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Transient dynamics of cold-rolled and subsequently thermally rejuvenated atactic-polystyrene using broadband dielectric spectroscopy

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Abstract
The effect of plastic deformation on the molecular dynamics of atactic polystyrene (α-PS) was studied by broadband dielectric relaxation spectroscopy (BDRS), Fourier-transform infrared spectroscopy (FTIR) and polarized-light microscopy. Sheets of α-PS have been subjected to cold rolling, that is, mechanical rejuvenation, followed by a quenching step and fast heating above its glass-transition temperature, resulting in thermal rejuvenation. Cold rolling revealed, in addition to the known α- and γ(I)-relaxations, four hitherto unknown relaxation processes (II, III, IV and V). Using the framework of craze formation and multiplicity of the glass transition (E. Donth, G. H. Michler, Colloid Polym. Sci. 1989, 267, 557–567), supported by an activation-enthalpy/entropy analysis (Starkweather, W. Howard, Macromolecules 1981, 14, 1277–1281), the following physical picture emerges: (a) processes I and II represent local conformation transitions γ referring to chains of two different degrees of stretching (T/G-ratio); and (ii) processes III and IV were identified as helix-inversion processes of T2G2 helices as reported earlier for syndiotactic-rich PS—an assignment supported by FTIR results. Finally, the relaxation V could be attributed to the onset of the fibrillar glass transition (within crazes), leading to stress release by collapse of the fibrils and hence dying out of process V. Polarized-light microscopy confirmed the creation of oriented structures and internal stresses upon cold rolling, and their removal upon thermal rejuvenation.

KEYWORDS
atactic polystyrene, glassy polymers, rejuvenation
1 | INTRODUCTION

One of the most fascinating subjects in condensed matter science is arguably the state of a glass. The frequent use of polymeric glasses in high-level applications, such as medical and aviation applications, makes understanding of their intrinsic mechanical response inevitable. Polymer glasses are out of equilibrium, and their evolution toward equilibrium is generally known as physical aging. The effect of physical aging can be erased by increasing the temperature above the glass-transition temperature of the material, that is, thermal rejuvenation. It is also generally accepted that with deformation far beyond the yield strain, the dynamics of a polymer glass undergo changes that also lead to the erasure of physical aging, a phenomenon called mechanical rejuvenation.

Thermally and mechanically rejuvenated glasses have similar macroscopic properties, however microscopically they may be rather different (e.g., anisotropy). A recent investigation on polymer glasses concluded that the thermally and mechanically rejuvenated glasses are in different states, and that mechanical deformation leads to an amorphous-amorphous phase transition. Their results are confirmed by positron-annihilation lifetime spectroscopy experiments on polycarbonate (PC) based on the fact that the free volume follows a different DSC trace as compared to the thermally rejuvenated ones. This idea has also been supported theoretically by other studies. In his thorough review on the subject of mechanical rejuvenation, McKenna discussed the possible interpretations of the erasure of history of glassy materials with deformation below and above the yield point. At least close to the glass transition temperature, the presented results of torsional dilatometry experiments prove that the free volume of the glass is not rejuvenated below the yield point. Deformation above the yield point leads to a different DSC trace as compared to a thermally rejuvenated polymer, a sub-glass transition minimum is observed for the deformed polymer for which the molecular picture is not fully understood. McKenna suggests that deformation above the yield point in the polymer leads to a polyamorphic phase transition and not to rejuvenation, based on the fact that the yield stress does not reach the same value after thermal rejuvenation and aging as compared to mechanical cycling and aging.

Intriguing observations have been reported on density measurements on various cold-rolled glassy polymers. Thermal rejuvenation is known to cause a decrease in the density, cold rolling, however, shows an increase in density. Increased segmental mobility upon mechanical deformation has been observed in various studies and modeling studies argue that the increased segmental mobility is associated to different explored energy landscape regions in contrast to thermal rejuvenation. A study by Donth and Michler proposes that the increased molecular mobility is a result of the formation of fibrillar structure crazes. According to their studies, two types of crazes are formed: (a) precrazes which are related to the molecular mobility of a confined flow zone and (b) proper crazes which relate to the molecular mobility of a flow transition zone.

