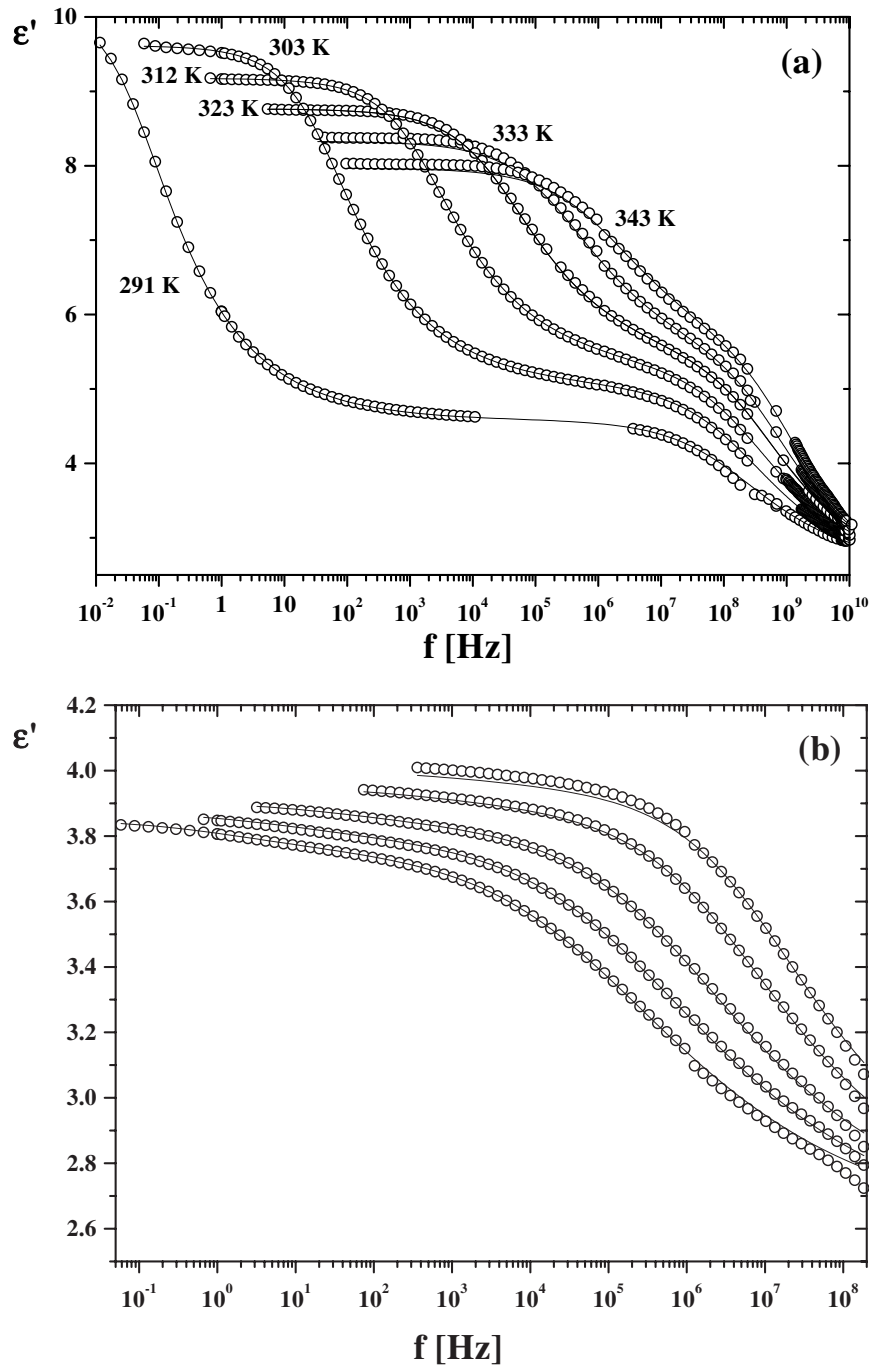


Figure 2. Real part ϵ' of the dielectric constant versus frequency at different temperatures (degrees Kelvin) both above (a) and below (b) the glass-transition temperature T_g (287 K). The solid lines are the fits obtained as the superposition of HN functions and the conductivity contribution (see the text).

