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Effect of Low-Temperature Physical Aging on the Dynamic Transitions of Atactic Polystyrene in the Glassy State

Kalouda Grigoriadi,1,2 Tristan Putzeys,3 Michael Wübbenhorst,3 Lambèrt C. A. van Breemen,1 Patrick D. Anderson,1 Markus Hütter1

1Polymer Technology, Department of Mechanical Engineering, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands
2Dutch Polymer Institute, PO Box 902, 5600 AX, Eindhoven, The Netherlands
3Department of Physics and Astronomy, KU Leuven, Celestijnenlaan 200D, B-3001 Leuven, Belgium

Correspondence to: M. Hütter (E-mail: m.huetter@tue.nl)

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ABSTRACT: The local and cooperative dynamics of atactic PS (a-PS) were studied by broadband dielectric relaxation spectroscopy (BDRS) and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR). The a-PS has been subjected to thermal rejuvenation and subsequent quenching, short-term aging (6 weeks), and long-term aging (1 year) at ambient conditions. Where for the rejuvenated sample only an α- and a γ-relaxation is observed, short-term aging results in an additional βα-relaxation that merges with the α-relaxation at longer aging times. The γ-relaxation is increasing in intensity and activation energy during aging. The α-process shows no spectral changes and shift in the relaxation time upon aging. This may be attributed to a possible erasure of history of the material during the temperature-sweep mode measurement. Fourier transform infrared spectroscopy (FTIR) results suggest that the energetically favorable trans-trans (tt) conformers are increased in population with aging. © 2019 The Authors. Journal of Polymer Science Part B: Polymer Physics published by Wiley Periodicals, Inc. J. Polym. Sci., Part B: Polym. Phys. 2019, 57, 1394–1401

KEYWORDS: ageing; annealing; amorphous; atactic; dielectric properties; FT-IR; molecular dynamics; polystyrene

INTRODUCTION Below the glass-transition temperature \( T_g \) glasses are known to be in a nonequilibrium state and their relaxation toward equilibrium is called physical aging. Physical aging causes a slow alteration of the physical structure of the material. This alteration often has a detrimental effect on the material properties. Macroscopically, a gradual increase of the yield stress of the material is observed, which causes embrittlement, resulting in a gradual loss of the design function and ultimate failure. These macroscopic changes make physical aging of enormous importance, both on a technical and research level.

Numerous studies have been done to examine the effect of physical aging on the macroscopic mechanical behavior of glassy polymers3–8 and similarly for the enthalpy changes upon aging.8–14 Most of the studies are trying to explain their results based on the free-volume theory, in which the changes of the properties of the material are interpreted solely by the changes in free volume.15–19 Other studies try to explain their results from the standpoint of segmental/chain mobility.20,21 However, the link between the molecular structure and intrinsic properties is still lacking.

Since many physical properties of glassy polymers are affected by physical aging, a large variety of techniques can be used to study them; however, only a few studies can follow the dynamics over a broad frequency range, which would be necessary for studying the effects of physical aging on small scales. One of these methods is broadband dielectric relaxation spectroscopy (BDRS), which covers more than 10 decades in time and frequency. Most of the research studies involve measurements of relaxations close to the glass transition, and only a few are dedicated to measure the effect of aging on the secondary relaxations below \( T_g \). Polystyrene (PS) is a material frequently used in both academia and industry. It is a particularly interesting material to study because (a) it is known for its fast aging kinetics and (b) it has been studied extensively by simulations.24–26 So far, dielectric relaxation spectroscopy has very limited use in studying aging of atactic polystyrene (a-PS) because the measurements are known to be difficult due to the weak relaxation strength of the material.

In this work, we study rejuvenated and fast cooled (cooling rate \( \approx 230 \text{ K/min} \)) a-PS using dielectric and ATR-FTIR
spectroscopy and compare the results with short- and long-term aged a-PS samples stored at room temperature. Complementary BDRS and ATR-FTIR studies allow us to relate changes in the molecular dynamics with changes in molecular conformations during physical aging.

EXPERIMENTS

Materials

Atactic PS with the commercial name N5000 was kindly supplied in pellet form by Shell. The molecular weight \( M_0 = 320.700 \) g/mol and poly-dispersion index (PDI = 2.22) were determined by high-performance liquid chromatography (HPLC) using a Shimadzu HPLC instrument (Prominence 4, LC 2030C 3D).

