Dielectric and dynamic-mechanical study of the mobility of poly(t-butylacrylate) chains in diblock copolymers: Polystyrene-b-poly(t-butylacrylate)

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ABSTRACT

Keywords:
Dielectric relaxation
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A calorimetric, dielectric and dynamic-mechanical study of the dynamics of the poly(t-butyl acrylate) (PtBa) chains has been carried out in a PtBa homopolymer and two polystyrene (PS)-b-PtBa block copolymers with different PtBa chain lengths. The DSC results show that the size of the cooperative rearranging regions is similar in the homopolymers and the copolymers, both for the PtBa rich- and the PS-rich regions. Therefore, no significant contributions are found arising from composition fluctuations in the copolymers. The relaxation map obtained from dielectric relaxation indicates that there are no differences in the temperature dependence of the α-relaxation of the PtBa block in the three samples studied. However, there are larger differences for the values obtained from DMTA experiments. Contrary to the α-relaxation, the relaxation map for the β-transition shows that the characteristic times for the PtBa blocks are smaller in the homopolymer than in the copolymers. In principle, these are unexpected results because the β-relaxations have a more local character than the α-ones. The width of the α-relaxation increases with T for all the samples, and it is slightly larger for the copolymers. The intensity of the α-relaxation is larger (between 3 and 4 times) for the homopolymer. Considering the molecular weights of the PtBa blocks, this effect has to be ascribed to the existence of frozen amorphous PtBa due to the existence of the glassy PS domains in the microphase separated copolymers. Molecular Dynamic Simulations (MDSs) for different sequences of the polymers under study were carried out. The conformational analysis was carried out between 1000 and 1700 K. The analysis of the variation of angles \( \phi \) and \( \psi \) of the ester group of PtBa points out the existence of a correlation between the conformational changes of the side group of the polymer chains and their relaxational behaviour.

1. Introduction

Block copolymers have attracted much attention due to their tendency to form ordered structures at the nanometer scale below the so-called order-disorder temperature \( T_{OD} \). The equilibrium thermodynamic state of an A-B diblock copolymer melt is determined by \( \chi N \) and the composition \( f = N_A / N \), where \( N_A \) is the number of segments of type A in the chain, \( N \) is the total number of segments in the copolymer chain, and \( \chi \) is Flory's interaction parameter between the two types of segments (\( \chi \) depends on \( 1/T \), \( T \) being the temperature). For values of \( \chi N \) greater than a critical value \( (\chi N)_c \), a microphase separation occurs, and different microdomains are formed depending on the value of \( f \). Dispersion of spheres or cylinders of one of the blocks in a continuous matrix of the other block, lamellar and bicontinuous phases has been described.

When both blocks have well separated values of the glass transition temperature \( T_g \), the dynamics of low-\( T_g \) blocks can be affected by the presence of a rigid phase, thus being different from the corresponding homopolymer. Kotaka and Adachi have found that the dynamics of the normal and segmental modes of poly(isoprene) blocks (PI) in PI-b-PS and PI-b-PS-b-PI copolymers (PS referring to polystyrene) is strongly affected by the morphology of the samples. Moreover, for \( T < T_g(PS) \), they concluded that the interchain cooperativity increases. Alig et al. found that the
The molecular weights of the PtBa and PS blocks are given in Table 1. Characteristics of the copolymers used.

### Table 1

<table>
<thead>
<tr>
<th>Polymer</th>
<th>M (PtBa)</th>
<th>M (PS)</th>
<th>M_{w}/M_{n}</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtBa</td>
<td>327,200</td>
<td>452,000</td>
<td>1.14</td>
</tr>
<tr>
<td>P305</td>
<td>203,800</td>
<td>206,200</td>
<td>1.20</td>
</tr>
<tr>
<td>P307</td>
<td>489,000</td>
<td>236,600</td>
<td>1.13</td>
</tr>
<tr>
<td>PS</td>
<td>–</td>
<td>220,000</td>
<td>1.10</td>
</tr>
</tbody>
</table>
and thus it has not been possible to obtain reliable values for the relaxation times. Similar results were obtained for the $\alpha$-relaxation of the other samples.