The interpretation of increased mobility with deformation below the yield point should be discussed attentively. McKenna indicates that the glassy structure is independent of the mechanical stress. Specifically, evidence is provided that the mechanical equilibration time of a glassy material is not changed after mechanical perturbation. However, mechanical measurements cannot, possibly, be conclusive, since it is known that the equilibrium time scales property dependent. Mechanical stress below the yield point accelerates aging and densifies the glass.

Time–strain superposition master-curves for polycarbonate are different than the time–temperature master-curves, implying that temperature and strain influence the relaxation response of the glass in different ways. O’conell et al. states: “Because time–temperature superposition has been successful and deviations from it usually reported to be only subtle, our preliminary conclusion here is that the time–strain master-curve is not the correct master-curve. Further work needs to be done to establish the apparent validity of the time–temperature master-curve.”

Regardless of the ongoing research concerning the effect of mechanical rejuvenation on mechanical and thermodynamical properties, there is little understanding from a microscopic viewpoint. Many techniques have been used to study the physical properties of mechanically deformed glass formers; nonetheless, only a minority can probe the dynamics in an extensive frequency or time range. Broadband dielectric spectroscopy is one of these few methods that can easily cover more than 10 orders of magnitude in time/frequency range. Most attention has been paid to the study of glassy polymers during deformation and is limited to the α- and β-transitions. Since α-PS is a weakly polar material resulting in a low strength of the dielectric relaxations, studies using dielectric relaxation spectroscopy are experimentally challenging and hence sparse. In this study, we report, for the first time, dielectric relaxation data on α-PS just after cold-rolling, and after subsequent thermal rejuvenation. To the best of our knowledge, no material has been studied in this way before. Supporting FTIR spectroscopy and polarized-light microscopy studies connect the molecular dynamics with changes in the molecular structure of α-PS.
2 | EXPERIMENTS

2.1 | Materials

Atactic PS with the commercial name N5000 was kindly supplied in pellet form by Shell. The molecular weight and poly-dispersity index of the a-PS were determined by High-Performance Liquid Chromatography (HPLC) using a Shimadzu HPLC instrument (Prominence-I, LC 2030C 3D). A comparison of these quantities prior to rolling ($M_w = 320.700 \text{ g/mol}$, $PDI = 2.22$) and after rolling ($M_w = 319.200 \text{ g/mol}$, $PDI = 2.23$) confirmed the absence of any significant change of the molecular weight (distribution) upon cold rolling as for example, caused by chain scission.

2.2 | Sample preparation

The preparation of films (0.13 mm thickness) was performed by compression molding at 185 °C under vacuum. Initially, the pellets were compressed in three steps of rising pressure from $\approx 23 \text{ MPa}$ up to $\approx 70 \text{ MPa}$. Thereafter, the mold was cooled down to room temperature at a pressure of approximately $23 \text{ MPa}$ between two cold metal plates.

To further reduce the surface roughness, the acquired films were recompressed between two Kapton foils at 185 °C at $\approx 70 \text{ MPa}$ for 10 min under vacuum. Eventually, the specimens were cooled down to room temperature at ambient pressure.

2.3 | Treatments

Cold rolling of the a-PS films was performed by rolling in a Durston DRM C100 two-roll mill (diameter of rolls 50 mm) until the thickness of the films was reduced by 20–30% of their initial thickness. The samples were then inserted into the dielectric sample cell that was precooled in advance to a temperature of $\approx -100 °C$ in order to arrest their cold-rolled state. In order to avoid moisture absorption during mounting of the sample, all sample handling around the dielectric cryostat took place under a flow of dry, gaseous nitrogen. Subsequently the sample was heated well above its $T_g$ (thermal rejuvenation) and then cooled down with the same rate of 3 K/min.

