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Dielectric relaxation of 2-ethyl-1-hexanol around the glass transition by thermally stimulated depolarization currents

S. Arrese-Igor,¹ A. Alegría,^{1,2} and J. Colmenero^{1,2,3}

¹Centro de Física de Materiales (MPC), Centro Mixto CSIC-UPV/EHU, Paseo Manuel Lardizabal 5, 20018 San Sebastián, Spain

²Departamento de Física de Materiales UPV/EHU, Apartado 1072, 20080 San Sebastián, Spain

³Donostia International Physics Center, Paseo Manuel Lardizabal 4, 20018 San Sebastián, Spain

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We explore new routes for characterizing the Debye-like and α relaxation in 2-ethyl-1-hexanol (2E1H) monoalcohol by using low frequency dielectric techniques including thermally stimulated depolarization current (TSDC) techniques and isothermal depolarization current methods. In this way, we have improved the resolution of the overlapped processes making it possible the analysis of the data in terms of a mode composition as expected for a chain-like response. Furthermore the explored ultralow frequencies enabled to study dynamics at relatively low temperatures close to the glass transition (T_g). Results show, on the one hand, that Debye-like and α relaxation timescales dramatically approach to each other upon decreasing temperature to T_g . On the other hand, the analysis of partial polarization TSDC data confirms the single exponential character of the Debye-like relaxation in 2E1H and rules out the presence of Rouse type modes in the scenario of a chain-like response. Finally, on crossing the glass transition, the Debye-like relaxation shows non-equilibrium effects which are further emphasized by aging treatment and would presumably emerge as a result of the arrest of the structural relaxation below T_g . © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4921655>]

I. INTRODUCTION

Hydrogen bonding has significant impact on the structure, the thermodynamics, and the dynamics of many important fluids with biological or technical applications. Due to the polar nature of these systems, dielectric relaxation is often used to study their behavior and properties. Special attention has long been paid to the strong electrical absorption, commonly referred to as Debye-like relaxation, shown by several liquids containing hydrogen bonds like monohydroxy alcohols (MAs) or secondary amides.^{1,2} The amplitude of this Debye-like relaxation exceeds the value expected on the basis of the molecular dipole moments contained in the samples, and it is more intense and slower than the non-exponential structural relaxation. It is broadly believed that the origin of the Debye-like relaxation is related to supramolecular structures or aggregates resulting from hydrogen bond interaction, although the detailed mechanism is still under debate.¹ The typical morphology of these supramolecular clusters in MA would be chain-like and ring-like structures as identified from computer simulations, with the majority of molecules forming chain-like aggregates.³⁻⁷ The size of these aggregates would predominantly be between 4 and 10 units although it is difficult to state a precise number due to the large variety of different aggregate lengths and types generally observed, with non-negligible populations of chains well above 10 units. Intermolecular orientational correlations can be indirectly assessed determining experimentally the Kirkwood correlation factor g_k sizing the deviations of the dielectric constant from the expectation on the basis of Onsager's theory, which assumes that the short-ranged orientational

correlations are negligible. $g_k > 1$ in hydrogen bonded liquids is interpreted as indicative of parallel alignment of dipoles forming chain-like structures, while $g_k < 1$ is understood as indicative of anti-parallel alignment as it would occur for ring-like structures. The first clue pointing to the formation of chain-like structures was the early observation of g_k values exceeding 1 in several MA exhibiting strong Debye-like relaxations.⁸ The observation of the Debye-like process by other techniques than dielectric relaxation has long remained elusive. Recent investigations, however, have reported the observation of the Debye-like relaxation by light scattering⁹ and the presence of a low frequency mode in addition to the structural relaxation by shear-modulus investigations.^{10,11} Gainaru *et al.* first and Hecksher *et al.* later found evidence for a short-chain polymer like rheological response on MAs which would be related to the Debye-like dielectric relaxation.^{10,11} The former authors identified the studied 2-ethyl-1-hexanol (2E1H) as short-chain polymeric liquid and used the analogy with linear polymers to estimate—by applying the Rouse model for chain dynamics¹²—the size of the hydrogen bonded aggregates, which turned to be around 9 units. The Rouse model¹² (the simplest approach for non-entangled polymeric chain dynamics) predicts the correlation function of the end-to-end vector $\vec{R}(t)$ to be

$$\langle \vec{R}(t) \cdot \vec{R}(0) \rangle \propto \sum_{p:odd}^{N-1} \cot^2\left(\frac{p\pi}{2N}\right) \exp\left(-\frac{t}{\tau_p}\right), \quad (1)$$

where N is the number of beads and τ_p is the relaxation time associated with the p th Rouse mode, which scales as $\tau_p = \tau_{p=1}/p^2$ in the relevant low- p range. By analogy with

polymer chain dynamics, the Debye-like relaxation could be nothing more than the signature of MA's chain-like relaxation, i.e., an analogous to polymers' normal mode (NM) relaxation. To time, most Debye-like relaxations have been reported to be "pure" Debye type, i.e., to correspond to a single exponential relaxation, in contrast to the expectation on the basis of a Rouse like chain dynamics. The absence of a multimode relaxation, however, is not at odds with the existence of chain-like aggregates, as the relaxation of the net end-to-end dipolar moment of the chain could effectively take place through another faster process. In the transient chain model proposed by Gainaru *et al.*,¹³ the successive loss and or gain of segments at the ends of the chain aggregates would ultimately relax the end-to-end net dipole of the chain. More generally, in the framework of molecular relaxations in fluctuating environments¹⁴ or in association-dissociation situations,¹⁵⁻¹⁷ the probability of the molecular relaxation and its time dispersion will depend on the relative timescales of the different dynamical processes involved. In spite of these results, Wang *et al.*¹⁸ reported non-pure Debye behavior for the prominent and slowest relaxation component in 2-butyl-1-octanol and 2-hexyl-1-decanol, two relatively long alkyl chain MA, which could be indicative of the Rouse-like chain dynamics.

