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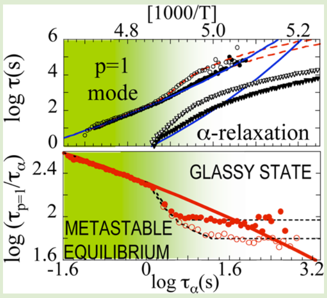
Chain Dynamics on Crossing the Glass Transition: Nonequilibrium Effects and Recovery of the Temperature Dependence of the Structural Relaxation

S. Arrese-Igor,*,† A. Alegría,†,‡ and J. Colmenero†,‡,§

†Centro de Física de Materiales (MPC), Centro mixto CSIC-UPV/EHU, Paseo Manuel Lardizabal 5, 20018 San Sebastián, Spain
‡Departamento de Física de Materiales UPV/EHU, Apartado 1072, 20080 San Sebastián, Spain
§Donostia International Physics Center, Paseo Manuel Lardizabal 4, 20018 San Sebastián, Spain

Supporting Information

ABSTRACT: In this paper we report thermally stimulated depolarization current results on the chain and segmental dynamics of two monodisperse polyisoprenes accessing both dynamics at ultralow frequency range and exploring the relationship between segmental and chain time scales when crossing the glass transition. In this range, we have recorded experimental evidence of nonequilibrium effects on the slowest chain mode dynamics. The nonequilibrium effects seem to occur simultaneously for both chain and α-relaxation. Moreover, detailed analysis strongly indicates the recovery of an even T-dependence for the chain and α-relaxation dynamics on crossing glass transition and in the glassy state. The obtained results can be understood taking into account the different temperature dependences of the length scales involved in the segmental and chain relaxations.



According to Rouse and reptation tube models[1−3] for polymer chain dynamics, the characteristic time of the chain motion is defined in terms of the so-called friction coefficient and its temperature variation. Traditionally this coefficient has been identified with that controlling the segmental motions of the polymer chain leading to the expectation that both chain dynamics and the structural α-relaxation have equal temperature (T)-dependences. However, systematic tests of this assumption have proven that this is not the case and that the α-relaxation shows a stronger T-dependence than chain modes especially as the temperature approaches the glass transition one, T_g.[4−7] The thermally stimulated depolarization current (TSDC) is a dielectric technique that has proven recently to be a very powerful tool allowing the study of chain dynamics in detail at ultralow frequencies[8] and at relatively low temperatures close to T_g—a range where chain end-to-end fluctuations detected by dielectric experiments have scarcely been explored. In this paper we report TSDC results on the chain and segmental dynamics of two monodisperse polyisoprenes accessing both dynamics at the ultralow frequency range and in this way exploring the relationship between segmental and chain time scales when approaching and crossing the glass transition. For low molecular weight polyisoprene (PI), nonequilibrium effects on the slowest chain mode are observed for the first time. Moreover, the detailed analysis of the results strongly indicates the recovery of an even T-dependence for the chain and α-relaxation dynamics on crossing T_g and deep in the glassy state.

Two monodisperse PI samples with molecular weights M_w = 10 500 Da, PI10, and M_w = 2900 Da, PI3, were investigated. PI3 is below the entanglement regime, while PI10 is right at the transition between entangled and nonentangled systems. The PI chain contains dipolar components parallel to the chain backbone yielding a net "end-to-end" polarization vector. This allows to follow chain dynamics by dielectric relaxation techniques, and as a consequence PI is a very well-studied polymer by broadband dielectric spectroscopy (BDS) in particular.[6,7,10,11] A TSDC experiment consists of: first, polarizing the sample at high temperature (where dipolar entities are mobile) and then freezing-in the orientational polarization by cooling down the sample with the field on; switching off the field at low temperature; and finally recording the electric current due to the thermally stimulated release of the polarization during a subsequent linear heating. A peak in the electric current is obtained when the molecular mobility becomes high enough to randomize dipolar orientation. 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.[14,15] The TSDC technique, however, is unique in the sense that we can vary the temperature at which the field is switched on (T_{on}) or off (T_{off}) during cooling to "remove" from the subsequent depolarization current curve the contribution from slow or fast relaxing entities and in this way isolate the response of a certain process of interest. This is referred to as a *partial polarization* (PP) TSDC experiment.[14,15] Here the PP TSDC technique has been used to isolate the response of the α-

