CHANGES IN SEGMENTAL DYNAMICS OF ISOPRENE IN STYRENE-ISOPRENE BLOCK COPOLYMERS UPON ELONGATION PROBED BY SOLID STATE CARBON NMR RELAXATION TIME MEASUREMENTS

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ABSTRACT

The segmental motion of isoprene within styrene–isoprene tri-block (SIS) copolymers (14 wt% and 22 wt% styrene) is reported as a function of elongation at three different temperatures (293K, 303K and 313K) using carbon solid state NMR spin-spin (T2) and spin-lattice (T1) relaxation time measurements. The results show that after a sample elongation by a factor of approximately 4, the segmental mobility decreases by a factor of 2 – 3. Also, the segmental mobility reveals a temperature behaviour which is strongly dependent on the relative amount of styrene within the styrene-isoprene tri-block polymers. The activation energy of the segmental motion is further discussed with respect to the B-parameter in the Vogel-Tammann-Fulcher (VTF) Equation; \( \log(\tau/\tau_0) = B/(T-T_0) \), where \( \tau \) is the segmental correlation time at the (absolute) temperature \( T \).

Keywords: Polysoprene, polystyrene, block copolymer, NMR relaxation, segmental motion.

1. INTRODUCTION

Block copolymers offer not only interesting morphological and material properties but also the opportunity to probe the molecular dynamics within multi-component systems. For instance, styrene-isoprene tri-block copolymers (SIS) possess some fascinating properties due to its elastomeric- (polysoprene) and thermoplastic properties (polystyrene) [1]. Due to the covalent linkage between chemically dissimilar segments, the rigid polystyrene domains may form a three-dimensional network of crosslink sites. Consequently, SIS copolymers exhibit mechanical properties that are, in many ways, comparable to those of a vulcanized (covalently cross linked) rubber [2]. Hence, molecular motion within the soft polyisoprene domain (SIS) is of significant interest due to its prominent influence on the stretching properties.

A number of research groups have reported on various properties of such block copolymer systems under external strain by applying Small Angle Neutron Scattering (SANS) [3], 2-Dimentional Small Angle X-ray Scattering (2D-SAXS) [4], Transmission Electron Microscopy (TEM) [4] and Fluorescence techniques [5] to elucidate the morphology and orientation of styrene-X-tri-block copolymers (where X represents any elastomeric component, i.e., isoprene or butadiene).

The phase transitions of triblock copolymers (SIS) have been reported using SAXS and TEM [6-9] by focusing on the properties of the polystyrene domain. Due to the characteristics of these tri-block copolymers, they can be considered to involve elastomeric properties (the polyisoprene domain) and thermoplastic capability (the polystyrene domain).

NMR has become an extremely powerful tool for characterizing polymer systems on a molecular level, including the portrayal of molecular motion. For instance, various relaxation time models, as reported by Hall-Helfand (HH-model) [10], Viovy-Monnerie-Brochon (VMB-model) [11] and Dejean-Laupretre-Monnerie (DLM-model) [12] have been employed to gain information on the molecular dynamics. Ediger [13] and co-workers combined spin-lattice relaxation time (T1) and nuclear Overhauser (NOE) measurements to extract the segmental correlation time of both styrene and isoprene within styrene-isoprene tetrablock copolymers (SISI) by combining the Kohlrauch-William-Watts (mKWW) autocorrelation function [14, 15] and the Vogel-Tammann-Fulcher (VTF) function [16-18]. Using computer simulation they modelled the segmental and global dynamics in disordered styrene-isoprene tetra-block copolymers [19] by implementing the Lodge/Mcleish model [20]. From these previous works, it appeared that the mKWW autocorrelation function combined with the VTF Equation represented a reasonable description of the molecular motion within styrene-isoprene block copolymers. Moreover, this combined experimental and modelling approach seemed feasible also to other polymeric materials [21], as well as to polymer
On this ground, we adopted the same analytical approach in analyzing the segmental motion within a polysisoprene chain of a tri-block SIS polymer during elongation. The present report represents a first attempt to pin down the details regarding segmental motion during stretching/elongation of a thermoplastic elastomeric (SIS) using solid state NMR. To probe the molecular motion within SIS, Chen and co-workers invented a simple, home-built device to monitor, in situ, the NMR characteristics during stretching [23] using solid state NMR under magic angle spinning (MAS) conditions[24].