From a practical point of view, the detailed study of the dispersion of characteristic times on the Debye-like and α relaxation by broadband dielectric spectroscopy (BDS) may be difficult due to the overlap of the typically much more intense Debye-process with the structural relaxation, leading to uncertainties in the determination of the dynamical parameters characterizing these dynamical processes. According to recent data,¹⁹ the timescale separation between these two processes varies non-monotonously as a function of temperature, but uncertainties in delineating the position (and shape) of the α relaxation can be high, specially at high and low temperatures where the two processes seem to overlap. Motivated by these difficulties, here, we explore new routes for characterizing the Debye-like and α relaxation by low frequency dielectric techniques. These include mainly the use of thermally stimulated depolarization current (TSDC) techniques and isothermal depolarization current (IDC) method. TSDC is a powerful tool²⁰ facilitating the resolution of overlapped processes, either because their response may show narrower than in a standard BDS experiment or because the weight of each process can be varied by means of partial polarization protocols. Likewise, TSDC explores ultralow frequencies allowing to study dynamics at relatively low temperatures close to the glass transition where the characterization of the Debye-like and the α relaxation is especially difficult and scarce. In particular, we have investigated the effect that different structural glassy states (samples with and without aging) have on the dynamics of the Debye-like and α relaxations on crossing the glass transition during a heating treatment. Finally, TSDC technique is very well suited for the detailed and precise study of the possible dispersion of relaxation times in the Debye-like process, and provides a natural way to analyze the mode composition of a chain-like response, as it has been recently demonstrated.^{21,22} With these ideas in mind, we have investigated here the dielectric response of the extensively studied 2E1H as an archetype of MAs to illustrate the potential application of

the experiments proposed for investigating the behavior of the Debye-like relaxation around the glass transition. Another goal of this work will be exploring to which extent the analogy of polymer chain dynamics is compatible with that of the chain-like aggregates formed by MAs.

II. EXPERIMENTAL DETAILS

2E1H was purchased from Aldrich and directly used without further processing. A parallel plate capacitor was prepared by sandwiching the alcohol between two gold-plated electrodes with 0.25 mm Teflon spacer thin strips in a specific liquid cell. Results were corrected from stray capacitance and area of the Teflon strips. IDC, TSDC, and BDS experiments were carried out on commercial Novocontrol set-ups, where the temperature was controlled by a nitrogen-jet stream. In the case of BDS experiments, isothermal measurements between 120-300 K were done with a temperature stability of ± 0.1 K. IDC experiments were conducted at temperatures between 155 and 142 K. TSDC experiments were performed at 3 K/min constant heating and cooling rates using a polarizing voltage of 150 V. Several experiments were done varying the voltage and the thickness of the sample to ensure that under the experimental conditions used, the response remains in the linear regime, i.e., that results do not depend on the applied field except for an amplitude factor proportional to the field. Calorimetric characterization of the sample was done at the same heating rate of the TSDC experiments and determining the reversible part of the heat capacitance by temperature modulated Differential Scanning Calorimetry (DSC).

A TSDC experiment consists on first, polarizing the sample at high temperature $-T_{on}$ - (where particular dipolar entities are mobile), then freezing-in the orientational polarization by cooling down the sample with the field on, switching-off the field at low temperature $-T_{off}$ -, and finally recording the electric current due to the thermally stimulated release of the polarization during a subsequent linear heating. When a sample is fully polarized after the first and second steps, the measured current contains contributions from all the dielectrically active relaxations, and the experiment is referred to as a *global* polarization TSDC experiment. By varying the temperature at which the field is switched-on and -off during cooling, it is possible to suppress the contribution of slow or fast relaxing entities to the subsequent depolarization current curve, and in this way, try to isolate the response of a certain process of interest. This is referred to as a *partial polarization* (PP) TSDC experiment.

For comparison with the experimental results, the depolarization current produced by a certain relaxation process, $I = -dQ/dt$, can be numerically calculated using a general stretched-exponential Kohlrausch-Williams-Watts (KWW) relaxation function for the charge, Q , and the reduced time formalism²³ as

$$Q(t, T) = Q_0 \exp \left[- \left(\int_{t_{off}}^t \frac{dt'}{\tau_p(t')} \right)^\beta \right], \quad (2)$$

where t_{off} is the time when the field is switched-off and β is the stretching parameter of the KWW function. In order to

generate the response equivalent to a PP-TSDC experiment or the presence of more than one process, the superposition principle applies so that

$$Q(T) = \sum_j Q_o^j \left\{ \exp \left[- \left(\int_{t_{off}}^t \frac{dt'}{\tau_j(t')} \right)^{\beta_j} \right] \right. \quad (3)$$

$$\left. - \exp \left[- \left(\int_{t_{on}}^t \frac{dt'}{\tau_j(t')} \right)^{\beta_j} \right] \right\}, \quad (4)$$

where the index j stands for the different types of relaxations and t_{on} for the time when the field is switched-on. On the other hand, by analyzing the experimentally recorded depolarization current of a process, one can extract the T-dependence of its characteristic times $\tau_{TSDC}(T)$ as²⁴

$$\tau_{TSDC}(T) = \beta \frac{Q(T)}{I(T)} \left[\ln \frac{Q_o}{Q(T)} \right]^{(1-1/\beta)}, \quad (5)$$

where

$$Q(T) = \frac{1}{q} \int_T^{T_{end}} I(T') dT', \quad (6)$$

and T_{end} is the temperature of the end of the heating ramp.

On the other hand, the information contained in a BDS experiment is generally extracted by fitting the measured permittivity to a sum of several relaxation processes (j) modeled by a Havriliak-Negami (HN) function—in the most general case—plus some dc-conductivity term when necessary,

$$\begin{aligned} \epsilon^*(\omega) &= \epsilon'(\omega) - i\epsilon''(\omega) \\ &= \epsilon_\infty + \frac{\sigma_{dc}}{i\omega\epsilon_o} + \sum \frac{\Delta\epsilon_j}{(1 + (i\omega\tau_j)^{a_j})^{b_j}}, \end{aligned} \quad (7)$$

where σ_{dc} refers to dc-conductivity and ϵ_∞ and ϵ_o to the high and low frequency limits of the dielectric constant, respectively. Each process j is characterized by its relaxation strength $\Delta\epsilon$, its relaxation time τ , and the shape parameters a and b , which determine the broadening and asymmetry of the loss curve with $0 < a, b \leq 1$.