Sample Preparation

Films of 0.13 mm thickness were prepared by compression molding under vacuum at a temperature of 185 °C. First, the pellets were heated for 5 min and then compressed in three steps of increasing pressure from \( \approx 23 \) MPa up to \( \approx 70 \) MPa. Afterward, the mold was cooled down to room temperature between two cold metal plates at a pressure of approximately 23 MPa.

The obtained films were recompressed between two Kapton foils under vacuum at 185 °C at \( \approx 70 \) MPa for 10 min to eliminate surface roughness. Afterward, the mold was cooled down at ambient conditions.

Treatments

The samples were prepared for the dielectric and ATR-FTIR spectroscopy measurements as follows. The PS films were thermally rejuvenated by heating them to 140 °C for half an hour and subsequently quenching them in liquid nitrogen (cooling rate \( \approx 230 \) K/min). The samples were flushed with nitrogen gas to avoid water condensation on their surface. Afterward, the films were aged for 6 weeks (called short-term aged hereafter) and 1 year (called long-term aged hereafter) respectively, at room temperature and relative humidity (RH) \( \approx 30\% \).

Broadband Dielectric Relaxation Spectroscopy

Dielectric measurements in a temperature/frequency sweep mode, from \( 10^{-1} \) Hz to \( 10^{6} \) Hz, and from \( -120 °C \) to \( 145 °C \) in steps of 5 K, leading to an effective heating rate of around 0.5 K/min. A high-accuracy dielectric analyzer (ALPHA analyzer, Novocontrol Technologies) in combination with a Novocontrol Quatro temperature system maintaining excellent control of the sample temperature (\( \leq 0.05 \) K) was used. The samples (40 mm in diameter and a thickness of 0.13 mm) were placed between polished stainless steel electrodes.

To determine the relaxation time \( \tau(T) \) and other relaxation parameters, the dielectric loss spectra \( \epsilon''(\omega) \), obtained for different temperatures (Fig. 1), were fitted to the imaginary part of the Havriliak-Negami (HN) relaxation function,

\[
\epsilon'' = -\text{Im} \left( \frac{\Delta \epsilon}{1 + (\omega \tau)^{a \beta}} \right) + \frac{\sigma}{\epsilon_s \omega} \tag{1}
\]

where \( \Delta \epsilon \) denotes the relaxation strength, while the two “shape parameters” \( a \) and \( b \) relate to the logarithmic slope of the low-frequency loss tail \( (a) \) and the high-frequency loss tail \( (a \beta) \). The second term of the right-hand side of eq 1 accounts for the Ohmic conduction, where \( \sigma \) corresponds to the conductivity, \( \epsilon_s \) to the vacuum permittivity and \( \omega = 2\pi f \) to the angular frequency. An extensive description of the analysis procedure for dielectric features can be found in the studies of Wübbenhorst and van Turnhout\(^{29}\) and van Turnhout and Wübbenhorst.\(^{30}\)

![FIGURE 1 Dielectric loss spectra \( \epsilon''(f,T) \) for various temperatures showing the dynamic glass-transition \( \alpha \)-process. [Color figure can be viewed at wileyonlinelibrary.com]](image1)

![FIGURE 2 Snapshot of dielectric spectra of loss tangent tan\( \delta \) versus temperature as measured at frequency 100 Hz for the thermally rejuvenated a-PS (black squares), short-term aged (red circles), and long-term aged (blue triangles) sample. [Color figure can be viewed at wileyonlinelibrary.com]](image2)
Fourier Transform Infrared Spectroscopy

ATR-FTIR spectroscopy in reflection mode (PERKIN ELMER Spectrum two spectrometer) was carried out on the PS films in the range from 400 to 4000 cm$^{-1}$ at a resolution of 4 cm$^{-1}$, with a total of 50 scans. Two such measurements were performed on each sample. A normalization protocol was applied to erase the effect of sample thickness in the absorbance spectrum. FTIR spectra contain absorption bands that are specific to both trans-trans and trans-gauche conformations, while other bands (ring modes) show no conformation sensitivity and thus provide an internal reference. Specifically, the original spectra of the conformationally sensitive 538 cm$^{-1}$ peak were normalized with the 1451 cm$^{-1}$ peak that does not represent conformational changes and thus is used as an internal reference.