2.4 | Broadband dielectric relaxation spectroscopy (BDRS)

Employing a high-precision dielectric ALPHA analyzer (Novocontrol Technologies) connected to a Novocontrol Quatro temperature system keeping control of the specimen temperature ($\leq 0.05 \text{ K}$), dielectric measurements were performed from $-130 °C$ to $180 °C$ in a continuous frequency-sweep mode from $10^6 \text{ Hz}$ to $10^9 \text{ Hz}$, while a temperature ramp at $3 \text{ K/min}$ was employed in both heating and cooling stages. The specimens ($20 \text{ mm}$ in diameter and thickness of $\approx 60 \mu \text{m}$) were clamped between polished stainless steel electrodes.

To determine the relaxation time $\tau(T)$ and other relaxation parameters, the dielectric loss spectra $\epsilon''(\omega)$ acquired at various temperatures were fitted to the imaginary part of the empirical Havriliak-Negami (HN) relaxation function,$^{[24]}$

$$\epsilon'' = -\text{Im} \left\{ \frac{\Delta \epsilon}{(1 + (i \omega \tau)^{a})^{b}} \right\} + \frac{\sigma}{\varepsilon_{\nu} \omega}, \quad (1)$$

where $\Delta \epsilon$ denotes the relaxation strength, while $a$ and $b$ (“shape parameters”) relate to the logarithmic slope of the low-frequency loss tail ($a$) and the high-frequency loss tail ($-ab$). The last term accounts for Ohmic conduction, with conductivity $\sigma$, vacuum permittivity $\varepsilon_{\nu}$ and angular frequency $\omega = 2\pi f$. A thorough description of the analysis of dielectric data can be found in the work of Wübbenhorst et al.$^{[25]}$ and Van Turnhout et al.$^{[24]}$

2.5 | Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR)

The a-PS films were measured in the range of 400–4,000 cm$^{-1}$ at a resolution of 4 cm$^{-1}$ and a total of 20 scans with a FTIR PERKIN ELMER Spectrum Two spectrometer in reflection mode. Two measurements were performed on each sample. For analysis of the data, the baseline-corrected spectra were normalized with the 1,451 cm$^{-1}$ peak which is conformationally insensitive and therefore used as internal standard. The difference spectrum was obtained by subtraction of the spectrum of the not-rolled from the cold-rolled specimens. Since the FTIR measurements were performed perpendicularly to the polymer film plane, possible effects arising from the in-plane anisotropy of the film are averaged out and are not manifested in the absorption spectra.

2.6 | Polarized-light microscopy

Polarizing-light microscopy measurements (Zeiss Axio Imager D1) were performed for observing the internal
stresses of the samples. The morphology was captured by a Zeiss AxioCam MRc 5 camera.

3 | RESULTS

3.1 Dielectric relaxations

Figures 1 and 2 show the effect of cold rolling and subsequent quenching to a temperature of approximately \(-100^\circ C\) on the molecular dynamics of a-PS. Six processes are detected, which are labeled in order of increasing temperature. Considering the isochronal loss curve for \(f = 61\) Hz, first, at \(-110^\circ C\) the \(\gamma\)-relaxation (I) is observed followed by a second, low-temperature process (II) located around \(-70^\circ C\). At higher temperatures, three additional relaxation modes (III), (IV), and (V) can be distinguished around \(20^\circ C, 50^\circ C,\) and \(75^\circ C\), respectively. Though hard to resolve in the first heating run, process IV becomes clearly visible in the second heating as a low-intensity, isolated relaxation process, (Figure 2a). A fifth transition (V) appears at around \(75^\circ C\) (61 Hz) and is followed by the dynamic glass transition, the \(\alpha\)-relaxation (VI) around \(120^\circ C\). Opposed to the primary \(\alpha\)-relaxation (VI) and the \(\gamma\)-process (I) that are known from earlier studies, the other identified processes (II, III, IV and V) have not been reported in literature before. The relaxation-time data, calculated either by the fit of isothermal spectra \(e^\omega(\omega)\) to Equation (1) or by using a 2D fit procedure,[25] are shown in the Arrhenius diagrams, see Figure 3. The main \(\alpha\)-process, easily discernable by its characteristic curvature in the temperature dependence of the relaxation time, \(\tau(T)\), was fitted to the Vogel-Fulcher-Tamman (VFT) law,[22]

\[
\tau = \tau_\infty \exp \left( \frac{E_V}{R(T-T_V)} \right),
\]

with \(E_V\) and \(T_V\) being the Vogel activation energy and the Vogel temperature, respectively. The parameters \(R\) and \(\tau_\infty\) denote the universal gas constant and the limiting relaxation time at \(T \to \infty\).