Although the case of 2E1H is not a particularly tough one, in general, the former analysis applied to MAs can be difficult due to the overlap of a strong Debye-like process with a relatively small intensity α relaxation, in addition to the low frequency conductivity contribution. In order to minimize the uncertainty in the determination of the parameters characterizing the α relaxation and its possible influence on the resolved width of the Debye-like process, in addition to the widespread method reflected in Eq. (7), we decided to extract information also from the derivative analysis of the real part of the dielectric permittivity. Derivative representation of the data helps to resolve strongly overlapped processes as they show narrower.²⁵ In order to translate the advantages of this representation also to the fitting procedure and at the same time preserve the widespread empirical relaxation models for permittivity, the derivative of the real permittivity was fitted to the analytical derivative of these empirical relaxation functions, i.e.,

$$\frac{d\epsilon'(\omega)}{d\log\omega} = \text{Re} \left\{ \frac{1}{\log e} \sum \frac{\Delta\epsilon_j a_j b_j (i\omega\tau_j)^{a_j}}{[1 + (i\omega\tau_j)^{a_j}]^{(b_j+1)}} \right\}. \quad (8)$$

Although the use of the derivative representation is not uncommon in the literature,²⁶ to our knowledge the derivative fitting approach has been scarcely exploited or not at least preserving the standard functional forms. For both fitting approaches, analysis of the real and imaginary parts by Eq. (7) and analysis of the derivative of the real part by Eq. (8), the same model for the permittivity was used. In the first instance, the functional shape for the Debye-like relaxation was left completely free (HN) and later on fixed to a Cole-Davidson (CD) ($a = 1$) functional form driven by the output of the first fitting. For the structural α relaxation, as this is known to be well described by an stretched-exponential relaxation function in the time domain, a KWW equivalent Havriliak-Negami (KWW_{HN}) function²⁷ was used, where the a and b shape parameters of the HN function are related to each other as $b = 1 - 0.8121(1 - a)^{0.387}$, and the equivalent stretching parameter is $\beta \simeq (a * b)^{0.813}$.

Finally, IDC data were analyzed in the conventional way fitting the resulting peak in $t * I$ to the corresponding expression for the case of a KWW relaxation,²⁸

$$I * t \propto t \frac{\beta}{\tau^\beta} \left[t^{(\beta-1)} e^{-(t/\tau)^\beta} - (t + t_p)^{(\beta-1)} e^{-((t+t_p)/\tau)^\beta} \right], \quad (9)$$

where t_p stands for the polarization time.

III. RESULTS

A. On the possible dispersive nature of the Debye-like process in 2E1H: PP-TSDC experiments

Until now, most Debye-like relaxations and that of 2E1H in particular have been reported to be “pure” Debye type, i.e., to correspond to a single exponential. This would rule out the presence of higher order modes (see Eq. (1)) for MAs in contrast to the expectation on the basis of a Rouse like chain dynamics used to interpret mechanical data. 2E1H displays a very prominent Debye-like relaxation with a value of g_k close to 5 at low temperatures,²⁹ strongly supporting the idea of the formation of chain-like aggregates, and thus being a good candidate to study the possibility of chain-like multimode relaxation. As commented in the Introduction, TSDC technique is very well suited for the detailed and precise study of the possible dispersion of relaxation times in the Debye-like process, and provides a natural way to analyze the mode composition of a chain-like response.^{21,22} For this purpose, a series of TSDC experiments were carried out where the polarizing field was switched-on at a sufficiently high temperature for the Debye-like process to be fully polarized, whereas T_{off} was systematically varied to later eliminate the contribution of faster modes. Figure 1(a) shows depolarization currents for 2E1H obtained by varying the polarizing temperature window. Contrary to the typical multimode chain response behavior in polymers,²¹ current curves do not narrow as T_{off} increases indicating the presence of a single exponential mode. Figure 1(b) compares the experimentally measured depolarization current for $T_{off} = 146$ K (a window broad enough to include the response of higher order modes) with the predictions of the Rouse model for the response of the $p = 1$ mode and the sum of

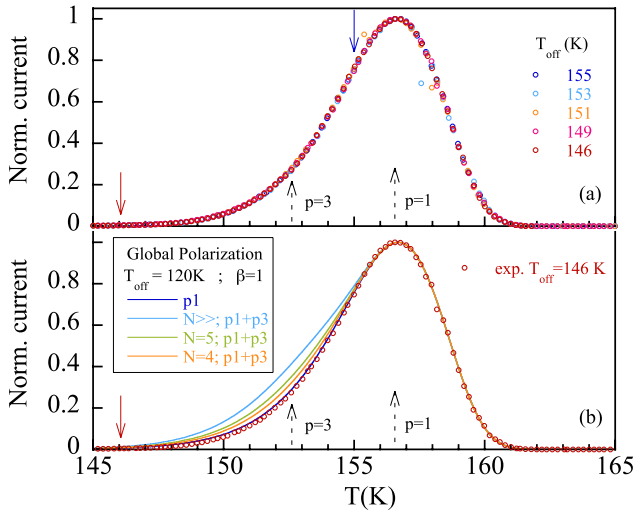


FIG. 1. Depolarization current curves measured for 2E1H with constant T_{on} and increasing T_{off} between 155 and 146 K (indicated with solid arrows). Lines in (b) represent depolarization current curves calculated within the Rouse model for various chain lengths considering only the first ($p = 1$) or the sum of the two first ($p = 1$ and $p = 3$) terms.

the first two modes ($p = 1$ and $p = 3$) for very large chains, and short chains of 5 and 4 units.³⁰ Calculated depolarization currents considering more than one Rouse mode are clearly broader than that experimentally recorded, which in turn is very well described by the current calculated under a single and exponential (Debye) mode.