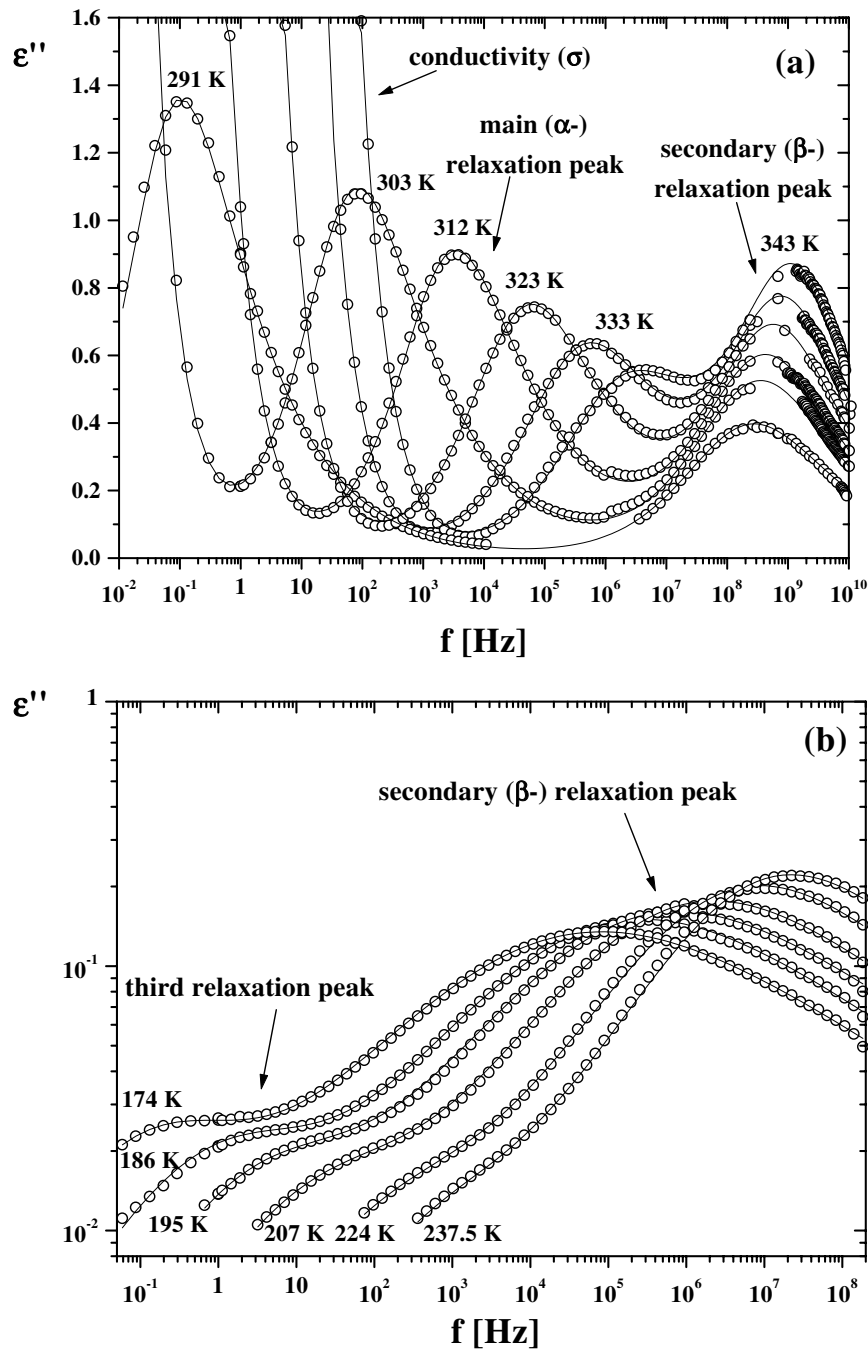


Figure 3. Imaginary part ϵ'' of the dielectric constant versus frequency at temperatures above (a) and below (b) T_g . For the spectra recorded at lower temperatures a log–log scale has been used in order to magnify the contribution of the third relaxation process. The solid lines represent the fits.

However, in order to allow a detailed comparison between the results obtained with the two approaches, also the analysis of the data according to Williams' *ansatz* is being performed, and the results will be presented in a forthcoming paper.