All processes except the primary \(\alpha\)-process and process V show Arrhenius-like behavior, each with different activation energies, \(E_A\), according to:

\[
\tau = \tau_\infty \exp \left( \frac{E_A}{RT} \right)
\]

The fit parameters for the six relaxations are listed in Tables 1 and 2. The six processes can be classified as follows: Starting from the lowest temperature (Figures 1a and 2), process I can be observed, its low activation energy of 33.8 kJ/mol is typical for a local conformation transition.[23] At a somewhat higher temperature, process II emerges, characterized by an activation energy of 60.6 kJ/mol (Figure 3). Around \(20^\circ C\) (at 61 Hz), the process III is spotted (Figures 1a and 2) (activation energy of 70.6 kJ/mol), followed by process IV located at around \(50^\circ C\) and characterized by similar activation parameters. At even higher temperatures, at around \(75^\circ C\) the relaxation mode V shows up, but disappears just after passing \(80^\circ C\) (cf. Figure 1), which goes simultaneous with a shift and fading out of process IV (Figure 4a). Strikingly, the
2D fit clearly revealed VFT-behavior for the relaxation mode V being indicative for a dynamic glass transition. As expected, the main $\alpha$-relaxation (VI) also obeys a VFT-behavior, characteristic for segmental mobility of bulk a-PS (Figure 4a). Heating the sample above its glass transition, thermal rejuvenation starts, resulting in a removal of the thermomechanical history of the sample and the restoration of the common dynamic pattern of a-PS consisting of two “usual” relaxation processes, namely the primary $\alpha$-relaxation and $\gamma$-relaxation processes (Figure 1b). Although the VFT-parameters for the thermally rejuvenated sample differ significantly from those of the freshly rolled film, the actual differences in the relaxation times are only significant at temperatures just above $T_g$ (Table 1 and Figure 4). In the 2nd heating run, the $\gamma$-process (I) is again weak in intensity and shows a reduced activation energy around 21 kJ/mol (Table 2).

The commonly used Arrhenius analysis provides us with information on the activation energies of the new processes, however due to complexity of these processes it is difficult to proceed to a microstructural interpretation.\[^{26}\]

**FIGURE 2** Dielectric spectra of tan $\delta$ versus temperature as measured at frequencies of 61 Hz (a) and 976 Hz (b) for the cold-rolled a-PS (blue circles) versus the second heating cycle of the same sample (red circles). The data correspond to the dotted lines in Figure 1 [Color figure can be viewed at wileyonlinelibrary.com]

**FIGURE 3** Measured and fitted loss curves $\varepsilon''(T)$ at $f = 3.8$ Hz (a) and 15 Hz (b) for cold-rolled a-PS, which were fitted to a unique set of three HN functions in combination with a temperature dependent relaxation time $\tau(T)$ assuming either Arrhenius-(III, IV) or VFT behavior (V). For this two-dimensional “global” fit procedure described in Wübbenhorst et al.,\[^{25}\] dielectric loss data were used in the temperature range from $-30$ °C to $70$ °C (orange symbols) at frequencies from 1.9 Hz to 13 kHz. Two examples of fitted data along the T-axis are displayed, however, equally low deviations between measured data and the fit function were achieved in the entire $f$- and T-range. Note that calculated fit data above $70$ °C have no physical meaning because of structural changes caused by the fibrillar glass transition (V) and are thus excluded from the fit [Color figure can be viewed at wileyonlinelibrary.com]
We therefore further analyzed the activation parameters in terms of their activation entropies ($\Delta S$) and activation enthalpies ($\Delta H^*$), using the analysis introduced by Starkweather\cite{26} and applied for example, by Meersman\cite{27} for plastic crystals. Here, $\Delta H^*$ has the meaning of the theoretical activation enthalpy associated with a zero activation entropy.