RESULTS

Dielectric Relaxations

The molecular dynamics of thermally rejuvenated, short- and long-term aged (ambient conditions) a-PS were studied by BDS. The relaxation behavior of the a-PS is given in Figures 2, 3, and 4. The representation of tanδ ($\varepsilon''/\varepsilon'$) is chosen, since tanδ eliminates uncertainties with samples thickness, while the peak shape is preserved due to the low relaxation strength of all processes.

In Figure 2, the tanδ as a function of temperature is represented for the thermally rejuvenated sample, a short-term aged (at 20 °C) sample and a long-term aged (at 20 °C) sample, as recorded at a frequency of 100 Hz. In Figure 5, the tanδ as a function of frequency in the temperature range where a specific process is visible are shown for the thermally rejuvenated sample, the short- and the long-term aged samples. The resulting spectra of thermally rejuvenated a-PS samples reveal the main $\alpha$-relaxation process, also found in the literature, whereas no second process, $\beta$, appears in the whole frequency range [Figs. 2 and 5(b)]. The $\gamma$-process appears at $-110$ °C (Fig. 2).

In contrast, both aged samples show an additional $\beta^*$-process just below the $\alpha$-relaxation and well above the $\gamma$-relaxation range. For longer aging times, this $\beta^*$-process becomes a shoulder of the main $\alpha$-relaxation process. At the measured frequencies and temperatures, not the whole peak but only the tail of the $\beta^*$-process is shown in Figure 5.

The dielectric input was examined by fitting isothermal spectra $\varepsilon''(\omega)$ to eq 1, to calculate the complete relaxation and thermal activation parameters. The relaxation-time data are shown in the Arrhenius diagram (Fig. 4). The $\alpha$-process distinguished by its representative curvature in the temperature dependence of the relaxation time, $\tau(T)$, was fitted to the Vogel–Fulcher-Tamman (VFT) law:

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

where $E_V$ and $T_V$ are the Vogel activation energy and the Vogel temperature, respectively. The additional two parameters $R$ and $\tau_\infty$ are the universal gas constant and the ultimate relaxation time, respectively. Contrary, the $\gamma$-relaxation data follow the Arrhenius equation, eq 3, suggestive for “simple” thermally activated response,

$$\tau = \tau_\infty \exp \left( \frac{E_A}{RT} \right),$$

with Arrhenius activation energy $E_A$ and ultimate relaxation time $\tau_\infty$. In order to translate the Vogel activation energy $E_V$ into an equivalent Arrhenius activation energy $E_A$, the apparent temperature-dependent activation energy, $E_{\text{app}} = E_V(1 - T_V/T)^{-1}$, is determined according to the procedure described in Van Turnhout and Wübbenhorst. The used temperature $T$ is defined as the temperature at which $\tau_\infty = 100s$, a convention widely used in the dielectric-spectroscopy community. All fit parameters for the three relaxations are noted in Table 1. The dielectric activation map for the $\alpha$- and $\gamma$-relaxations for all the reference and aged samples is shown in Figure 3. Evidently, the effect of aging is different for each molecular relaxation in a-PS. The width and the relaxation times of the $\alpha$-relaxation do not change significantly with aging [Figs. 2 and 5(a,c) and Table 1], while the Vogel activation energy of this process is in agreement with other studies. The $\beta^*$-process did not appear in a rejuvenated sample [Figs. 2, 5(b), and 3(a)], although, for 6 weeks of aging, the peak of this process appeared at 73 °C (100 Hz). After 1 year of aging at room temperature, the $\beta^*$-process peak increased in intensity [Fig. 5(f)] and became a shoulder of the $\alpha$-process [Fig. 3(c)]. Moreover, the $\beta^*$-process for both short- and long-term aged samples shows a peculiar behavior: the losses increase with increasing temperature up to 70 °C [Figures 5(d–f)]. Increasing the temperature from 70 °C to 90 °C, the losses decrease. Unfortunately, only the tail of the