B. Structural relaxation of 2E1H

Although there was a time when the prominent and slowest Debye-like dielectric relaxation of MAs was linked to the α relaxation of the liquid, nowadays it is well established that this is not the case and that the structural relaxation manifests as a more or less resolved low intensity shoulder at the high frequency side of the Debye-like relaxation. Figure 2 shows as an example a BDS frequency sweep of 2E1H at 180 K: (a) $\epsilon''(\omega)$; (b) $\epsilon'(\omega)$ on the left axis and $d\epsilon'(\omega)/d\log f$ on the right axis; and (c) $d\epsilon'(\omega)/d\log f$. A prominent process corresponding to the Debye-like relaxation is observed at low frequencies together with an approximately two orders of magnitude smaller α relaxation at higher frequencies. Derivative representation of the real part helps to best resolve these two processes (panels (b) and (c)). In this way, the α relaxation is manifested as a clearly separated peak so that peak frequency can be determined with much less uncertainty.

When using TSDC, due to the relatively low intensity of the α relaxation the differences between a global depolarization current response (containing all contributions) and that of a PP polarization experiment designed to isolate the response of the Debye-like relaxation are better highlighted in a logarithmic representation. The depolarization intensity obtained when the field is switched-off 2 K below the maxima of the global TSDC experiment (empty symbols in Figure 3(a)) is clearly different from that of a global experiment (filled symbols). The intensity difference at low temperatures between these two experiments is ascribed to the contribution

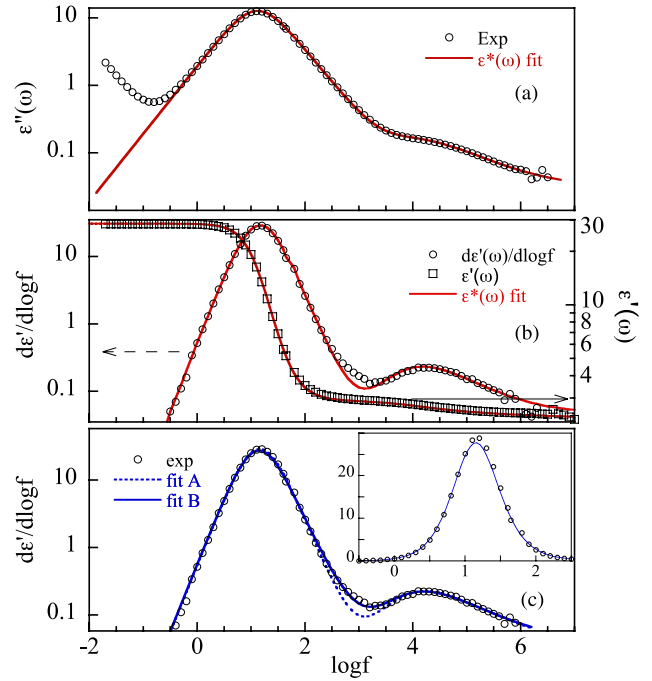


FIG. 2. BDS sweep at 180 K. (a) \circ : $\epsilon''(\omega)$; lines: fits of $\epsilon^*(\omega)$. (b) \square : $\epsilon'(\omega)$ on the right axis, \circ : $d\epsilon'(\omega)/d\log f$ on the left axis, and lines: fit of $\epsilon^*(\omega)$. (c) \circ : $d\epsilon'(\omega)/d\log f$; lines: fits of $d\epsilon'(\omega)/d\log f$; inset: detail of the quality of fit B at the linear scale.

of the α relaxation to the global depolarization current. A series of PP-TSDC experiments with decreasing polarization temperature T_{on} were performed with the aim of resolving the structural α relaxation by decreasing the contribution of slower relaxation components. Figure 3(b) shows the results of such experiments where T_{off} was maintained constant at 120 K. It can be seen that as T_{on} decreases, the Debye-like contribution decreases and the depolarization current shows a clear bimodal response. The position of the maxima of

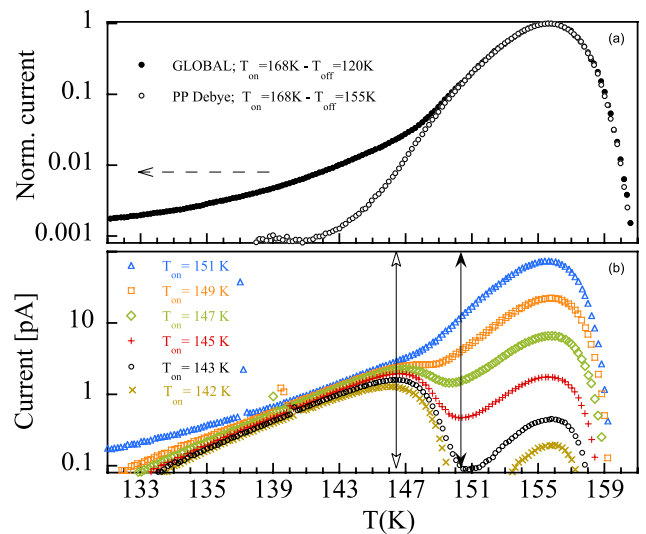


FIG. 3. Depolarization currents for 2E1H. (a) Global experiment \bullet and PP-TSDC experiment \circ designed to reflect only the response of the Debye relaxation. (b) Evolution of the depolarization current upon decreasing T_{on} . Vertical arrows indicate calorimetric glass transition at the onset (empty) and maximum change (filled) of the reversible calorimetric heat flow.

the high temperature peaks corresponding to the Debye-like contribution do not move upon decreasing T_{on} , as it is expected for a pure exponential relaxation. Consistent with the assignment of the low temperature peak to the α relaxation, the location of this peak resolved by decreasing T_{off} matches very well calorimetric glass transition.

C. T-evolution of timescales

Characteristic times for the Debye-like and α relaxation were determined from BDS, IDC, and TSDC measurements. In the case of BDS, these were obtained model-free, i.e., directly reading the position of the maxima from the $d\epsilon'/d\log f$ representation. The so obtained values are included in Figure 4(a) by dark filled symbols. IDC data were analyzed by means of Eq. (9) and the resulting characteristic times are represented by white filled symbols in the same figure. The characteristic times obtained isothermally by BDS and IDC measurements for both Debye-like and α -relaxation were fitted to a standard Vogel Fulcher Tamman (VFT) equation,³¹ which have been represented by solid lines in Figure 4(a).