Table 3 shows the values for $T_{11Hz}$, the temperature at which the peak of the corresponding process is located at a frequency of 1 Hz (obtained from fitting), $\Delta H^*$, $\Delta S$, $T_{11Hz} \Delta S$, $E_A = T_{11Hz} \Delta S + \Delta H^*$ and $T_{11Hz} \Delta S/E_A$ for the IV-, III-, II- and I($\gamma$)-relaxations of cold-rolled a-PS. A process where $T_{11Hz} \Delta S/E_A$ is less than 10% can be considered as “practically non-cooperative”, while relaxations substantially exceeding the 10% limit are characterized by a significant entropic contribution to $E_A$.

Now, starting from low temperatures, it appears that the I($\gamma$)-relaxation has an entropic contribution $T_{11Hz} \Delta S/E_A$ of 7%, supporting its earlier assignment to a non-cooperative, local conformation transition.\cite{26} In contrast, relaxations...
II and III clearly show an entropic barrier as indicated by values $T_{1Hz} \Delta S/E_A$ of 28% and 15%, respectively.\[26\]

Noteworthy, as indicated by its low $T_{1Hz} \Delta S/E_A$ of 3%, the process IV seems to be of noncooperative nature.

### TABLE 3

<table>
<thead>
<tr>
<th>Relaxation</th>
<th>$T_{1Hz}$ (K)</th>
<th>$\Delta H^*$ (kJ/mol)</th>
<th>$\Delta S$ (kJ/mol K)</th>
<th>$T_{1Hz} \Delta S$ (kJ/mol)</th>
<th>$E_A$ (kJ/mol)</th>
<th>$T_{1Hz} \Delta S/E_A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV</td>
<td>314.4</td>
<td>75.0</td>
<td>0.007</td>
<td>2.3</td>
<td>77.2</td>
<td>0.030 (3%)</td>
</tr>
<tr>
<td>III</td>
<td>252.4</td>
<td>59.7</td>
<td>0.043</td>
<td>10.8</td>
<td>70.6</td>
<td>0.154 (15%)</td>
</tr>
<tr>
<td>II</td>
<td>185.6</td>
<td>43.4</td>
<td>0.092</td>
<td>17.1</td>
<td>60.6</td>
<td>0.283 (28%)</td>
</tr>
<tr>
<td>I</td>
<td>136.1</td>
<td>31.5</td>
<td>0.017</td>
<td>2.4</td>
<td>33.8</td>
<td>0.070 (7%)</td>
</tr>
<tr>
<td>I (rejuv.)</td>
<td>98.4</td>
<td>22.5</td>
<td>-0.012</td>
<td>-1.2</td>
<td>21.3</td>
<td>-0.056 (−6%)</td>
</tr>
</tbody>
</table>

Note: $T_{1Hz} \Delta S/E_A$ is the entropic barrier in comparison to the apparent activation barrier (Arrhenius). Processes III and IV are fitted with a two dimensional fitting procedure.\[25\]

### FIGURE 5

(a) Normalized peak intensity ($I/I_{1451}$) ATR-FTIR spectra of a-PS before rolling (black line), after rolling (red line) and their difference spectrum (blue line); and spectra focused on (b) conformationally sensitive region 450–620 cm$^{-1}$ and (c) 720–800 cm$^{-1}$ [Color figure can be viewed at wileyonlinelibrary.com]