In this paper, we present $^{13}$C CP/MAS spectra and relaxation time data ($T_1$ and $T_2$) on styrene-isoprene tri-block copolymers (SIS) under various draw-ratios (stretching/elongation) and temperatures. We will implement a Cole-Davidson distribution function [25] which has an analogy to the mKWW function, to estimate the segmental correlation time of the $\beta$, $\gamma$- and $\delta$-carbon atoms within the polyisoprene chain. The difference in sensitivity between the $^{13}$C spin-spin relaxation time ($T_2$) and $^{13}$C spin-lattice relaxation time ($T_1$) upon elongation is discussed with respect to the Bloembergen-Purcell-Pound (BPP) Equation. An empirical Equation relating the segmental correlation time to the degree of elongation is proposed, which represents a “fingerprint” of the segmental correlation time as a function of elongation. Finally, we attempt to estimate the trend in activation energy of the segmental motion as a function of elongation, based on the VTF Equation.

2. EXPERIMENTAL

2.1 Materials

Two commercial styrene-isoprene triblock copolymers (SIS), containing 14 wt. % and 22 wt. % of styrene were purchased from Aldrich Chemical Company, Inc. According to the $^{13}$C CP-MAS spectra, both cis- and trans-conformations of PI were observed. Peaks are assigned from information based on previous reports[26-28]. To identify the two samples we adopt the notation SIS-14 and SIS-22, respectively.

2.2 Elongation

In situ, $^{13}$C-NMR MAS experiments on stretched samples were performed by means of a simple, home-made device in which the sample was strained and fixed on a cylinder device, using Teflon strings [23]. This device was subsequently inserted into the rotor, which hindered the sample from contracting during the experiment.

2.3 NMR

$^{13}$C measurements were performed on a Bruker DSX-300 spectrometer operating at 300.13 MHz proton frequency, corresponding to a carbon resonance frequency of 75 MHz. The $\pi/2$ pulse length ($^{13}$C) was set to 4$\mu$s. $^{13}$C spectra were obtained using cross polarization (CP) and magic angle spinning (MAS; spinning rate of 5 kHz) with a proton $\pi/2$-pulse of 4.2$\mu$s, followed by a 3.0 ms contact time. Spin-lattice relaxation ($T_1$) and spin-spin relaxation ($T_2$) times were measured by traditional $^{13}$C NMR techniques using a standard inversion recovery ($\pi$-t-$\pi/2$) pulse sequence and a spin echo ($\pi/2$-t-$\pi$-t) pulse sequence with $^1$H TPPM decoupling during the $^{13}$C data acquisition. The latter parameter ($T_2$) was determined by applying, $T_2$ measurements were carried out at room temperature (293 K), only. The relaxation delay between each scan was 5 times the longest relaxation time of the carbons of interest. A total of eight (8) delay times were used to obtain the relaxation curves, which was fitted to a single exponential function. The corresponding relaxation curves obtained from the spin-lattice relaxation measurements were fitted to a three parameters model to obtain an estimate of $T_1$. Both peak intensities and peak areas were used in the model fitting. However, no significant differences in derived relaxation times were noted between these two different approaches.

The number of scans was set to more than 1K in each experiment in order to achieve a reasonable signal-to-noise ratio. $T_1$ measurements were performed at 293K, 303K and 313K at four different elongations/stretching, or draw ratios. Throughout the text we will use the term stretching or elongation synonymously, to mean the fraction of elongation of the polymer film relative to its initial, non-elongated form. The symbol $\lambda$ is introduced to represent the degree of stretching/elongation, i.e., $\lambda = 1$ means no stretching.