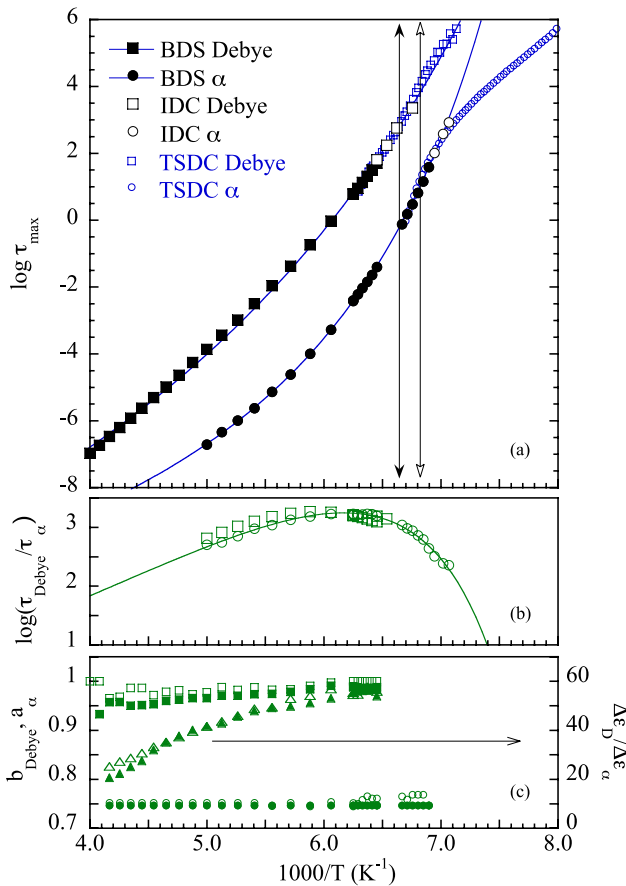


FIG. 4. (a) Characteristic times obtained from BDS data (dark filled symbols), IDC data (white filled symbols), and TSDC data (empty symbols). Lines correspond to VFT fits of BDS and IDC data all together. Empty and filled arrows represent calorimetric T_g at the onset and maximum change of the reversible heat flow, respectively. (b) τ_{Debye}/τ_α ratio, symbols, experimental data, and line values from fitted VFT laws. (c) $\Delta\epsilon_{Debye}/\Delta\epsilon_\alpha$ ratio (triangles), shape parameter for the Debye-like b_{Debye} (squares) and α relaxation a_α (circles). Filled symbols correspond to fits on ϵ^* and empty symbols to fit A on $d\epsilon'(\omega)/d\log f$.

When comparing the timescales of both relaxations, as it can be seen in Figure 4(b), the temperature variation of the τ_D/τ_α ratio is non-monotonous. Previously reported in the literature, the tendency of the timescales of the two processes to approach each other at high temperatures¹⁹ is here corroborated. Moreover, the low frequency data obtained here evidence a much stronger variation at low temperatures close to the glass transition with a marked tendency of both times scales to approach to each other.

In the case of TSDC measurements, characteristic times for the Debye-type process were extracted by means of Eq. (5) and assuming $\beta = 1$ from the experimentally recorded non-isothermal depolarization current curve, particularly that corresponding to $T_{off} = 155$ K in Figure 1. The so obtained τ_{TSDC-D} times are represented by empty squares in Figure 4(b). Similarly, $\tau_{TSDC-\alpha}$ times were extracted for the α relaxation (empty circles in Figure 4(a)) from the analysis of the PP-TSDC depolarization current curve with $T_{on} = 143$ K and $T_{off} = 120$ K, and using in Eq. (5) a β value of 0.47 according to the results of BDS data analysis (see Sec. IV). As it could be expected, the $\tau_{TSDC-\alpha}$ times extracted from the intrinsically non-isothermal TSDC measurements display specific features related to the glass transition. The T-dependence of $\tau_{TSDC-\alpha}$ times show a crossover from a milder Arrhenius-like behavior at low temperatures $T \ll T_g$ to the isothermally determined VFT law at higher temperatures $T > T_g$. This phenomenology occurs as a result of the evolution of the sample from an out of equilibrium glassy state below T_g to an equilibrium state at higher temperatures on crossing the glass transition along the non-isothermal measurement. Similar results are well documented in the literature for other glass forming systems.^{22,24,32}

Although not as prominent as in the case of the α relaxation, the characteristic times obtained for the Debye-like relaxation by TSDC also show deviations with respect to the VFT fit of the isothermal data at low temperatures below the calorimetric glass transition (data at a reduced scale are included in Figure 5(c)). These small deviations have its reflect in the depolarization current. Figure 5(a) compares in a logarithmic scale the depolarization current predicted for an exponential relaxation with characteristic times defined by the VFT law in Figures 4(a) and 5(c) and the current intensity experimentally recorded. The comparison is very favorable at high temperatures whereas there exist systematic differences below the calorimetric glass transition. These subtle differences observed between the experimental results and the calculations under equilibrium conditions point to the emergence of non-equilibrium phenomena affecting also the Debye-like relaxation dynamics. Motivated by these signs, we estimated it constructive to study in detail the behavior of Debye-like relaxation on crossing T_g , using thermal annealing (aging) as a tool to create a sample state closer to equilibrium below T_g , which would exhibit a more dramatic crossover from the glassy state to the supercooled metastable state upon heating from below T_g .