FIGURE 3 Activation diagram showing the peak relaxation times $\tau_\alpha$ and $\tau_\gamma$ for three different treatments of a-PS: thermal rejuvenation (black squares), short-term aging (red circles), and long-term aging (blue triangles). Lines: fit with eq 2 and eq 3, respectively. Note: the $\beta^*$-relaxation data points are obtained from the respective peak-positions in the $\varepsilon'(T)$-graphs at constant frequency $f$ (not shown), and using $\tau = 1/(2\pi f)$. [Color figure can be viewed at wileyonlinelibrary.com]
\(\beta^*\)-process appears in a short-frequency range (\(10^{-1}\) to \(10^6\) Hz) only [Fig. 5(d–f)], which makes the determination of the relaxation time and activation energy of this relaxation process unreliable. The \(\gamma\)-process had a profound increase in intensity of tan\(\delta\) and activation energy with aging (Figs. 2 and 3, Table 1). The thermally rejuvenated \(\alpha\)-PS had a \(\gamma\)-process with an activation energy of 20.94 \(\pm\) 8.75 kJ/mol, when after 6 weeks of aging the intensity of this process as well as its activation energy (23.64 \(\pm\) 0.5 kJ/mol) increased. After 1 year of aging, its intensity was increased more with an activation energy of 29.33 \(\pm\) 0.3 kJ/mol. The activation energies of the \(\gamma\)-process have values lower but comparable to the ones in the study of Wypych et al.\(^{27}\) There, the authors state that

**FIGURE 4** Three-dimensional representation of the dielectric loss tangent tan\(\delta(f,T)\) for (a) the thermally rejuvenated, (b) short-term aged, and (c) long-term aged \(\alpha\)-PS. [Color figure can be viewed at wileyonlinelibrary.com]
the activation energy is about 35 kJ/mol for the thermally rejuvenated a-PS and increases to 45 kJ/mol after 10 months of aging at room temperature.

**ATR-FTIR Spectra**

The bands in the 500–600 cm\(^{-1}\) region are due to out-of-plane deformation of the phenyl ring and they are conformationally sensitive. The broad 538 cm\(^{-1}\) band due to amorphous components is assigned to the out-of-plane deformation mode of the phenyl ring in trans-conformation segments with four and more monomeric units. The increase in trans-trans conformation between the rejuvenated and aged a-PS was confirmed by ATR-FTIR measurements. Figure 6 presents the peak intensity of normalized mid-infrared ATR-FTIR spectra of the thermally rejuvenated, short- and long-term aged a-PS.

It is evident that the intensity of the 538 cm\(^{-1}\) band was increased during aging, showing that the trans-trans conformation segments were also increasing in population with aging.

**TABLE 1 Activation Parameters and Their Standard Deviation for the \(\alpha\)- and \(\gamma\)-Processes Found in a-PS for the Different Treatments; the Apparent Temperature-Dependent Activation Energy \(E_{app}\) is Included as well**

<table>
<thead>
<tr>
<th>Treatment</th>
<th>(\alpha)-Process</th>
<th>(E_V) (kJ/mol)</th>
<th>(E_{app}) (kJ/mol)</th>
<th>(T_V) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermally rejuvenated</td>
<td>(-11.86 \pm 0.04)</td>
<td>10.7 \pm 0.2</td>
<td>1236 \pm 24</td>
<td>327.270 \pm 0.008</td>
</tr>
<tr>
<td>Short-term aged</td>
<td>(-11.78 \pm 0.06)</td>
<td>10.1 \pm 0.3</td>
<td>1364 \pm 34</td>
<td>330.220 \pm 0.012</td>
</tr>
<tr>
<td>Long-term aged</td>
<td>(-11.55 \pm 0.05)</td>
<td>9.8 \pm 0.3</td>
<td>1306 \pm 32</td>
<td>330.000 \pm 0.001</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Treatment</th>
<th>(\gamma)-Process</th>
<th>(E_A) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermally rejuvenated</td>
<td>(-9.99 \pm 1.75)</td>
<td>20.9 \pm 8.7</td>
</tr>
<tr>
<td>Short-term aged</td>
<td>(-11.10 \pm 0.10)</td>
<td>23.6 \pm 0.5</td>
</tr>
<tr>
<td>Long-term aged</td>
<td>(-12.51 \pm 0.06)</td>
<td>29.3 \pm 0.3</td>
</tr>
</tbody>
</table>
The phenyl rings. A noncooperative monodisperse polystyrene, and is attributed to the rotation of α torsion, a couple of relaxation processes are described in the literature. 