3.1. Characteristic relaxation times

The characteristic time of the main relaxation process, in the whole investigated temperature range, is well described by a VFT equation having the parameters $D = 6.08 \pm 0.22$ (thus the system is a fragile glass former), $T_0 = (245 \pm 1)$ K, $\tau_{02} = (2.47 \pm 0.95) \times 10^{-14}$ s (figure 4). From the VFT fit, it was possible to extrapolate the temperature behaviour of the α -relaxation time in order to determine the glass transition temperature T_g , conventionally defined as the temperature at which τ_α reaches 10^2 s. For our compound, T_g is (287 ± 3) K.

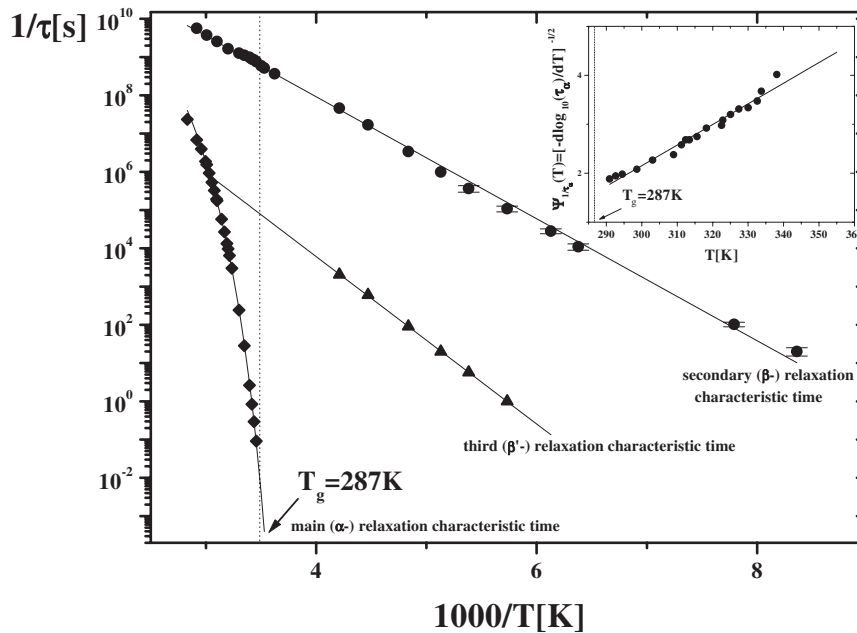


Figure 4. The inverse of characteristic relaxation times for the α - (diamonds), β - (circles) and β' - (up triangles) relaxation processes, determined in the range 290 K–343 K, 120 K–343 K and 174 K–237 K respectively, versus the reciprocal temperature, $1000/T$. The solid lines represent the fits by VFT for τ_α , and an Arrhenius law for τ_β and $\tau_{\beta'}$. The vertical line identifies T_g . The inset shows the Stickel-plot of the quantities $\Psi_{1/\tau_\alpha}(T)$ defined in the text. The solid line in the inset represents the fitting straight line, according to the equation $\Psi_x(T) = (DT_0 \log_{10} e)^{-1/2} (T - T_0)$.

A more sensitive analysis to check whether the temperature dependence of the time constant changes in the explored temperature interval was proposed by Stickel *et al* [20–22]. This analysis uses the quantity $\Psi_x(T) = [d \log_{10}(x)/dT]^{-1/2}$, which yields the following linear temperature dependence, provided that a VFT behaviour, $x = x_0 \exp[-DT_0/(T - T_0)]$, holds:

$$\Psi_x(T) = (DT_0 \log_{10} e)^{-1/2} (T - T_0). \quad (5)$$

This representation permits us to reveal changes in the dynamics in several glass-forming materials [13–15, 20–22]. The thus observed crossover temperature T_B , the splitting