The relaxation curves have been fitted to a sum of $n$ contributions

$$\varepsilon_{\text{dipolar}}(\omega) = \varepsilon_{\infty} + \left( \frac{\sigma_{\text{dc}}}{i\omega 2\pi f} \right)^s + \sum_{i=1}^{n} \frac{\Delta \varepsilon_i}{[1 + (2\pi f \tau_{i,\text{HN}})^{\delta_{i}}]^{\gamma_i}}$$

where the first term of the right hand side (r.h.s.) represents the high-frequency limit of the dielectric permittivity, the second term accounts for the ionic conductivity found at high temperature (see Fig. 2b), $\sigma_{\text{dc}}$ being the direct current conductivity, and $\varepsilon_0$ is the dielectric permittivity of the vacuum. The exponent $s \leq 1$ takes into account the complexity of the conductivity processes that appear in the low-frequency region. For the simplest ohmic process $s = 1$. The last term of the r.h.s. of Eq. (1) describes for the contributions of the segmental (or $\alpha$-) relaxation and of the subvitreous (or $\beta$-) relaxation. For the last two contributions we have used a Havriliak-Negami function, in which $\Delta \varepsilon_i$ is the intensity of the relaxation, $\tau_{i,\text{HN}}$ is a characteristic time, and the parameters $\delta_i$ and $\gamma_i$ are dimensionless parameters that describe the symmetric and asymmetric broadening of the loss function $\varepsilon''(\omega)$, respectively. They are constrained such as $0 < \delta_i, \gamma_i < 1$. We have found that for the three samples studied the $\beta$-relaxation can be described with a Cole–Cole function, i.e. $\gamma = 1$. The fits are the lines in Fig. 2. Fig. 2b shows that the d.c. conductivity contribution can be described with $s = 1$.

Fig. 3 shows the imaginary part of the elastic modulus of one of the samples at temperatures close to the $\alpha$-relaxation of the PtBa blocks. Physical aging experiments of Shelby and Wilkes have suggested the existence of a weak $\beta$ process in PS. This might overlap with the $\alpha$ process of the PtBa blocks, thus leading to an increase of the width and height of the relaxation peak. Fig. 4 shows the same magnitude for temperatures close to the $\alpha$-relaxation of the PS block in the PS05 copolymer, similar results were found for the two other samples. Two facts are clearly visible: On one side the scattering of the data appears to be larger than for those of Fig. 3. On the other hand, for some temperatures, the existence of two or more than one relaxation appears to be clear. Fig. 5 shows that it is possible to build a master curve with the DMTA results of one of the copolymers near the $T_g$ of the PtBa block (similar results were found for the other samples, but not for the results near the $T_g$ of the PS block). This means that from the mechanical point of view the PtBa blocks can be considered as thermorheologically simple materials, and that the shape of the $\varepsilon''(\omega)$ curves does not change with $T$. Similar results were obtained by Alig et al. for PS-b-poly(isoprene) copolymers. However, it was not possible to build a similar master curve with the dielectric results since, as it will be discussed below, the shape of the $\varepsilon''(\omega)$ curves is a function of $T$. The shift factor $a_T$ of the frequency axis needed for building the master curves for the three samples (for the $\alpha$-relaxation of the PtBa block) has been fitted to a Williams–Landel–Ferry equation

$$\log_{10} a_T = -\frac{C_1(T - T_0)}{C_2 + T - T_0}$$

The constants $C_i$ and $T_0$ are given in Table 3. However, one cannot discard the possibility that the good results obtained in building the

Scheme 1. Model structures for (a) P(305); (b) P(307); and (c) PtBa.

Scheme 2. Representation of boxes for MDS in periodic boundary conditions using Consistent Valbond Force Field (CVFF).
4. Discussion

A key concept in the fluctuation approach to the \( \alpha \)-relaxation is that of the cooperatively rearranging region (CRR) [16], defined as the smallest volume element that can relax to a new configuration independently of the neighboring regions. According toDonth et al. [17] the volume of a CRR is given by

\[
V_a(\delta T, T) = \frac{k_B T^2 \Delta (1)}{\rho(\delta T)^2} 
\]

(3)

where \( \rho \) is the density, and usually \( C_p \) is approximated by \( C_p \), \( \Delta T = T - T/2.5 \), with \( T \) obtained from the \( C_p \) curves as indicated in Fig. 1b. The values calculated from the DSC experiments according to Fig. 1b are given in Table 2. The values of \( \xi_a \) found in the case of the homopolymers are slightly larger than for the block copolymers, although the differences between the samples are close to the calculated uncertainties. These values are similar to those previously reported for other polymers. The fact that \( \xi_a \) is slightly smaller for the block copolymers than for the homopolymers may be due to the microphase separated morphology of the latter. It has been already demonstrated in semicrystalline polymers that when the amorphous phase is subject to geometrical constraints the size of the CRR decreases. In fact Hong et al. found that there is a correlation between \( \xi_a \) and the interlamellar separation. In the PS-b-PtBa copolymers, the amorphous PtBa phase is constrained by the glassy PS phase.