DISCUSSION

To identify the molecular mechanism that links the emergence of a β*-relaxation upon short-term aging and its merging with the main α-relaxation, as well as the increase of intensity and activation energy of the γ-relaxation with long-term aging, we discuss the findings of the previous sections in more detail.

Below the glass-transition region, manifested by the α-relaxation, a couple of relaxation processes are described in the literature: a β*-process is detected directly below the main α-relaxation at around 47°C (f = 110 Hz) for atactic polydisperse polystyrene and at around 67°C (f = 110 Hz) for atactic monodisperse polystyrene, and is attributed to the rotation of the phenyl rings. 

A noncooperative α**-relaxation is found in ultrathin a-PS films at around 10°C (f = 0.7 Hz) which is attributed to surface dynamics. The peculiar β1- and β2- relaxation processes (at about 90°C and 180°C, respectively, and f = 100 Hz) have been reported for a-PS with a solvent history and are attributed to the dynamics of helical “rods” formed by syndiotactic sequences. 

A γ-process is detected at much lower temperatures (−120°C, f = 100 Hz) and is assigned to torsional motion of methylene sequences formed in the backbone of the chain. 

Time-of-flight and backscattering studies suggest that the origin of this relaxation is localized low-amplitude angular fluctuations. Heading to even lower temperatures, the γ’- and δ-relaxations of PS may appear due to defects in chemical structure.

In this study, first of all, the α-relaxation appeared to have the same spectral shape [Figs. 2, 5(a,c,e) and 3] and relaxation times in rejuvenated and aged samples. Isothermal aging at 25°C for 6 weeks resulted in an emergence of the peak of the β*-process [Figs. 2, 5(d,f), and 3], as it was also seen by mechanical spectroscopy on PS and amorphous Polyethylene naphthalate (PEN). This result contradicts a large amount of research, which has shown a significant impact of aging on the α-relaxation 41–44 at aging temperatures close to the Tg. 