3. PRELIMINARY REMARKS

For proton bearing carbons like C$_{\beta}$, C$_{y}$ and C$_{\delta}$ in the isoprene unit (Figure 1), the dipolar mechanism will be the dominant course of relaxation.
From the BPP model the following relaxation times may be derived [29].
\[ \frac{1}{T_{1i}} = K_1 [\omega_H - \omega_C + 3(\omega_H + \omega_C)] \]  
\[ \frac{1}{T_{2i}} = K_1 [2(\omega_H - \omega_C) + 3(\omega_H + \omega_C)] \]  
where \( i \) represents the carbon number and \( K_1 \) defines its corresponding “rigid lattice constant”, as defined by:
\[ K_1 = \frac{h^2}{2} \sum_{ij} \frac{\gamma_i \gamma_j}{R_{ij}^5} = K \Sigma 1/R_{ij}^5 \]  
\( R_{ij} \) represents the distance between a proton nucleus “\( j \)” (bonded to carbon “\( i \)”) and the carbon nucleus “\( i \)” in question, with \( h^2 \gamma_i \gamma_j \) = 2.05 10^9 s^-3Å^6. For a single C-H bond possessing a sp^3-hybridization \( R_{ij} \) = 1.102 Å, while for a single C-H bond possessing a sp^2-hybridization \( R_{ij} \) = 1.085 Å [12]. Corresponding bond distances for C-C and C=CH are 1.54 Å and 1.33 Å, respectively [29]. Using simple geometric arguments we may obtain the following approximate K-values; \( K_{ij} = 2.64 \times 10^9 \) s^-2, \( K_{ij} = 2.66 \times 10^9 \) s^-2 and \( K_{ij} = 2.64 \times 10^9 \) s^-2, respectively. Our calculated K-value for a single C-H bond amounts to \( K = 2.32 \times 10^9 \) s^-2 and is in excellent agreement with the reported value of 2.29 \( \times 10^9 \) s^-2 [28].
From basic NMR theory, the quantitative connection between molecular motion and relaxation is made through the orientation autocorrelation function \( G(t) \) which describes the reorientation of the inter-nuclear vector (C-H), i.e.;
\[ J(\omega) = \frac{1}{2} \int_{-\infty}^{\infty} G(t) \cdot \exp(-i\omega t) \]  
\( J(\omega) \) defines the spectral density function, which is the key parameter in the relaxation functions, Equations 2 and 3.
Due to the complexity of the polymer structure, the molecular dynamics will be rather complicated. Hence, it is reasonable to describe the molecular dynamics by introducing a distribution of correlation times. A number of different distribution functions have been applied in the literature, among which the modified Kohlrausch-William-Watts (mKWW) orientation autocorrelation function [14, 15] has been applied with success [30]. This function is composed of an exponential term characterizing the fast libration motion of the C-H bond, and a stretched exponential term representing the slower segmental motion (Equation 5);
\[ G(t) = a_{lib} \exp(-t/\tau_{lib}) + (1-a_{lib}) \exp\left[-(t/\tau_{seg})^\beta\right] \]  
Since the libration motion is much faster than the segmental motion (\( \tau_{lib} \ll \tau = \tau_{seg} \)), we may exclude the first term in Equation 5. Hence, the second term (in Equation 5) represents the final autocorrelation function to be applied in the segmental motion analysis. However, from a numerical point of view, such an approach is not very tractable since the calculation of the spectral density \( J(\omega) \) from Equation 4 involves a series expansion which converges slowly and, in addition, involves terms which are differences of rather large numbers [21, 32]. After some trial and error we found that a better alternative is to replace the second term in Equation 5 by a Cole-Davidson distribution function [25] which can be represented as a spectral density function of the form [33];
\[ J_{cd}(\omega, \tau) = \frac{1}{(1+\omega^2\tau^2)^{\beta_{cd}}/2} \sinh(\beta_{cd}) \times \arctan(\omega\tau) \]  
where \( \beta_{cd} \) characterizes the width of the distribution (0 < \( \beta_{cd} \) \leq 1). In particular, we note that in the extreme narrowing limit (\( \tau \ll 1 \)), Equation 6 can be Taylor expanded to obtain \( J_{cd}(\omega, \tau) = \beta_{cd}\tau \), which (for \( \beta_{cd} = 1 \)) equals the spectral density function of the BPP equation. Likewise, for long correlation times (\( \tau > 1 \)) and \( \beta_{cd} = 1 \) we obtain \( J_{cd}(\omega, \tau) = 1/\omega^2 \tau \), which is again identical to the BPP spectral density function. As a consequence, the final spectral density function becomes equal to equation 6, if multiplied by the factor (1 – a_{lib}). If knowing the three parameters \( a_{lib}, \tau = \tau_{seg} \) and \( \beta_{cd} \) we may calculate the relaxation rates 1/\( T_{1(2)} \) by combining Equations 1, 2 and 6 for any proton bearing carbon within the isoprene monomer unit (Figure 1).
To compensate for the libration motion of the CH-bonds we may set \( a_{lib} \) equal to its pure homopolymer value, i.e., \( a_{lib} = 0.23 \) [30]. In this work we chose to use an average value for the libration constant \( a_{lib} \) based on simulations performed by Theodourou et al [32] with \( a_{lib} = 0.24 \) (C_1), \( 0.17 \) (C_2) and 0.25 (C_3), respectively. This enables us to determine \( \beta_{cd} \) and \( \tau_{seg} \) at any temperature and for any draw-ratio or elongation factor by model fitting Equations 1 and 2 (with \( J(\omega) \) replaced by Equation 6) to the observed relaxation rate data.
In order to constrain the fit more effectively all relaxation data of the different carbon nuclei (β-, γ- and δ- carbons) were fitted simultaneously, thereby reducing the number of adjustable parameters. Within experimental error - no significant change in \( \beta_{cd} \) was detectable when varying the temperature or when altering the draw-ratio (λ).
Of particular concern, however, the theoretical expression for $1/T_2$ (Equation 2) had to be multiplied by a factor $k$ different from 1 in order to be consistent with $1/T_1$ (Equation 1). The reason for this is – at present - not understood and needs further investigation. One should keep in mind, however, that Equation 2 is strictly valid for “fast” motion. For slower motion, i.e., when the correlation time becomes longer ($\tau > 1$), $T_2$ will ultimately level off towards a limiting value, denoted the rigid lattice $T_2$-value. However, the analytical expression relating $T_2$ to the correlation time for such slow motion is rather subtle and complex.