temperature at which the characteristic time-scales of secondary and main relaxation process, respectively, definitely separate, and the critical temperature T_C predicted by MCT, appear to fall in the same temperature region as T_B [37, 38]. These findings support the idea of the existence of a narrow temperature interval, well above T_g , where the transport mechanisms in the supercooled liquid change. For TPMTGE, in the whole investigated temperature range, $\Psi_{1/\tau}(T)$ is approximately linear without any change in slope (see the inset in figure 4), therefore, if any change in dynamics occurred, it should be localized above the highest temperature measured. In fact, the crossover and the splitting temperature for most of the fragile glass-formers are usually located around $1.2\text{--}1.3 T_g$, but for TPMTGE, due to the chemical stability, the highest temperature investigated was $1.22 T_g$, so no prediction about dynamic transition can be cast in this system. Actually, by comparing the dynamics of TPMTGE with those of previously investigated epoxy systems [13, 14, 16], one can appreciate that, while the secondary relaxations have almost the same characteristic time scales, the α -process of TPMTGE is much slower, which produces a higher value of the glass transition temperature and a larger spectral separation between the main and the secondary process. So, the slowness of the α -relaxation is also mainly responsible for the fact that a complete merging of the main and the secondary process is not reached, even at the highest temperature to which the system can be driven without being damaged. Indeed, a particular splitting topology, in which no complete merging of the two relaxation processes occurs, was identified by Donth *et al* [39], who suggested that the onset of the main relaxation in a separate time scale respect to that of the secondary process can be caused by the existence of a minimal degree of molecular cooperativity necessary for it. In the present case, it is not possible to assign certainly the investigated system to that particular topology because, as for the change of the dynamic regime, a complete merging region could exist, even if being placed at too high temperatures with respect to those experimentally investigated.

The slowness of the dynamics of the main relaxation may be due to the more complex molecular structure of our compound, which produces a rise of the cooperativity and consequently a rapid slowing down of the structural dynamics with decreasing of temperature. Actually, in previous experiments [40] León *et al* found a direct relationship between the molecular weight of propylene glycol and its oligomers and the shape parameter, n , of the stretched exponential, $\Phi_\alpha(t) = \exp[-(t/\tau_\alpha)^{1-n}]$, which describes the main relaxation. Moreover, in the framework of the coupling model (CM) [28, 40, 41], Ngai and coworkers proposed a connection between the stretching parameter, n , and the degree of cooperativity. In fact, they supposed that only for times longer than a temperature-independent characteristic time (≈ 2 ps) intermolecular interactions have an influence on relaxation processes. Therefore, at shorter times the decay of polarization is well described by an exponential relaxation function, while at longer times a stretched exponential, $\Phi_\alpha(t) = \exp[-(t/\tau_\alpha)^{1-n}]$, is more suitable. So, the degree of cooperativity is characterized by the value of the stretching parameter, n : a higher n corresponds to a stronger cooperativity. Further experiments on the mono-, di- and poly-epoxy corresponding to TPMTGE are in progress in our laboratory, in order to check the predictions of Ngai's coupling model.

The temperature dependence of the characteristic times of the other relaxation processes of TPMTGE is weaker than the structural one. The time constant of the β' -relaxation exhibits an Arrhenius behaviour having a pre-exponential factor $\tau_{0\beta'} = (2.88 \pm 0.39) \times 10^{-13}$ s and an activation energy $\Delta E_{\beta'} = (41.9 \pm 0.3)$ kJ mol $^{-1}$. A third relaxation process was also observed in a similar tri-epoxy compound [14], but in that case it appeared as coupled to the structural dynamics. In TPMTGE, in contrast, the relaxation follows an ARR law like a secondary relaxation, and it is probably related to an internal degree of freedom of the quite complex molecule.

Concerning the β -relaxation, the relaxation time τ_β can be fitted by an Arrhenius equation providing a pre-exponential factor $\tau_{0\beta} = (4.57 \pm 0.69) \times 10^{-15}$ s and an activation energy ΔE_β of (30.6 ± 0.3) kJ mol $^{-1}$, close to the values observed for secondary relaxation processes in other epoxy compounds [13, 14, 16].

Another intriguing feature of the α - β scenario is the constancy of the ratio $\Delta E_\beta/RT_g$, between the activation energy, ΔE_β , and the glass transition temperature, T_g (R is the molar gas constant), for a set of different epoxy compounds [13, 14, 16]. We find

$$\frac{\Delta E_\beta[\text{kJ mol}^{-1}]}{RT_g[\text{K}]} \simeq 13. \quad (6)$$

In particular for TPMTGE, $\Delta E_\beta/RT_g = 12.8$. A similar phenomenological relationship was previously suggested by Rössler and coworkers [10–12]. However, there a ratio $\Delta E_\beta/RT_g \simeq 24$ was found for a large group of glass formers, where most of the systems comprised rigid molecules, and consequently the secondary relaxations observed there should be Johari–Goldstein processes. Thus, it is not evident whether one has to discriminate different classes of glass formers, on the basis of different rigidity of the molecules, or whether the relationship between ΔE_β and T_g cannot be generalized. One may also speculate whether the β' -relaxation observed here is the actual Johari–Goldstein process (for this process $\Delta E_{\beta'}/RT_g \simeq 18$ is found).