The reason behind this difference may be that this study is concerned with aging at only low temperatures (Tg ~80 K). Hodge and Huvard45 have already shown, by enthalpy relaxation experiments, that when aging far below Tg, the enthalpy overshoot remains unaltered and a second endothermic peak is observed. More recently, Wypych et al.27 have shown differential scanning calorimetry results for low-temperature aged PS, where the α-relaxation remains unaltered in the course of 10 months; however, these observations were not discussed. More proof about the insensitivity of the α-relaxation to low-temperature aging has been seen in polymers 46 and metallic glasses,47 indicating that there are different mechanisms present to recover to equilibrium far from and close to Tg specifically mentioning that aging far below Tg is disconnected from the α-process. Contrary, creep experiments on PS by Struik48 showed that PS ages in temperatures far below Tg obeying time–temperature superposition. We believe that the results shown by Struik48 may display the macroscopic intertwined aging kinetics of the β*- and α-processes as it has been observed by Van Breemen et al.49 Nevertheless, the reason for that the α-process seems to be insensitive to aging in this study could be the complicated thermal history of the samples studied, which Struik named “downquench-storage-upquench” history. Here, we rapidly quench the samples from a temperature above Tg to a temperature close to 0°C, subsequently age the samples at room temperature and then measure the samples by heating them with a rate of about 0.5 K/min. Heating the sample has an effect on the relaxation times: During heating, the samples age, their internal dynamics slow down with increasing aging, and finally the history of the material may be (partly) erased by the heating scan at temperatures close to Tg. According to Struik,48 fast processes exist that contribute to the volume relaxation which have a lower transition temperature than the Tg of the material. Consequently, when a material is heated, even at a temperature far below Tg, the physical aging that has occurred can be partially erased; the α-process observed seems not being affected by aging. Furthermore, the dynamics delayed by aging may not be observed in the frequency window in which the measurements are done. Second, isothermal aging at 25°C for 1 year leads to the increase of intensity and the merge of the β*-process with the main α-process, in agreement with mechanical spectroscopy findings on PS.40 Moreover, a very peculiar behavior can be seen for the β*-process [Fig. 5(d,f)]. The losses increase with increasing temperature from 55°C to 70°C. Increasing the temperature from 70°C to 90°C shows a decreasing trend of the losses. This behavior may be the evidence that at around 70°C, there is the transition temperature of the fast processes contributing to the volume relaxation as mentioned by Struik.49 Heating...
above 70 °C, around 30 K below \( T_g \) of the material, the thermomechanical history of the specimen is already starting to be erased. Low-frequency Raman spectroscopy (LFRS) on a-PS has shown that the Raman scattering around the Boson peak is weaker for aged samples at room temperature for 10 months compared to the rejuvenated PS. The Boson peak was interpreted as an indication of more cohesive nano-domains surrounded by soft zones. Decreasing intensity of the Boson peak was explained as decreasing contrast between the cohesive nano-domains and the soft surrounding medium (softer channels). Hence, the decrease of the Boson peak intensity with aging suggests that the glass nanostructure becomes more homogeneous. The merge of the \( \beta^* \)-process with the main \( \alpha \)-relaxation upon long-term aging could be related to the decrease of mobility of the previously high mobility domains due to better packing. Having the LFRS picture in mind, one could interpret that these high mobility domains were "locked in" upon fast cooling, leading to no appearance of a \( \beta^* \)-process in the dielectric spectrum [Figs. 2, 5(b), and 3]. We speculate that with short-term aging, the domains of collective rearranging zones responsible for the main \( \alpha \)-relaxation process develop into domains of high mobility for the more local sub-\( T_g \) relaxation motions, thereby "un-locking" the \( \beta^* \)-process. Third, interestingly, also the \( \gamma \)-relaxation seems to be affected by aging, as can be seen from its increase in both intensity and activation energy, as it was also seen in a previous study by dielectric spectroscopy on a-PS. Molecular dynamic simulations by Boulougouris and Theodorou suggested that the most probable candidate of the \( \gamma \)-process motion is the vibration of the phenyl stem and ring. This motion is immensely random. These authors speculated that the low mobility occurs in regions with a high degree of local tactivity along the a-PS chain.

The comparison between the ATR-FTIR spectra for the 538 cm\(^{-1} \) band, which is representative of the \textit{trans-trans} conformations, for the thermally rejuvenated, short- and long-term aged a-PS is presented in Figure 6. Clearly, there is an intensity increase upon aging, that implies an increasing number of \textit{trans-trans}-conformers, which is in agreement with results reported for polycarbonate and poly(\( \ell \)-lactide). Upon physical aging of polycarbonate, it has been suggested that the \textit{trans-cis} conformers rearrange into the \textit{trans-trans} counterparts by comparing the spectral intensity of the characteristic bands. The \textit{trans-trans} conformations of polycarbonate are known to be energetically more stable than the \textit{trans-cis} counterparts, allowing closer packing of the polymer chains. Similar tendencies of the conformational rearrangements from the high- to low-energy conformers upon physical aging have also been reported for poly(ethylene terephthalate) (PET), polystyrene (PS), poly(vinyl chloride) (PVC), and poly(\( \ell \)-lactide) (PLLA). It is suggested that the conformational changes, which appear during physical aging could lower the potential energy of a glassy polymer as it was discussed by Debenedetti and Stillinger.

**CONCLUSIONS**

Using BDRS, the emergence of a \( \beta^* \)-relaxation by short-term aging and its intensity increase and merging with the \( \alpha \)-process upon long-term aging together was revealed for low-temperature aged a-PS for the first time by this technique. A progressive increase of the intensity and activation energy of the \( \gamma \)-relaxation was observed with aging. By ATR-FTIR spectroscopy an energetically favorable increase of the \textit{trans-trans} population was observed, upon aging.

This suggests that the physical aging favors the formation of low-energy molecular states, rationalized on the basis of the energy landscape concept. With rejuvenation and fast cooling, the system is falling into a local minimum, with relatively few \textit{trans-trans}-conformers. Aging leads the system into ever deeper minima with increasing number of \textit{trans-trans}-conformers.

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**REFERENCES AND NOTES**