In summary, in the final model fitting procedure we used $k$ as an adjustable fitting parameter and assumed the parameter $\beta_{cd}$ to be dependent only on the relative amount of styrene within the block copolymer.

4. RESULTS AND DISCUSSION

The room temperature $^{13}$C MAS NMR spectra of samples SIS-14 and SIS-22 are shown in Figures 2A and 2B for $\lambda = 1$ (no elongation). The peak assignment is based on information presented elsewhere [26-27]. The change in spectral appearance upon elongation is illustrated on Figures 2C and 2D, for both concentrations. Only the chemical shift range of the cis-polyisoprene peaks ($\alpha$, $\beta$- carbons) between 115 ppm and 140 ppm is shown, for clarity. Moreover, only the segmental motion of this conformer is reported in this work. The corresponding segmental motion of the trans conformer will be presented elsewhere.

The two relaxation times $T_1$ and $T_2$ were derived from inversion recovery- and a spin-echo pulse sequences, respectively, and are illustrated in Figure 3 for sample SIS-14. The two relaxation curves were acquired at 293 K under no external stress (no elongation).

![Figure 2](image-url)

**Figure 2.** Room temperature $^{13}$C CP/MAS spectra of sample SIS-22 (A) and sample SIS-14 (B) under no external forces. Room temperature $^{13}$C CP/MAS spectra as a function of elongation ($\lambda$) are depicted on Figures C (SIS-22) and D (SIS-14), respectively. Only the chemical shift range of the cis-polyisoprene peaks ($\alpha$, $\beta$- carbons) between 115 ppm and 140 ppm is shown, for clarity. The increase in signal intensity of the $\beta$-carbon with increasing elongation is clearly evidenced.

The two relaxation times $T_1$ and $T_2$ were derived from inversion recovery- and a spin-echo pulse sequences, respectively, and are illustrated in Figure 3 for sample SIS-14. The two relaxation curves were acquired at 293 K under no external stress (no elongation).

![Figure 3](image-url)

**Figure 3.** Illustration of the $T_1$ (A) and the $T_2$ relaxation curves (B) for the $\delta$-carbon of polyisoprene (sample SIS-14) under no external forces (no stretching). The solid curves show non-linear least squares fits to the functions $M(t)=M(0)[1-2\exp(-t/T_1)]$ and $M(t)=M(0)\exp(-t/T_2)$, respectively.
The temperature dependence of the two relaxation times is shown in Figure 4 with a standard error less than approximately 5% (represented by error bars in the Figure). The solid curves were obtained by model fitting the relaxation data of all three carbons (β, γ and δ) simultaneously using Equations 1, 2 and 6. The dotted curves in Figure 4A were obtained by excluding the T₂-relaxation data in the model-fit.