Previous aging experiments on 2E1H^{33,34} were devoted to study the timescale of the structural recovery by recording the time evolution or equilibration of isothermal dielectric loss curves or NIR spectrum near T_g , demonstrating that the α process governs the physical aging. Figure 5(c) includes the

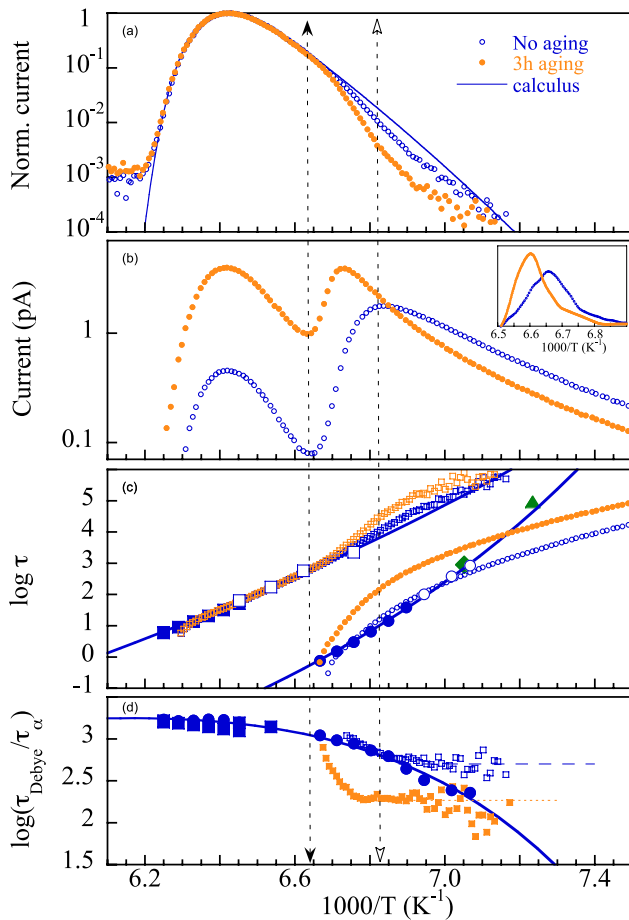


FIG. 5. (a) Depolarization currents corresponding to PP-TSDC experiments ($T_{on} = 168$ K and $T_{off} = 155$ K) aimed at resolving the Debye-like relaxation without aging and after 3 h long aging treatment. (b) Depolarization currents corresponding to PP-TSDC experiments ($T_{on} = 143$ K and $T_{off} = 110$ K) aimed at resolving the α relaxation without aging and after 3 h long aging treatment. Inset at (b): derivative of the reversible heat flow without aging and after 3 h long aging treatment. (c) Characteristic times (\square : Debye-like, \circ : α relaxation) extracted from the depolarization curves in panels (a) and (b) together with isothermal BDS and IDC data (same symbols as in Figure 4(a)) and their respective VFT laws. Triangle and diamond represent structural recovery time constants from Refs. 33 and 34, respectively. (d) $\tau_{Debye}/\tau_{\alpha}$ ratios, big symbols correspond to isothermal measurements, lines to VFT fits, and small symbols to TSDC times obtained after 3 h (filled) and 0 h (empty) long aging treatments. In all panels, filled (empty) symbols for TSDC or DSC data correspond to 3 h (0 h) long aging treatments.

time scales of the structural recovery measured by BDS and NIR equilibration measurements in Refs. 33 and 34. As it can be seen, the points nicely agree with the VFT law extracted from isothermal measurements corroborating that during the recovery experiments, the structural equilibrium was fully established. A sample in such a state should have significantly reduced mobility with the result of a more dramatic crossover phenomena (from glassy to metastable equilibrium) when heated across T_g . Thus, we have studied the temperature behavior of the α and Debye-like relaxations on crossing the T_g for a sample that has been nearly equilibrated a few degrees below the glass transition.

In order to study the behavior of the α and Debye-like relaxations on crossing the T_g , we performed several PP-TSDC experiments as those described in Secs. III A and III B, involving 3 h long aging treatment at 140 K

during the cooling step of the PP-TSDC measurements. In the case of the α relaxation, depolarization currents were recorded by polarizing at $T_{on} = 143$ K and $T_{off} = 120$ K without aging (empty symbols) and after 3 h long aging treatment at 140 K (filled symbols), and results are shown in Figure 5(b). The effect of thermal annealing on the α relaxation was complementarily tested by calorimetric measurements under the same conditions (rates, aging temperature, and aging times) and the results are depicted in the inset of Figure 5(b) as the derivative of the heat flow. Consistent with the outcome of calorimetric measurements, the depolarization current peak corresponding to the α relaxation narrows, gets more intense, and moves towards higher temperatures upon aging. Note that the relative contribution of the Debye process (whose contribution is not completely eliminated by the PP-TSDC procedure) to the overall measured intensity and under the same polarizing conditions increases with aging. Since for this PP-TSDC experiment the aging is carried out with the field on, this allows a more efficient polarization of the slower Debye-like process for the aged sample.

Regarding the PP-TSDC experiments performed to study the Debye-like relaxation on crossing T_g , Figure 5(a) shows the depolarization currents obtained after a PP-TSDC protocol with $T_{on} = 168$ K and $T_{off} = 155$ K without aging (empty symbols) and after 3 h long aging at 140 K (filled symbols). Note that for this PP-TSDC experiments, the aging is carried out once the polarizing field is switched-off, but the aging time is still about hundred times shorter than the dielectric relaxation time of the Debye-like process at this temperature. Comparing the TSDC data of the two experiments (see Figure 5(a)), a nice superposition is found at $T > T_g$ but at lower temperatures, the current of the aged sample is noticeably smaller than that of the unaged one. As expected, annealing treatment emphasizes the non-equilibrium effects so that the current of the aged sample deviates more dramatically from the expectation under an exponential relaxation with characteristic times defined by the VFT law determined from isothermal measurements.

Figure 5(c) shows the characteristic times extracted from the depolarization curves depicted in panels (a) and (b) together with the VFT laws presented in Figure 4(a). When plotted in a wider scale compared to that in Figure 4(a), the τ_{TSDC-D} times extracted from the intrinsically non-isothermal TSDC measurements below T_g clearly deviate from the extrapolated VFT law obtained fitting isothermal data. In both cases (aged and non-aged), τ_{TSDC-D} times conform well to the VFT law at high temperatures, whereas they seem to crossover to a different T-dependence at temperatures below T_g . Noteworthy, the observed phenomenology mimics the behavior of the α relaxation on approaching the glass transition. When the ratio between the relaxation times of the Debye-like and α relaxation processes is determined with TSDC data what is found is that it remains essentially constant below T_g (see dashed and dotted lines in Figure 5(d)). This finding strongly suggests that on crossing the glass transition, the structural relaxation governs the way in which the Debye-like relaxation changes with temperature. Interestingly, the nearly constant $\tau_{TSDC-D}/\tau_{TSDC-\alpha}$ ratio at low temperatures crosses the same quantity determined by extrapolation from

isothermal experiments (at metastable equilibrium condition) approximately at T_g for the non-aged sample and at $T_a = 140$ K for the aged one.