3.2. Conductivity

Classical hydrodynamics is based on the fact that microscopic time-scales and lengths of the liquid molecules, among which the diffusion takes place, are many orders of magnitude smaller than those characteristic of the moving particle. Under such a hypothesis, the Fokker–Planck equation for the conditioned probability of the position of the particle reduces to a diffusion equation, in which the translational diffusion coefficient D is connected to viscosity η by the Stokes–Einstein equation: $D \propto \eta^{-1}T$ [42]. According to the Einstein equation, $D \propto \sigma T$, the conductivity is proportional to the inverse of the shear viscosity:

$$\sigma \propto \eta^{-1}. \quad (7)$$

This result leads to the conclusion that also the conductivity should have a super-Arrhenius temperature behaviour. Conductivity data of TPMTGE in the temperature range 299–343 K are shown in figure 5 as taken from the fits in figure 2. They are well fitted by a VFT-like equation, $\sigma(T) \propto \exp[-D_\sigma T_\sigma/(T - T_\sigma)]$, having the following parameter values: $D_\sigma = (5.50 \pm 0.99)$ and $T_\sigma = (238 \pm 6)$ K. Within the experimental errors, the value of both the strength parameter, D_σ , and the Vogel temperature, T_σ , seems to agree with those obtained for the main relaxation time data. This result is mainly just a consequence of the uncertainty of the VFT fit because, as shown in the next subsection, actually the conductivity and the α -relaxation characteristic time do not have the same temperature dependence.

The temperature behaviour of the quantity $\Psi_\sigma(T)$ (cf equation (5)), is linear and no change of slope is observable (inset in figure 5), thus confirming the analogous result for $\Psi_{1/\tau}(T)$, that a single VFT law is able to describe the experimental data in the whole investigated temperature range.

3.3. Relation between relaxation time and conductivity

By taking into account equation (7) and the Debye–Stokes result, $\tau \propto \eta T^{-1}$ [43], a link between the conductivity and the main relaxation time, expressed by the following Debye–

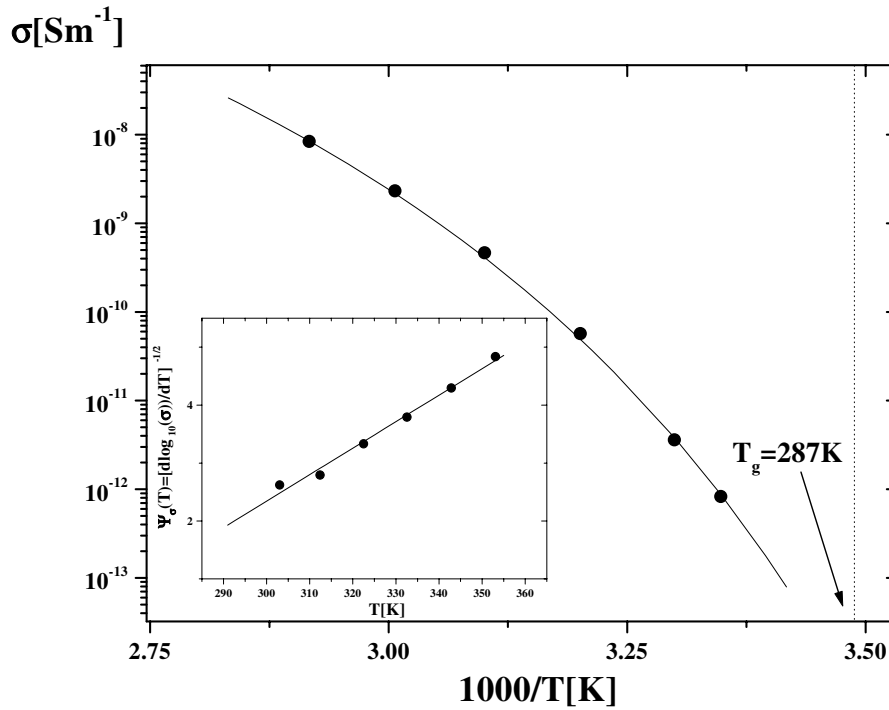


Figure 5. The dc conductivity versus the reciprocal temperature $1000/T$, with the solid line representing the VFT fitting function superimposed. The inset shows the Stickel-plot of the quantities $\Psi_\sigma(T)$, with the superimposed solid line representing the fits according to $\Psi_x(T) = (DT_0 \log_{10} e)^{-1/2} (T - T_0)$.