As can be inferred from the model fit, the sensitivity in the spin-lattice relaxation as a function of elongation (λ) is rather small, and probably originates from T₁ being close to its minimum. The spin-spin relaxation time T₂ seems to be more sensitive to the molecular motion on this time scale and is probably a better parameter to use when probing the segmental correlation time as function of elongation. One way of improving the lower sensitivity in T₁ would be to perform relaxation time measurements at a different magnetic field strength, i.e., at a lower magnetic field. However, no low field magnet was available during this study.

The derived parameters β_{cd} and k are summarized in Table 1. An error estimate of each parameter was calculated by constructing a set of synthetic relaxation data by a random, statistical procedure (by applying Equation 7 and implicitly assuming a Gaussian error distribution for the relaxation times);

$$T_{1,2\text{new}} = T_{1,2} \cdot [1 + 3.5 \cdot (\rho - 1/2)] \cdot \sigma/100$$

where ρ is a random number (0 < ρ < 1) and σ represents the standard error (%) of the relaxation time (σ was set to 5). A minimum of 6 data sets were generated and the error (standard deviation) was calculated by standard statistical procedures. The derived β_{cd} parameter (see Table 1) is in excellent agreement with the one reported by Ediger et al [30] of 0.45. Moreover, the same authors reported on a slight decrease in β_{cd} with decreasing amount of styrene. However, the estimated error in β_{cd} was too large to reveal any such concentration dependence.

A)

B)

Figure 4. Spin-lattice relaxation time T₁ (A) and spin-spin relaxation time T₂ (B) of the β, γ and δ carbons within the isoprene unit of a SIS triblock copolymer as a function of elongation/stretching (λ) at 293 K. The continuous curves (solid/dotted) represent model fits to Equations 1 and 2 (including Equation 5) for all the different carbons, simultaneously. The error bars represent 5%. The solid curves were obtained by model fitting the relaxation data of all three carbons (β, γ and δ) simultaneously using Equations 1, 2 and 6. The dotted curves in Figure 4A were obtained by excluding the T₂-relaxation data in the model-fit.
In order to determine the average segmental correlation time one has to keep in mind that our model assumes a distribution of correlation times, as characterized by $\beta_{\text{cd}}$. However, the two parameters $\tau_{\text{cd}}$ and $\beta_{\text{cd}}$ in Equation 6 can be combined into a single average correlation time $\tau_{\text{seg, c}}$ which is denoted an overall segmental correlation time [30].

$$\tau_{\text{seg, c}} = (1 - a_{\text{tu}}) - \frac{\tau_{\text{seg}}}{\beta_{\text{cd}}}$$

(8)

The resulting segmental correlation time as a function of elongation, temperature and the relative amount of styrene within the triblock copolymer is shown in Figure 5.

The data analysis suggests that the average segmental correlation time may be linked to the elongation factor $\lambda$, according to:

$$\tau_{\text{seg}}(\lambda) = \tau_{\text{seg}}(1) + (\tau_{\text{seg}}(4) - \tau_{\text{seg}}(1)) \frac{\lambda}{\beta_{\lambda}} \exp \left( -\frac{\left(\lambda - \lambda_{\text{m}}\right)^2}{2\sigma_{\gamma}} \right) d\lambda$$

(9)

We have adopted Equation 9 to represent the segmental correlation time as a function of elongation ($\lambda$). The size of $\sigma_{\gamma}$ gives information on the width of the $\gamma$-region at which the correlation time changes significantly upon stretching. The smaller the $\sigma_{\gamma}$, the narrower is the elongation region in which a significant change in correlation time takes place. The parameter $\lambda_{\text{m}}$ represents the stretching factor at which the segmental correlation time has increased by 50% relative to the correlation time at $\lambda_{\text{max}}$. In short, we claim Equation 9 to represent a “fingerprint” of the segmental correlation time as a function of elongation. It must be kept in mind that Equation 9 is only tentative and has no profound theoretical basis. Actually, this expression implicitly assumes that the change in the segmental correlation time upon elongation ($d\tau_{\text{seg}}/d\lambda$) is symmetric about $\lambda = \lambda_{\text{m}}$ and follows a Gaussian behavior with respect to $\lambda$. We simply note that this model gives a good fit to the observed data. However, the number of data is too few to evaluate the goodness and reliability of the model.