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relaxation from that of the chain dynamics on the one hand and to isolate the response of the slowest chain mode $p = 1$ from faster α-relaxation and higher-order chain modes on the other. The latter is based on the Rouse equation[1] describing the end-to-end vector's $\vec{R}(t)$ correlation function as a discrete superposition of several mode components $\langle \vec{R}(t)\cdot\vec{R}(0)\rangle \propto \sum_{p:\mathrm{odd}}^{N-1} \cot^2((p\pi)/(2N)) \exp(-t/\tau_p)$ (where N is the number of beads forming the chain, and $\tau_p = \tau_1/p^2$ is the relaxation time associated with the p^{th} mode).[33] The slowest $p = 1$ mode dominates the correlation function due to the $\sim 1/p^2$ weighting factor. Moreover, it is 9 times slower than any other mode contributing to the polarization and consequently can be confidently isolated by PP TSDC experiments.[8]

Dielectric relaxation of the samples investigated is typical of type-A polymers in general and PIs in particular.[6,10,11] As an example, the global TSDC curves measured for PI10 at different heating rates are shown in Figure 1 (for further experimental details please see Supporting Information). The peak situated at lower temperature corresponds to the fast α-relaxation, whereas the peak at higher temperatures corresponds to the slower chain dynamics. As the TSDC experiment is performed in nonisothermal conditions, the response of the sample depends both on the heating rate and on the T-dependence of the characteristic times. Figure 2 shows with open squares the characteristic times for the chain and α-relaxations calculated from the position of the maxima (vertical lines) in Figure 1 (see Supporting Information for further details). There, we also include relaxation times for segmental and chain dynamics (Δ) extracted by standard fitting procedures of isothermal BDS and time-domain relaxation data, showing good agreement.

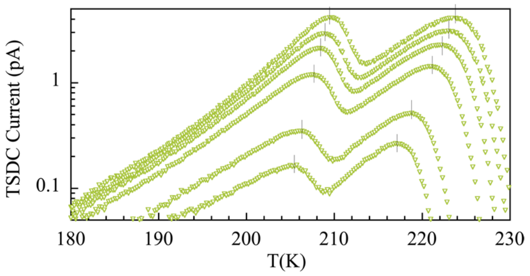

Figure 1. Global depolarization current curves for PI10 recorded at 10, 7, 5, 3, 1, and 0.5 K/min (from top to bottom) heating rates. Vertical lines indicate maxima position.

As commented on before, PP in TSDC allows to isolate specific contributions by applying a temperature cutoff in the polarizing field. In particular, we have designed experimental protocols to isolate the response of the first $p = 1$ chain mode on the one hand[8] and the response of the α-relaxation on the other. Figure 3 shows the result of such experiments on PI10 (-○- for the $p = 1$ chain mode and -▽- for α-relaxation). The outcome of a TSDC experiment can be numerically calculated assuming a general stretched-exponential Kohlrausch–Williams–Watts (KWW) function for the relaxation of the polarization and using as inputs stretching exponent β and T-dependent relaxation times (see Supporting Information). For instance, the depolarization current curve corresponding to the $p = 1$ chain mode in PI10 can be calculated using as inputs: (i) the Williams–Landel–Ferry (WLF)[12] law for the characteristic times extracted by fitting isothermal BDS measurements (solid line in Figure 2a) and (ii) $\beta = 1$.[8] The so-calculated current curve compares extremely well with the result of the PP experiment designed to isolate the $p = 1$ mode in PI10, strongly supporting the suitability of this procedure[8] (see Figure 3). What is more, the result of a calculation using the same WLF law as input but including this time up to $p = 9$ Rouse modes and the polarization conditions used in the real experiment is also indistinguishable from the experimental data and the calculated global $p = 1$ current curve. In addition, from the experimental TSDC data T-dependent characteristic times, $\tau_{\mathrm{TSDC}}(T)$, can be obtained directly by analyzing the measured depolarization current as a function of temperature (see Supporting Information). The so-obtained times for the PP experiment of the $p = 1$ chain mode in PI10 using $\beta = 1$ are included in Figure 2a as circles. As can be seen, the agreement with the WLF law deduced from isothermal measurements is again very good, as already foreseen by the good concordance between calculated and experimental depolarization curves in Figure 3. Noteworthy, this analysis of TSDC data for the $p = 1$