Stokes–Einstein equation (DSE), is obtained:

$$\sigma \tau = \frac{\text{const}}{T}. \quad (8)$$

Usually, if the previous expression is applied to supercooled liquids the T^{-1} dependence is neglected because of the much stronger temperature dependence of σ and τ . However, many relaxation experiments showed that DSE diffusion regime is not verified in supercooled liquids approaching the glass transition [14, 15, 37, 44–53] and, in some cases, the conductivity and the relaxation time are connected by a fractional DSE law:

$$\sigma \tau_\alpha^s = \text{const}. \quad (9)$$

Among other experimental techniques, dielectric spectroscopy allows a cogent check of the DSE model [13–15] as both conductivity and main relaxation time can be determined by the same spectra, so avoiding systematic error. The data of the conductivity, σ , and of the relaxation time, τ_α , of TPMTGE were fitted by using equation (9), obtaining the fractional value $s = (0.741 \pm 0.008)$ (figure 6).

Even if this behaviour were observed in several systems [14, 15, 50, 52–54], a comprehensive explanation of its origin is still not available. The fractional DSE law can be derived by a free-volume [23–25] calculation, provided that the exponent, s , represents the ratio between the critical sizes necessary for translational and rotational diffusion, respectively. However, the free-volume concept does not provide any explanation of why a difference between the translational and rotational critical volumes exists. Also in the framework of

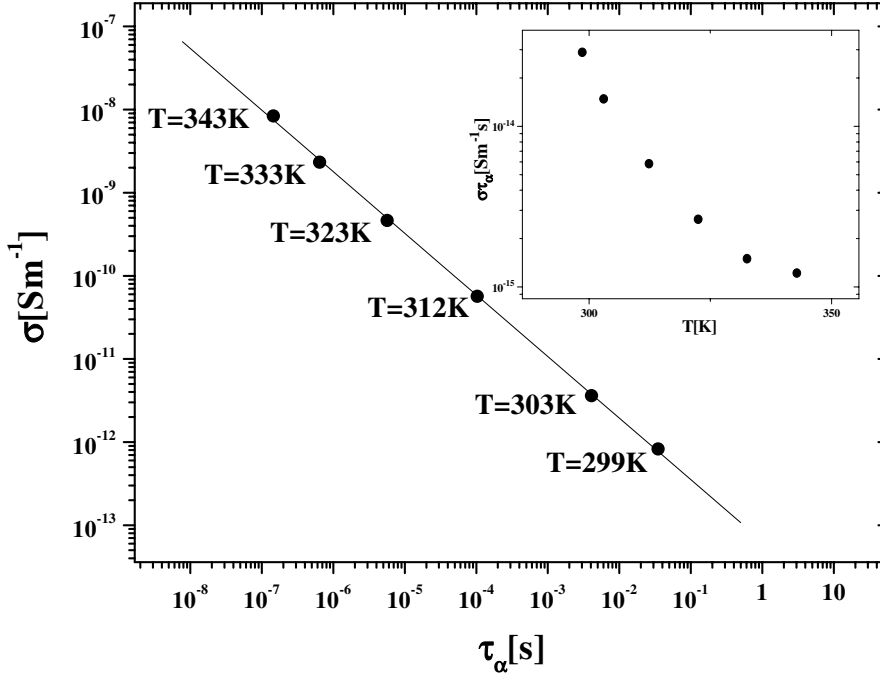


Figure 6. Log–log plot of the conductivity σ versus the main characteristic relaxation time τ_α at several temperatures. The solid line represents the fitting function according a fractional DSE law (see the text). The inset shows the temperature dependence of the product $\sigma\tau_\alpha$, which is not constant as temperature is varied.

cooperativity theories, some pictures were proposed in order to explain why translational motion is easier than rotational one [55]. Moreover, several other efforts, based on different approaches, have been performed [48, 51, 56–58].