The observed change in segmental correlation time of isoprene in the triblock copolymer of sample SIS-14, as defined by the difference in correlation time at the maximum elongation and the correlation time in the absence of any elongation, is only about 20% at $T = 293$ K and 313 K with a doubling at $T = 303$ K. In contrast, the sample containing the higher relative amount of styrene (SIS-22) shows a monotonic increase of the segmental correlation time with increasing temperature by a factor of 0.5 to 2 when increasing the temperature from 293 K to 313 K. At maximum elongation ($\lambda = \lambda_{\text{m}} = 4$) the segmental correlation time is always shorter in sample SIS-22 compared to sample SIS-14 by a factor of 1.2 and 3 at 293 K and 303 K, respectively. At the highest temperature this factor increases to about 6. No systematic change in $\lambda_{\text{m}}/\sigma_{\gamma}$ can be distinguished at this lower temperature. As illustrated by Figure 6, the sample containing the higher amount of styrene (SIS-22) reveals a more significant change in the segmental correlation time upon elongation.

### Table 1. Parameters derived by fitting Equations 1 and 2 to the observed relaxation time data by a simultaneous model fit.

<table>
<thead>
<tr>
<th></th>
<th>SIS-14</th>
<th>SIS-22</th>
</tr>
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<tbody>
<tr>
<td>$\beta_{\text{cd}}$</td>
<td>0.45 ± 0.07</td>
<td>0.51 ± 0.11</td>
</tr>
<tr>
<td>$k$</td>
<td>1.92 ± 0.24</td>
<td>1.92 ± 0.24</td>
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![Figure 5](image-url)
Only a marginal change in $\lambda_m$ and $\sigma_m$ appears when decreasing the temperature from 313 K to 303 K. However, a further decrease in temperature to 297 K leads to a substantial increase in both $\lambda_m$ and $\sigma_m$, implying that a significant change in the segmental correlation time occurs within a rather small elongation region. Interesting is the significant increase in the segmental correlation time when increasing the relative amount of styrene by approximately 60% (SIS-14 to SIS-22).

5.2 Activation energy of the segmental motion

The Vogel–Tammann–Fulcher (VTF) Equation is an empirical Equation frequently used to characterize the temperature dependence of the relaxation in polymers, and reads:

$$\tau_{\text{seg}} = \tau_0 \cdot \exp \left( \frac{B}{T-T_0} \right)$$  \hspace{1cm} (10a)

where $T_0$ is the temperature at which structural mobility ceases (and configurational entropy vanishes). B is the Angell parameter that measures the strength of the glass [34]. Angell also argued that $T_g$, $T_0$ and B are related by the Equation:

$$T_g = T_0 + 0.0271 \cdot B$$  \hspace{1cm} (10b)

with $T_0$ equal to 185 K and 178 K for SIS-22 and SIS-14, respectively ($T_0$ was estimated from the data presented by Ediger et al [30]). By applying the information presented in Figure 6 we may calculate the segmental correlation time $\tau_{\text{seg}}$ of isoprene at any temperature and any elongation $\lambda$ for samples SIS-14 and SIS-22. The results are illustrated in Figure 7 which shows the segmental correlation time as a function of the inverse “corrected” absolute temperature $1/(T-T_0)$. The solid, thick curve was calculated from the literature data of a block copolymer of the same styrene concentration as investigated in this work (22 wt% styrene), after shifting the pre-exponential factor $\tau_0$ from 1ps to 4 ps [30]. As can be noted, the B-value is within experimental error equal to the B value of sample SIS-22 investigated in this work (in the absence of elongation). Moreover, the data in Figure 7 indicates that the B-value of sample SIS-14 is independent on elongation, which is in contrast to sample SIS-22, which suggests that B is dependent on elongation.

**Figure 6.** The segmental correlation time is described by a Gaussian distribution with respect to the stretching factor ($\lambda$), according to Equation 8. The value of $\lambda$ at which the correlation time has changed by 50% is denoted $\lambda_m$. The width of the distribution is denoted $\sigma_m$. The variation of these parameters as a function of temperature is illustrated on the above figure.