### 3.2 ATR-FTIR spectra

Figure 5 exhibits the normalized and difference infrared ATR-FTIR spectra for a-PS before and after cold rolling.
The negative bands in the difference spectrum are connected to the vibrational modes of the main chain at 2,848 cm\(^{-1}\) (CH\(_2\) symmetric stretching\(^{28,29}\)) and 2,923 cm\(^{-1}\) (CH\(_2\) asymmetric stretching)\(^{28,29}\). The positive bands are associated with the phenyl groups. Two bands that change considerably with cold rolling are the bands appearing at the difference spectrum at around 538 cm\(^{-1}\) and 754 cm\(^{-1}\) which show a positive change. The 538 cm\(^{-1}\) band is associated with the δ-form helical structure of syndiotactic polystyrene\(^{30–32}\) which is considered to be a short helix consisting of 7–12 monomeric units.\(^{33}\) The 754 cm\(^{-1}\) band is also considered to be associated with δ-form helices.\(^{32}\) These helices are formed by T\(_2\)G\(_2\) conformational sequences.\(^{34–36}\)

### 3.3 Polarized-light microscopy

In Figure 6, the polarized-light microscopy photos for a-PS subjected to cold rolling (Figure 6a) and subsequent thermal rejuvenation (Figure 6b) are shown. The effect of cold rolling on the creation of orientation and internal stresses in the polymer is observed by the color pattern under polarized light. Thermal rejuvenation erases the internal stresses of the a-PS films, as can be seen in Figure 6b.

### 4 DISCUSSION

The wealth of relaxation data obtained for freshly cold-rolled a-PS provides the unique chance to derive a microstructural model that rationalizes all molecular dynamics features. A cartoon of our new model is shown in Figure 7 and will be discussed in the following.

(a) \(\gamma\)-process (I). The \(\gamma\)-process, visible in (Figures 1a and 2), is a well-known dielectric relaxation process of a-PS and has been reported by several authors before.\(^{23,37,38}\) Its strength and activation energy are very sensitive to the microstructure as demonstrated by recent aging experiments\(^{38}\) as well as by results of this study. While the freshly rolled film showed an activation energy of 33.8 kJ/mol (Table 2), its value substantially dropped to 21 kJ/mol after thermal rejuvenation. Interestingly, such low value was also found by Arrese et al.\(^{39}\) by neutron scattering experiments, concluding that the \(\gamma\)-relaxation of a-PS is associated with localized low-amplitude motions. The low activation entropy found in this study once more emphasizes the noncooperativity of this relaxation\(^{26,40}\) (see Table 3).

(b) \(\gamma'\)-process (II). As seen in the Arrhenius diagram 4b, another secondary relaxation appears in just rolled a-PS, which is slower than the \(\gamma\)-process and characterized by a substantially higher activation energy of 60.6 kJ/mol (Table 2). Moreover, process II exhibits a very low pre-exponential factor \(\log(\tau_\infty) = -17.8\) that is far beyond any physical meaning in terms of a phonon-frequency being typically around \(10^{12}\) Hz. Closer inspection of Figure 4b actually reveals that all three Arrhenius dependences seem to converge to a single point where all curves intersect, a behavior known as compensation law\(^{41}\) or Meyer-Neldel rule\(^{42}\) indicating a correlation between the pre-exponential factor and the (apparent) activation energy. In terms of the Eyring and Starkweather approach, compensation behavior links relaxation processes that mainly differ in their activation entropy while the energetic contribution is varying only a little. From Table 3 we indeed see that \(\Delta S\) is the essential parameter that distinguishes process I from II. Consequently, we
think that both relaxations essentially share the same molecular mechanism of a $\gamma$ process (i.e., conformation transition$^{[43]}$) originating from chain segments in different conformational states affecting the activation entropy. The limited variation in $\Delta H^*$ can be rationalized by changes of intermolecular interactions as the result of different chain-packing and thus density, while intramolecular (predominantly rotational) energetic contributions might be maintained. The co-existence of two processes having a common nature, I and II (consequently labeled as $\gamma_0$) is a first strong hint for the formation of a heterogeneous microstructure in a-PS upon cold-rolling, comprising a moderately deformed matrix together with highly oriented fibrillar structures as reported and extensively studied by Donth and Michler.$^{[16]}$ In this scenario, based on its higher activation entropy ($\Delta S = 0.092 \text{ kJ/(mol K)}$), the $\gamma'$-process should be assigned to highly stretched chains located in the fibrillar fraction. Though direct imaging of fibrils was not possible in the framework of this study, experimental evidence for optical anisotropy and heterogeneity was provided by polarized microscopy (Figure 6a) as well as by FTIR showing a negative difference spectrum of the vibrations connected to the symmetric and asymmetric stretching of main-chain bands (Figure 5a).