3.4. Relaxation strengths

The overall strength and the partial strengths of the three observed relaxation processes are shown in figure 7. The temperature behaviour of both the total relaxation strength, $\Delta\varepsilon(T)$, and the main one, $\Delta\varepsilon_\alpha(T)$, is well described by the equation (in which $T > T_g$)

$$\Delta\varepsilon(T) = a + b/T \quad (10)$$

which describes the temperature dependence of the relaxation strength in many glass formers including epoxy compounds [13–16]. The fit of the overall strength data of TPMTGE by equation (10) provides $a = -6.59$ and $b = 4.13 \times 10^3$ K, and that of the structural relaxation strength yields $a = -15.99$ and $b = 6.26 \times 10^3$ K. The fact that the parameter a is not equal to zero indicates that the interactions among dipoles in the system are not negligible, which is confirmed by the estimate of the Kirkwood correlation factor g_K , according to the equation

$$g_K = \frac{9k_B T (\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)}{4\pi N \mu^2 \varepsilon_0 (\varepsilon_\infty + 2)^2} \quad (11)$$

where N is the density of dipoles of moment μ of the system; k_B is the Boltzmann constant and ε_0 and ε_∞ are the static and the high frequency limit of ε' , respectively. As expected, the

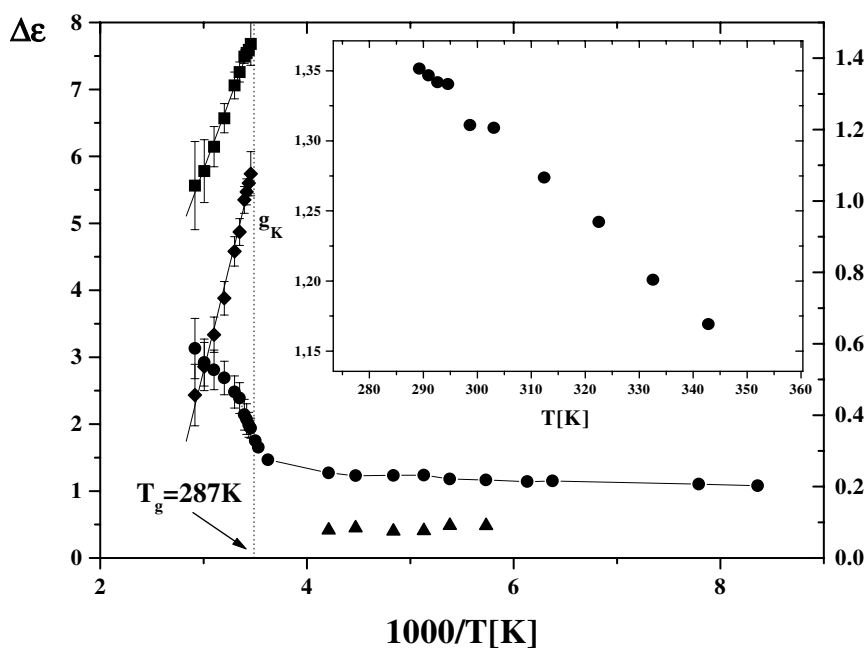


Figure 7. Strengths of the overall (squares), the α - (diamonds), the β - (circles) and the β' - (up triangles) relaxation process, versus the reciprocal temperature $1000/T$. The β' - (up triangles) data are referred to the right axis. The solid lines superimposed to the overall and the main relaxation data represent a fit by the function, $a + b/T$, the parameters of which are in the text. In contrast, the solid line on the secondary relaxation data is a guide for the eyes only. The vertical dotted line corresponds to the glass-transition temperature T_g . The inset shows the temperature dependence of the Kirkwood correlation factor g_K , estimated by equation (11) with $N \approx 4 \times 10^{21}$ and $\mu \approx 2.2$ Debye. In this plot we did not report the error bars, as the calculation of g_K is already approximate.

Kirkwood factor decreases with temperature towards unity, as the correspondent degree of the orientational correlation decreases (inset in figure 7).