IV. DISCUSSION

The above results show the main characteristics of the Debye-like and α relaxation components in 2E1H in a broad frequency and temperature range, with emphasis in the ultra-low frequency range accessed by time domain techniques. The main focus of our investigation has been the temperature dependence of the corresponding relaxation times in the vicinity of T_g . As a result, it was possible, for example, to establish beyond any doubt the dramatic tendency of the Debye-like and α relaxation's timescales to approach to each other upon decreasing temperature. The relaxation times in Figure 4(a) obtained isothermally were extracted in an essentially model-free way and the results obtained do not depend on the details of the data analysis. Contrary, the evaluation of the other quantities characterizing the relaxation processes (relaxation strength and shape) do actually depend on several factors. As explained in Sec. II, BDS data were analyzed by fitting $\epsilon^*(\omega)$ to Eq. (7) on the one hand and $d\epsilon'(\omega)/d\log f$ to Eq. (8) on the other, using in both cases the same model for $\epsilon^*(\omega)$. As it can be seen in Figure 2, the result of the $\epsilon^*(\omega)$ fit is visually satisfactory, for both the imaginary (panel (a)) and real (panel (b)) parts. Comparison of the derivative of ϵ'_{exp} and the derivative of ϵ'_{fit} (panel (b)) however, reveals that the fitting is not as high quality as it could seem. Direct analysis and fitting of the derivative of the real part, $d\epsilon'(\omega)/d\log f$, by means of Eq. (8) (panel (c)) evidences that the disagreement shown in panel (b) is intrinsic to the sample response and it does not result from problem originated by multiple parameter fitting and overlapped signals. When the fitting procedure minimizes errors in the logarithmic scale (fit B), the obtained curve once again seems to describe well the data, but clear differences are evident to the eye when comparing the fitted curve and the experimental data in the linear scale (see inset in panel (c)). If another fitting criteria which minimizes the error around the well defined maxima for the two processes in the linear scale is taken (fit A), then by no means does the model reproduce the region between the Debye-like and α relaxation.

With all, in the case of 2E1H, fitting details of BDS data analysis do not substantially change the main conclusions reached for the properties of the Debye-like relaxation along the different works in the literature. Since the position of the experimental maxima are relatively well resolved for this MA, the model-free characteristic times (τ_{max}) obtained directly reading the position of the maxima do not differ from those obtained from different fitting approaches. Regarding the dispersion of the Debye-like process in 2E1H, precise details will depend on the fitting model and procedure but all of them (including those in the literature) come to the same conclusion, i.e., that it has exponential or at least very close to exponential behavior (see Figure 4(a)). We have found a slight tendency for the b_{Debye} parameter to increase with decreasing temperature: between 0.95 and 0.99 in the $\epsilon^*(\omega)$ fittings and between 0.97 and 1 in the fit A of $d\epsilon'(\omega)/d\log f$, for example.

These values are in excellent agreement with the exponential behavior observed by PP-TSDC in Sec. III A.

On the other hand, in the case of the α relaxation, there is no significant variation of the β parameter with temperature (see Figure 4(a)). The values obtained for the different fitting options all lay within $\beta = 0.47 \pm 0.01$, which is a typical value observed for the structural relaxation of glass forming systems. Finally, the relative intensity of the Debye-like and the α relaxation has an unquestionable trend to decrease upon increasing temperature. Despite this trend is reproduced in all the analysis, specific $\Delta\epsilon_{Debye}$ and $\Delta\epsilon_{\alpha}$ values will depend on (i) the functional form (Debye, Cole-Cole (CC), CD, HN...) used to describe Debye-like and α relaxation, (ii) the way data is weighted during the fitting, i.e., if it is performed in a logarithmic or lineal scale, and (iii) the magnitude under fit ($\epsilon', \epsilon'', d\epsilon'/d\log f$...). In practice, the last two points in particular modify the weight or importance of the various observed features (inflexion points, maxima, valleys...) on the fitting procedure. In addition to inherent experimental errors, all these factors will produce uncertainties on the resulting absolute values of $\Delta\epsilon_{Debye}$ and $\Delta\epsilon_{\alpha}$ and on the magnitudes derived from them, as, for example, on the Kirkwood correlation factor g_k .

When going into more details, the analysis of BDS data leaves some open questions regarding the description of the permittivity in the region between the Debye-like and the α relaxations. We did not find in the literature any reference to this kind of effects, and will comment on the possible reasons. On the one hand, we have seen that divergences only emerge when attention is paid to details, and more remarkably in the $d\epsilon'/d\log f$ representation which provides a improved resolution. Second, logarithmic representation of the data and their fit might give a wrong impression of the quality of the agreement. Finally, all the works we examined (see Refs. 19, 29, 35, and 36 for example) assumed CC or HN functional forms to model the permittivity of the α relaxation plus a pure Debye function for the Debye-like relaxation. When using the CC or HN functions, a broad low-frequency extension of the relaxation is allowed, which opens a way to "fill" the region in between the Debye-like and the α relaxation, blurring deeper an already tiny effect. In comparison, the KWW_{HN} function used by us, which works generally well describing measurements by various relaxation techniques, provides a rather sharp cutoff of the relaxation at low frequencies and consequently the description of the "valley" becomes worse. The influence of the low-frequency tail of the α relaxation on the determination of the characteristics of the Debye-like relaxation is even more critical for other MAs with less intense Debye relaxation and closer timescales. The lack of intensity of the model we used ($CD_{Debye} + KWW_{HN\alpha}$) in the region between the Debye-like and the α relaxation could be interpreted as indicative of an underlying low intensity relaxation process. Obviously, the introduction of an additional relaxation process (an exponential one for simplicity for example) improves the quality of the fitting but, in principle, has no other clear physical justification. One could speculate that this signal could be related to the dynamics of the OH group detected by nuclear magnetic resonance,^{13,37} which was also reported to have a timescale in between those of the Debye-like and