(c) Process III. Toward higher temperatures, a broad and strong III-relaxation is observed ($-16 ^\circ\text{C}$ to $30 ^\circ\text{C}$ at 61 Hz) (Figures 1a and 2) with an activation energy of around 70.6 kJ/mol (Table 2). This unfamiliar process has a similar activation energy as the $\beta_1$- and $\beta_2$-processes found in a-PS and s-PS by Lupas¸cu et al.$^{[22]}$ who attributed these relaxation modes to a defect mechanism (helix inversion) of T$_2$G$_2$ helices (Table 4). Despite its very similar activation energy, the process III is about two decades faster than the $\beta_1$-process. The presence of T$_2$G$_2$ helices could indeed be confirmed by ATR-FTIR, see the difference spectra in Figure 5, favoring the idea of defect fluctuations within syndiotactic helices as the molecular mechanism behind process III.$^{[22]}$ An explanation for the high activation energy and substantial activation entropy of process III is a relaxation mechanism involving T$_2$G$_2$ helices. Considering the findings on oriented fibrillar material reported by Li et al.$^{[44]}$ we speculate that the observed helices in the ATR-FTIR spectra (Figure 5) together with the highly activated III-process may point to helical structures being part of the highly stretched fibrils. Additional support for this idea comes from the observation (cf. Figure 4a) that relaxation III significantly slows-down upon softening of the fibrils around 70 $^\circ\text{C}$ (see Section 4) suggesting a certain sensitivity of the helix inversion process to chain stresses. Alternatively, the same observations might be rationalized by assuming helices located at the (large) fibrillar surface, resulting in surface enhanced segmental mobility along with a peculiar relaxation mode similar to process III as found for ultrathin films of a-PS.$^{[45]}$

With the removal of strain softening, glassy polymers display ductile behavior.$^{[46,47]}$ The presence of defects in crystals of i-PP (isotactic polypropylene) creates high ductility and flexibility because of polymorphic transformations that occur during deformation.$^{[48]}$ By combining these two observations, we propose that a similar mechanism is responsible for the ductile

<table>
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<th>$T$ (K)</th>
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<th>$\Delta S$ (kJ/(mol K))</th>
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<td>314.4</td>
<td>77.2</td>
<td>75.0</td>
<td>0.007</td>
</tr>
</tbody>
</table>

FIGURE 7 Molecular assignment of all relaxation processes to microstructural features for cold-rolled a-PS [Color figure can be viewed at wileyonlinelibrary.com]
behavior of mechanically rejuvenated PS in which, during deformation, the \textit{trans-trans} (amorphous) sequences are forming short-length defect helices that create the macroscopically observed flexibility.

(d) Process IV. Inspecting Figure 4a and Table 2, we clearly recognize the similarity between processes III and IV regarding their activation parameters. While process III was actually found to be faster than the \(\beta_1\)-relaxation known for s-PS, the activation parameters of process IV unambiguously identify this relaxation as \(\beta_1\)-relaxation\cite{22} ascribed to the helix inversion dynamics of single helices under bulk conditions. This helical fraction might be located either in the polymer matrix or in the inner part of the fibrils.

(e) \(\alpha^*-\text{process (V).}\) This prominent relaxation is a key feature of the dielectric relaxation pattern of just rolled a-PS. According to our two-dimensional fit procedure, process V is characterized by VFT behavior being the signature of a dynamic glass transition (Figures 2, 3, and 7). Below 70 °C, this relaxation process becomes visible in a small temperature window as rapidly moving (highly activated) relaxation process, which starts to vanish abruptly after exceeding 70 °C. The latter phenomenon is particularly striking and manifests itself as a frequency independent peak in the dielectric loss as seen in the isochronal representation \(\varepsilon''(f, T)\) (cf. Figure 2), suggesting the action of a thermal transition at around 75 °C.