In contrast to the strength of the main relaxation, the strength of the β -relaxation increases with temperature with a rate becoming significantly higher at temperatures above T_g . This result is an indication that the glass-transition of epoxy resins, besides the α -relaxation, strongly affects also the β -relaxation. A complete explanation of its phenomenology should help to understand the connection between the secondary relaxation and the microscopic mechanism, which influences the structural dynamics of the systems.

3.5. Shape parameters

The shape of the relaxation function is directly determined by the molecular interactions in the supercooled liquid. Therefore, the observation of the temperature behaviour of the shape parameters will assume particular importance if one looks at molecular interactions responsible of the cooperative mechanism driving the liquid to the glassy state.

The shape of HN relaxation function is ruled by two parameters m and n , which are the exponent of the low and the high frequency power law of $\varepsilon''(\omega)$, respectively [59], and are related to α - and β -parameters appearing in equation (3) by the simple relations $m = 1 - \alpha$ and $n = (1 - \alpha)\beta$. As a consequence, the temperature behaviour of m and n accounts for the long-range and the short-range (i.e. local) molecular interactions, respectively.

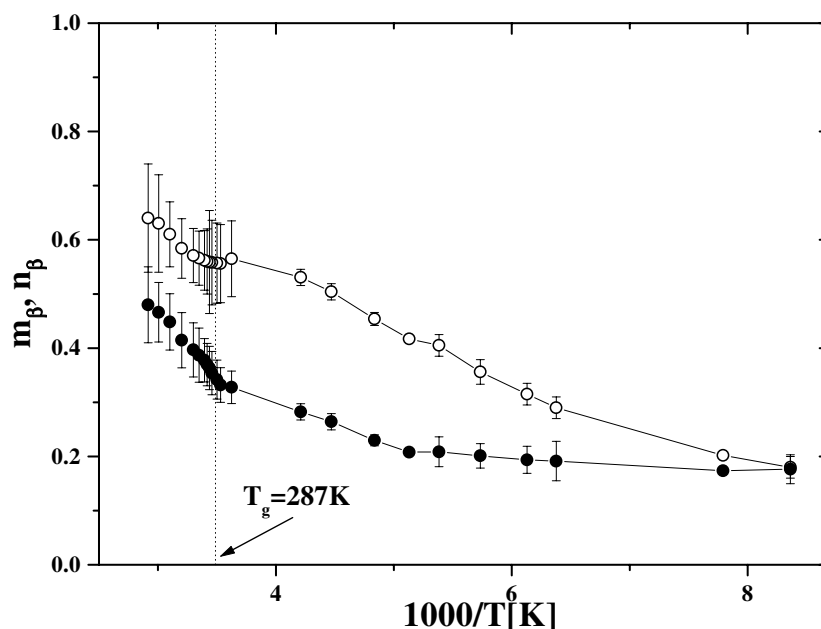


Figure 8. Shape parameters m_β (open circles) and n_β (solid circles) of the secondary frequency-domain relaxation function versus the reciprocal temperature $1000/T$. Their temperature dependence becomes more evident at temperatures higher than the glass-transition temperature T_g (indicated by the dotted vertical line).

In our system, both the shape parameters, m_β and n_β of the secondary relaxation increase with temperature (figure 8), approaching a Debye-like process ($m = n = 1$) as temperature increases. It is noteworthy that the rise becomes more appreciable for $T > T_g$, as occurred for the relaxation strength. The fact that not only the strength, but also the shape, of the β -relaxation is strongly affected by the glass transition was previously observed also in other epoxy systems [13, 14, 16]. This feature appears to be a further indication that a connection between the β -relaxation behaviour and the glass transition undoubtedly exists.

4. Conclusion

The dynamics of the tri-epoxy system, TPMTGE, was studied by performing a complete dielectric analysis on the data acquired over 12 decades. The approach of analysing all the dielectric parameters, i.e. relaxation times, conductivity, strengths and shape parameters, proved to be a powerful tool for studying the supercooled liquids near the glass transition. As it concerns the secondary relaxation, we observed changes in the temperature behaviour of the relaxation strength and of the shape parameters in proximity of T_g , which support the idea that not only the structural dynamics, but also the local motion, with which the β -process is associated, can be influenced by the glass transition. A single VFT dynamics of the main relaxation was observed, and the fractional DSE diffusive regime was proved to be valid throughout the investigated temperature range. These results are coherent with previous findings about changes of dynamics in similar supercooled epoxy systems [13–16].

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