the α relaxation. Unfortunately, TSDC measurements are not sensitive enough to support or deny the existence of this hypothetical contribution due to its low intensity (even lower than that of the α relaxation) and relatively close timescale to those of the Debye and α relaxations. When looked at the logarithmic scale, a narrowing of the depolarization current curve is discernible upon increasing T_{off} mainly due to the presence of the α relaxation (see Figure 3(a), for example), and we do not have enough information at hand to discard some minute contribution to the depolarization in addition to that of the α relaxation. In any case, TSDC experimental results impose an upper limit for the contribution of any additional mode, which should be less than 1% of the peak intensity recorded for the Debye-like relaxation, taking into account the good agreement between the experimental data and the calculated current under the exponential model.

Even though the current experiments cannot judge the presence of additional modes of very small amplitude relative to the principal exponential response, the results in Sec. III A remain a critical test on the dispersive nature of the Debye-like relaxation. The fact that the depolarization current curve does not significantly change upon varying T_{off} rules out the relevance of Rouse type modes (or any other type of modes with similar amplitude) and confirms the actual exponential nature of the Debye-like relaxation at low temperatures. The discordance/mismatch between the measured Debye-like relaxation and the relaxation expected under a Rouse model, however, is not at odds with the existence of chain-like aggregates, as the relaxation of the net end-to-end dipolar moment of the chain could effectively take place through another faster process, like association-dissociation processes in the case of supramolecular living polymers,^{38–40} for example. In the framework of molecular relaxations in fluctuating environments¹⁴ or in association-dissociation situations,^{15–17} there is an additional time-dependent process (fluctuations or association-dissociation processes) so that the probability of the molecular relaxation and its time dispersion will depend on the relative timescales of these two processes. In the limiting situation where this additional process is fast enough, the molecular relaxation exhibits a single correlation time.^{14,17} These scenarios provide a possible explanation for the pure exponential behavior of the Debye-like relaxation in 2E1H regardless the formation of chain aggregates. In the transient chain model by Gainaru *et al.*,¹⁵ the second process that comes into play would be the successive loss and or gain of segments at the ends of the chain aggregates, which would ultimately relax the end-to-end net dipole of the chain. Interestingly, the models for molecular relaxations in fluctuating environments or in association-dissociation situations predict time dispersion when the rates of the two processes are comparable,^{14,15,17} which seems not to be the case for 2E1H. The fact that the relaxation process as detected by TSDC looks as a single purely exponential mode implies that the polymer-like chain dynamics in the absence of fluctuations or association-dissociation processes would be much slower than the actually measured dielectric relaxation time since; if this was not the case, some signature of the presence of chain modes would be detectable. According to the limits related to the TSDC sensitivity, we envisage

the slowest time of the polymer-like chain dynamics, if any, to be at least 10 times slower than the relaxation actually measured, and so around 10^4 times slower than the structural relaxation. Although this timescale relation would imply rather large chains for a purely linear polymer melt (n about 100), the reported presence in the MAs of chains with different architectures (branched) but shorter could be the ultimate reason for a rather slow chain dynamics. We envisage as a future work the extension of the present study to those MA which were reported in the literature to have non-exponential Debye-like relaxation in order to test this ideas.

Regarding the structural relaxation, the application of PP-TSDC techniques provides another approach to identify the high frequency low intensity component of the dielectric response with the α relaxation: (i) the depolarization currents measured for this component show the characteristic imprint of the structural relaxation when measured by TSDC (very extended and nearly straight wing at low temperatures and a sharp decrease of the intensity nearby calorimetric T_g) and (ii) the characteristic times for this process show a crossover from an Arrhenius-like behavior deep in the glassy state towards a VFT-like one at higher temperatures as a consequence of the transition from a non-equilibrium state ($T < T_g$) to a metastable equilibrium one on crossing T_g .

Finally, close inspection of the TSDC data at temperatures close to T_g indicates the presence of non-equilibrium phenomena affecting also the Debye-like relaxation. Moreover, aging experiments in 2E1H reveal clear changes in the way the depolarization current of the Debye-like relaxation crossovers to the metastable equilibrium state upon aging, i.e., reveal a dependence on the glassy structural state. Modestly in non-aged experiments and more pronounced in aged ones, below the glass transition temperature τ_{TSDC-D} , times deviate from the VFT law determined isothermally at high temperatures. These deviations would be originated by non-equilibrium effects on the Debye relaxation caused by the arrest of the structural relaxation on crossing the glass transition during cooling. Noteworthy, both α and Debye-like relaxations vary with temperature in a very similar way at $T < T_g$ giving rise to a nearly constant $\tau_{TSDC-D}/\tau_{TSDC-\alpha}$ ratio.

It is interesting to note that the observed phenomenology is very much analogous to that found for the normal mode of a linear polymer, polyisoprene,²² on crossing the glass transition. In that case, the constant τ_{NM}/τ_{α} ratio observed below T_g was rationalized appealing to the characteristic length scales of each process and their variation with temperature.⁴¹ The typical length scale controlling chain fluctuations is of the order of the radius of gyration which remains essentially T-independent. Contrary, the characteristic length scale of the α relaxation is T-dependent and increases rather dramatically on approaching T_g , where it reaches a value close to the Kuhn length. The idea is that when cooling below T_g , the α relaxation length scale cannot longer increase so that both length scales remain T-independent and therefore both dynamical processes are expected to follow a similar T-dependence below T_g . To establish a direct analogy for the case of 2E1H is not straightforward because the exact mechanism leading to the Debye-like relaxation is unknown and therefore, the definition of a characteristic length scale is uncertain. Nevertheless,

if this length scale does really exist and is not changing much with temperature, the same arguments would explain the present results on 2E1H.

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