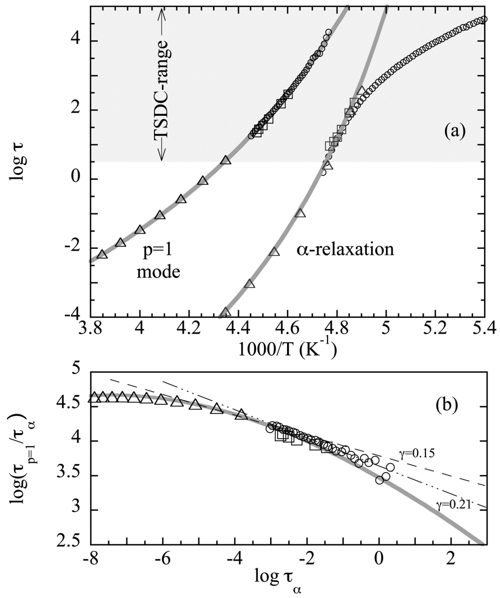

Figure 2. Panel (a) $\tau(T)$ for the $p = 1$ chain mode and α-relaxation of PI10 and (b) the ratio $\tau_{p=1}/\tau_\alpha$. (Δ) isothermal measurements; (□) variable rate global TSDC; (○) PP-TSDC. The lines in (a) are WLF and VFT law fits of the isothermal measurements and their ratio in (b). Dashed and dotted dashed lines in (b) show the power law description valid in limited ranges.

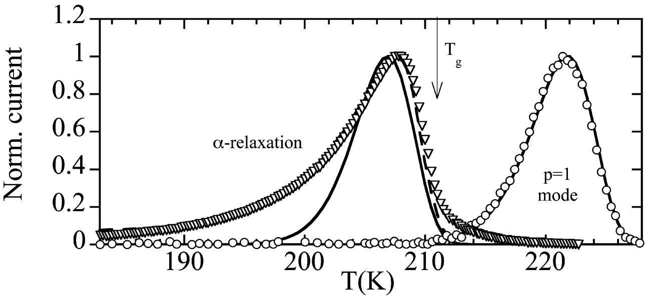

Figure 3. PP current curves for PI10: (○) experimental $p = 1$ chain mode; (▽) experimental α-relaxation; solid lines are calculations from VFT and WLF time laws in the metastable equilibrium; dashed line is calculation from actual times extracted from the analysis of the experimental α-relaxation current. Solid arrow represents calorimetric T_g at the inflection point of the DSC scan.

chain mode allows accessing relaxation times as high as ~10^5 s without noticing clear deviations from the behavior extrapolated from conventional isothermal experiments as seen in Figure 2a.