The observation of a thermal transition around that temperature has been reported before by calorimetry. A series of custom-made Deformation Calorimetry (DC) experiments\cite{49} on glassy polymers such as polystyrene (PS), polycarbonate (PC) and poly (methyl methacrylate) (PMMA) revealed that plastic deformation below the bulk glass transition results in high internal energy storage, that is released upon heating of the sample and appears as an exothermic abnormality in the region below \(T_g\) in DSC\cite{49,50}. Molecular Dynamic simulations\cite{10} also confirmed that the stored internal energy in PS and PC glasses after plastic deformation is remarkably high. Such behavior is explained in terms of localized shear transformation zones (STZ's)\cite{51}. We think that the process V actually represents the onset of segmental dynamics of highly stretched fibrils, which have a substantially lower \(T_g\) because of their large surface-to-volume ratio (confinement effect) similar to ultrathin polymer films.\cite{45} Once the fibrils are heated above their \(T_g\), the fibrils soften and subsequently collapse by virtue of retraction of stretched segments to their random coil configuration. As a consequence, the fibrillar structures fuses and internal surfaces within the crazes disappear, a process that goes along with a dynamic freezing of the former fibrillar fraction by concurrent up-shifting of its glass transition temperature (physical aging).\cite{16}

(f) \textit{Primary \(\alpha\)-relaxation process (VI).} As already discussed above, the \(\alpha\)-process of the just rolled sample nearly coincides with that after thermal rejuvenation. Little differences in the relaxation time \(\tau_\alpha\) are restricted to temperatures just above the volumetric glass transition \(T_g\), while at about 120 °C the relaxation time curves collapse (Figure 4a). This observation is in fact not surprising and just confirms that heating well above the bulk \(T_g\) restores bulk dynamics at the time- and length scale of segmental motions. In other words, there is no evidence that chain deformations arising from prior plastic deformation persist after high temperature treatment.

5 \textbf{CONCLUSIONS}

By the results presented above, yet unknown dynamics of cold-rolled a-PS, a polymer widely used in industry and broadly investigated in academia, have been uncovered. Using fast dielectric relaxation spectroscopy, four new relaxation processes II, III, IV, and V for atactic polystyrene after cold rolling and quenching, are unveiled for the first time. Subsequent thermal rejuvenation suppresses all these peculiar processes and restores the typical relaxation behavior of a-PS, the \(\alpha\)-relaxation and a weak \(\gamma\)-process. A detailed discussion of all relaxation processes in the framework of craze formation and multiplicity of the glass transition,\cite{16} supported by an activation enthalpy/entropy analysis by Starkweather,\cite{46} yields a detailed physical picture about the structure/dynamics relationship in cold-rolled PS: (a) processes I (\(\gamma\)) and II (\(\gamma'\)) represent local conformation transitions, referring to chains of two different degrees of stretching (T/G-ratio); (b) processes III and IV were identified as helix-inversion processes of \(T_2G_2\) helices as reported earlier for syndiotactic-rich PS – an assignment that was supported by FTIR results showing indeed the formation of \(T_2G_2\) helices upon cold rolling. Finally, the relaxation V could be attributed to the onset of the fibrillar glass transition (within crazes) around 70 °C, leading to abrupt stress release by collapse of the fibrils and hence dying out of process V. Polarized-light microscopy confirmed the creation of oriented structures and internal stresses upon cold rolling, and their removal upon thermal rejuvenation. This work provides first data and a physical picture regarding the (transient) molecular dynamics in mechanically rejuvenated compared to thermally rejuvenated a-PS, which might help to unravel the mechanism of temporary toughening in a-PS induced by cold-rolling in the near future. A possible mechanism behind the
macroscopic ductility of mechanically rejuvenated samples is proposed. Our findings could be corroborated via other experimental techniques to obtain more information on mechanisms underlying the mechanical rejuvenation, for example, X-ray scattering or nuclear magnetic resonance spectroscopy. Moreover, in the context of molecular dynamic simulations, our findings suggest that the initial conditions should be carefully chosen, taking into account the spatial heterogeneities.

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