**Figure 7.** Illustration of the segmental correlation time as a function of the “corrected” inverse absolute temperature $1/(T-T_0)$ for the isoprene unit within two different tri-block copolymers (SIS-14; — and SIS-22; –) exposed to four different stretching factors ($\lambda = 1$, 2, 3 and 4; from top to bottom). $T_0$ (185 K for SIS-22 and to 178 K for SIS-14) was extracted from the literature [30]. The thick, solid curve represents the corresponding correlation-time/temperature behavior of a styrene (22 wt%)-isoprene block copolymer sample [30], after shifting the pre-exponential factor in Equation 10a from 1 ps to 4 ps.
Finally, the derived B-value (using the data in Figure 7) is plotted as a function of elongation for both samples (SIS-14 and SIS-22) and shown in Figure 8. The B-value for sample SIS-22 decreases monotonically with increasing elongation, implying that at a specific temperature the segmental correlation time decreases with increasing elongation. In short, two identical polymer samples (SIS-22) experiencing different elongation may reveal the same segmental correlation time, however, at different temperatures.

Concerning sample SIS-14, the segmental correlation time will decrease with increasing temperature, independent on elongation (since B is temperature independent) and is in agreement with the findings presented in Figure 5 and implies that the pre-exponential factor \( t_0 \) in Equation 10a is rather temperature insensitive for this sample. Regarding sample SIS-14, by inserting the constant B-value \((= (832 \pm 17) \text{ K})\) and \( T_0 = 178 \text{ K} \) into Equation 10b results in glass transition temperature of approximately \((200 \pm 17) \text{ K}\), which is within experimental error – in agreement with the reported glass transition temperature of various polyisoprenes [35].

According to Pikal and coworkers [36], the activation energy \( \Delta H \) of the segmental motion may be expressed by:

\[
\Delta H = R \cdot B \left[ \frac{T_g}{T_g - T_0} \right]^2 = R \cdot B \left[ \frac{1}{1 - T_0/T_g} \right]^2
\]

(10c)

where \( R \) is the universal gas constant. Assuming Equation 10b to be applicable also during elongation, we obtain by insertion:

\[
\Delta H = R \left[ \frac{T_g}{0.0271} \right]^2 \frac{1}{B}
\]

(10d)

Due to the rather few temperature/correlation time data obtained in this work and the relatively high inherent uncertainty in the derived correlation times, it was not possible to obtain reliable values of \( T_0 \) and \( T_g \) (from Equation 10b) by model fitting. However, assuming tentatively the temperature parameters \( T_g \) to be rather insensitive to elongation, Equation 10d predicts that the activation energy is proportional to the inverse of \( B \) and implies that the activation energy of the segmental motion of sample SIS-22 increases with increasing elongation. In contrast, sample SIS-14 reveals no change in the activation energy upon elongation.

E. A. Egorov and coworkers [37] have argued that as a result of the decreasing molecular motion within the amorphous regions in the presence of an elongating force, the actual glass transition temperature is increased and can significantly exceed that of the unstressed polymer. From Equation 10d, we see that this would qualitatively result in a more significant increase in the activation energy with increasing elongation.

5. CONCLUSION

\(^{13}\text{C}\) solid state spin-lattice \((T_1)\) and spin-spin \((T_2)\) relaxation time measurements of the \( \beta-, \gamma- \) and \( \delta \) carbons within styrene–isoprene tri-block (SIS) copolymers have been performed to probe the segmental motion upon elongation and temperature. Since \( T_1 \) is close to its minimum value, the sensitivity in the segmental correlation time for this relaxation time is poorer compared to \( T_2 \).

Both samples reveal a decreasing segmental mobility by a factor of \( 2 - 3 \) after elongating the sample by a factor of 4.

The two samples reveal distinctly different behaviours upon elongation, as reflected by their different temperature dependence on the segmental motional characteristics. Fitting the segmental correlation time to temperature, according to the VTF Equation; \( \log(\tau/\tau_0) = B/(T-T_0) \) shows that \( B \) is approximately constant and independent on
elongation for the low-styrene concentration sample (SIS-14). In contrast, a significant decrease in B with increasing elongation is observed for the high-styrene concentration sample (SIS-22). A further analysis suggests that the activation energy for the segmental motion within the sample containing the higher styrene concentration (SIS-22) increases by more than 50% after stretching the sample by a factor of 4. Within experimental error, the low-styrene concentration sample (SIS-14) reveals no such change in activation energy upon elongation.

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