The fact that α-relaxation shows a stronger T-dependence than chain modes at $T \gtrsim T_g$ is very clear when low-frequency measurements of the chain dynamics by TSDC or time domain techniques are added to the conventional BDS frequency range. Differences in the T-variation of $\tau_{p=1}$ and τ_α are further evidenced when plotting the ratio $\tau_{p=1}/\tau_\alpha$ as a function τ_α. In Figure 2b the dissimilar T-variation is obvious when approaching T_g, while it seems to vanish at much higher temperatures (where $\tau_{p=1}/\tau_\alpha \sim$ constant). Sokolov et al.[9] approximated the ratio $\tau_{p=1}/\tau_\alpha$ close to T_g by an effective power law $\tau_{p=1}/\tau_\alpha \propto (\tau_\alpha)^{-\gamma}$ and obtained $\gamma \simeq 0.15$ for PI.[16] Our data clearly present some curvature so that the γ value depends on the fitted τ_α range and varies for instance from $\gamma \simeq 0.15$ for log τ_α between −6 and −2 to $\gamma \simeq 0.21$ for log τ_α between −4 and 0 (see Figure 2b). In this context, it has been reported that chain modes become nonexponential when their time scale approaches that of the structural α-relaxation.[8] The origin of the disparate T-dependences of the chain and α-relaxation, however, cannot be attributed to this effect. The $p = 1$ chain mode for PI10 and higher molecular weight PI's is found to be exponential,[8] while their chain and α-relaxation clearly show different T-dependences (see for example Figure 2b and ref 9).

When the TSDC data of the α-relaxation are analyzed, clear nonequilibrium effects are manifested at $T < T_g$. The $\tau_{\mathrm{TSDC}\alpha}(T)$ times calculated from the depolarization current curve of the α-relaxation for PI10 using $\beta = 0.48$ (determined from isothermal measurements) do not follow in the whole T-range the Vogel–Fulcher–Tamman (VFT)[13] line determined by fitting isothermal measurements at metastable equilibrium conditions (equilibrium from now on). Contrarily, $\tau_{\mathrm{TSDC}\alpha}(T)$ times show a crossover from an Arrhenius-like behavior deep in the glassy state ($T \ll T_g$) toward a VFT-like one at higher temperatures. Accordingly, the TSDC curve calculated assuming the VFT line in equilibrium and $\beta = 0.48$ clearly fails in describing the experimentally recorded current (see solid line in Figure 3), evidencing that during the experiment the characteristic times of the α-relaxation at $T \ll T_g$ do not follow the VFT law assumed in this calculation. This is not an unexpected result as, in practice, within the experimental time scale it is not possible to infinitely undercool the melt, and eventually the system will go out of the supercooled metastable equilibrium into the glassy state when the α-relaxation time reaches values in the range 1−100 s. The effect of crossing the glass transition on the α-relaxation time scale is well documented (see ref 17 and references therein). A crossover from VFT to a milder Arrhenius-like T-dependence was reported by numerous studies and several experimental techniques.[19−27] The question of whether this crossover only occurs for not fully equilibrated glasses is a topic of intense research activity[28] but out of the scope of this work.

At this point the question arises if similar nonequilibrium effects on crossing the glass transition can be observed for the chain dynamics, something that to our knowledge has never been directly measured before for the slowest chain mode. Even in the ultralow frequency range accessed by TSDC ($\lesssim 10^5$ s), the characteristic times for the $p = 1$ chain mode of PI10 do not show significant deviations from the equilibrium behavior extrapolated from isothermal measurements. Taking the crossover of the α-relaxation as a reference, it seems that the chain relaxation times where such nonequilibrium effects would be expected exceed the accessible time range by TSDC for the PI10 sample considered so far. Since by lowering molecular weight chain dynamics becomes significantly faster, a lower molecular weight PI sample (PI3) was investigated using the same approach. Figure 4 shows the result of PP TSDC experiments designed to isolate the response of the $p = 1$ mode and the α-relaxation of PI3 (panels a and b) together with the characteristic times extracted from these data (panel c). When analyzing these depolarization curves, $\beta = 0.48$ was assumed for the α-relaxation, whereas for the $p = 1$ chain mode $\beta = 0.87$ was used according to the results in ref 8. Contrary to the PI10 case, when the experimental data for the $p = 1$ chain mode are compared with the expectation for a mere extrapolation of the equilibrium behavior (solid line in Figure 4b) some differences are observed in the low-temperature side, namely, below T_g. Trying to confirm that the observed deviations are truly related to nonequilibrium effects, new experiments involving annealing below T_g were performed. Since annealing the glassy material below T_g results in a structural recovery (physical aging) approaching the supercooled metastable equilibrium state, the final glassy state obtained after cooling the aged sample should have a reduced mobility with the result of a more dramatic crossover phenomena on approaching T_g.[18] The experimental data obtained under these conditions (open symbols in Figure 4) confirm more prominent effects not only on the α-relaxation but, more importantly, also on the $p = 1$ chain mode. The

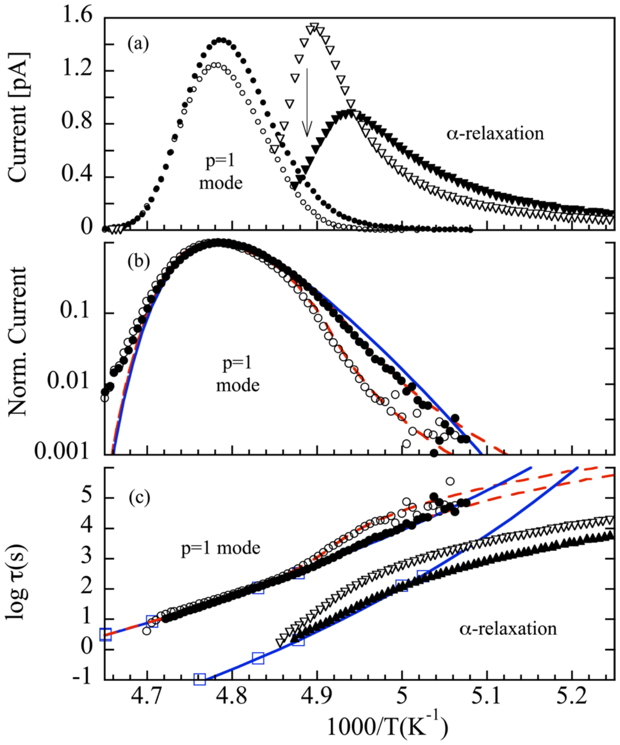

Figure 4. PP-TSDC currents and τ_{TSDC} times for $p = 1$ chain mode (circles) and α-relaxation (triangles) with (empty symbols) and without (solid symbols) aging. Solid lines represent VFT or WLF laws in equilibrium in (c) or the currents calculated on their basis in (b). Dashed lines represent ad-hoc times for $p = 1$ chain mode (see text) in (c) and the currents calculated on their basis in (b). Squares in (c) represent characteristic times determined at equilibrium condition by isothermal measurements. Solid arrow in (a) represents calorimetric T_g at the inflection point of the DSC scan.

difference between the depolarization curve predicted for a $p = 1$ mode relaxation following the equilibrium WLF law in the whole temperature range (solid line) and the experimental data of the aged sample is now very obvious. Even more, when the relaxation times for these annealed samples are evaluated the crossover phenomenon is clearly visible also for the slowest chain mode, mainly at the lowest temperatures. Results in Figure 4 prove the emergence of nonequilibrium effects on the slowest chain mode when crossing the glass transition. Similar to the phenomenology observed for the α-relaxation, at $T \lesssim T_g$ the $p = 1$ chain mode deviates from the extrapolation of the WLF law deduced from higher temperature experiments covering the more conventional frequency range, whereas at $T \gtrsim T_g$ it nicely follows it. Furthermore, this crossover is more dramatically manifested when the polymer is annealed below T_g.

As already commented, the connection between the polymer chain dynamics and the α-relaxation has been investigated in detail, in particular the problem of the thermorheological complexity, referring to the different T-dependences of these two dynamics. It has been found that, whereas at temperatures well above T_g both follow approximately the same T-dependence, there is a clear decoupling on approaching T_g. The current understanding of the physics behind this different evolution with temperature remains unclear.[16,29−32] In general different explanations put the accent on: (i) the *spatially heterogeneous dynamics* of the α-relaxation in contrast to an averaged effect of nanoscale heterogeneities on the chain relaxation or (ii) the very *distinct T-evolution of the length scales* involved on the chain dynamics and the α-relaxation, which for the case of the latter rapidly increases as temperature approaches T_g. The results presented herein indicate that around T_g chain dynamics and α-relaxation both present a similar crossover and alike T-dependences below T_g. A detailed analysis of this range never explored before should shed new light on the issue.

Figure 5 shows the $\tau_{p=1}/\tau_\alpha$ values for PI3 obtained by TSDC measurements during continuous heating through the T_g range as well as those obtained by isothermal measurements at equilibrium. For values of τ_α lower than a few seconds ($T > T_g$) the $\tau_{p=1}/\tau_\alpha$ ratio conforms with the extrapolated equilibrium line. On the contrary the appearance of the data in the "out of equilibrium" range, $\tau_\alpha > 1$ s, changes rather dramatically. There, it becomes evident that the ratio between the chain and the α-relaxation time scales in both nonannealed and well-annealed samples no longer follows the monotonous variation expected from the extrapolation of equilibrium measurements. Data look nearly constant at the lowest temperatures and cross over abruptly toward the equilibrium behavior at higher temperatures. The flattening of the data at the lowest temperatures is indicative of a trend to fully recover the pairing of the T-dependences of both dynamical processes deep in the glassy state. This idea is further sustained by the fact that assuming ad-hoc $\tau_{p=1}(T)$ times (dashed lines in Figure 4c) yields calculated (using $\beta = 0.87$) currents for the $p = 1$ chain mode that describe very well the experimentally measured ones, in both nonannealed and well-annealed PI3 (see dashed lines in Figure 4b). These ad-hoc times for the $p = 1$ chain mode were constructed starting from experimental $\tau_{\mathrm{TSDC}\alpha}(T)$ times and assuming the $\tau_{p=1}/\tau_\alpha$ ratios indicated by dashed lines in Figure 5, that is, the same T-dependence below T_g and then smooth crossover to equilibrium values.

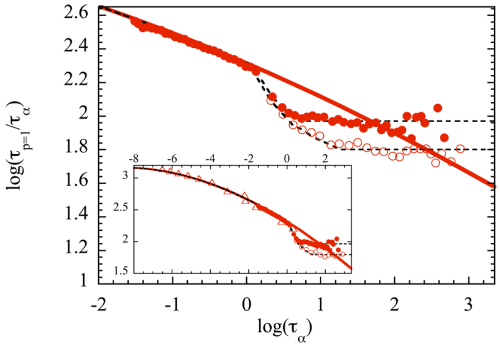

Figure 5. $p = 1$ chain mode and α-relaxation characteristic times ratio: solid lines, VFT and WLF laws obtained fitting isothermal measurements; (●) nonaged PI3; (○) well-aged PI3; dashed lines ad-hoc $\tau_{p=1}$ times (see text). The inset represents the same in a wider scale including also isothermal data (Δ).

The restoring of the same T-dependence of the chain and segmental dynamics well below T_g is an expected result when the thermorheological complexity is explained as originated by the very distinct T-dependence of the length scales involved.[29] The argument of this interpretation is based on the general idea that the length scale characteristic 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. Contrarily, the typical length scale controlling chain fluctuations is of the order of the radius of gyration which remains essentially T-independent. This would explain the stronger T-dependence of τ_α when approaching T_g and the nearly constant $\tau_{p=1}/\tau_\alpha$ ratio at high temperatures (see inset of Figure 5) as a result of the rather weak T-dependence of both length scales in this range. With these same arguments in mind, when cooling below T_g the α-relaxation length scale can no longer increase, and consequently both dynamical processes are expected to follow a similar T-dependence. Similarly, regarding the role of dynamic heterogeneities on the emergence of thermorheological complexity, the present results would put the accent on the T-evolution of their amplitude or length scale (which would arrest or freeze upon crossing T_g) rather than on their mere presence.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental and data analysis details. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: waaarirs@ehu.es.

Notes

The authors declare no competing financial interest.

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