We have calculated the retardation times characteristic of the \( \alpha \) and \( \beta \)-relaxations for the PtBa blocks from the fits of the dielectric relaxation spectra to Eq. (1). In order to compare the characteristic times of the dielectric and mechanical experiments one has to consider that \( E^* \) is a modulus while \( r^* \) is a compliance. As a consequence the times obtained from \( E^* \) are relaxation times, while those from \( r^* \) are retardation times. Richert and coworkers have recently discussed the relationship between the average relaxation, \( T_m \), and retardation times, \( T_\infty \), obtained from \( r^* \) and from the dielectric modulus \( M^* = 1/r^* \). For a Debye-like relaxation they concluded that \( T_m/T_\infty = 1/f_\infty \), where \( f_\infty \) and \( f_\infty \) are the low- and high-frequency limits of the dielectric constant for the relaxation under study.

For a relaxation described by the Havriliak–Negami equation no closed expression exists for \( T_m/T_\infty \). However, the expression corresponding for the Debye case is an upper limit for the ratio of the relaxation and retardation times. We have calculated \( T_\infty \) from the average retardation times calculated from the fits to Eq. (1). The temperature dependence of the retardation times has been described by Eq. (2), and the corresponding constants are given in Table 3. The retardation map shown in Fig. 6 points out that the difference between the two copolymers and the PtBa homopolymer in the \( \alpha \)-relaxation is rather small, almost within the scattering of the data. This means that there is almost no mixing effect at the segmental level, as expected in the strong segregation regime. However, clear differences were found for the times corresponding to the \( \beta \)-relaxation, the relaxation times of the copolymers being larger than those of the homopolymer. These results are unexpected because the \( \beta \)-relaxation has a more local character than the \( \alpha \)-one, and contrast with the results found for other copolymers. The results found cannot be attributed to any possible coupling between the different contributions in Eq. (1). In fact, as it can be observed in Fig. 2a, there are temperatures for which the different samples present only contribution from the \( \alpha \)-relaxation, and thus it is possible to determine the relaxation time without any perturbation from the \( \beta \)- or the conductivity contributions. Fig. 6 also includes the temperature dependence of \( \xi_a \) calculated from the DMTA experiments using Eq. (2) and the parameters collected in Table 3 for PtBa and P307 (the results for P305 are intermediate and are not shown for the sake of clarity). The figure shows that there is a reasonable agreement between the temperature dependencies predicted by

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**Table 2**

Parameters’ characteristic of the DSC traces of the different polymers in the glass transition region. Some of the values are given in Fig. 1b. \( T_m \) is the radius of cooperative rearranging regions calculated from Eq. (3).

<table>
<thead>
<tr>
<th>Property</th>
<th>PtBa</th>
<th>PS</th>
<th>P305</th>
<th>P307</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_m )/K</td>
<td>317</td>
<td>378</td>
<td>319</td>
<td>381</td>
</tr>
<tr>
<td>( \Delta T / K )</td>
<td>3.6</td>
<td>6</td>
<td>7</td>
<td>6</td>
</tr>
<tr>
<td>( \Delta C_p )/J g(^{-1})K(^{-1})</td>
<td>0.2</td>
<td>0.29</td>
<td>0.15</td>
<td>0.085</td>
</tr>
<tr>
<td>( C_p )/J g(^{-1})K(^{-1})</td>
<td>1.09</td>
<td>2.52</td>
<td>1.16</td>
<td>1.36</td>
</tr>
<tr>
<td>( \xi_a )/nm</td>
<td>3.8 ± 0.4</td>
<td>3.1 ± 0.4</td>
<td>2.7 ± 0.5</td>
<td>2.5 ± 0.3</td>
</tr>
</tbody>
</table>

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Fig. 1. (a) DSC thermograms for the two homopolymers: PtBa (1) and PS (2), and the two block copolymers P305 (3) and P307 (4). The heating rate was 10 K/min. The \( C_p \) scale was calibrated with a sapphire standard. (b) Construction used to calculate the size of the cooperative rearranging regions according to

\( C_p / J \) g\(^{-1}\)K\(^{-1}\)
Fig. 2. Imaginary part of the dielectric permittivity $\varepsilon''$ as a function of temperature $T$ and linear frequency $f$ for the P307 copolymer in two different temperature ranges. The temperature difference between two consecutive curves is $2\,\text{K}$. Notice that in the high temperature range there is an important conductivity contribution in the low-frequency range. The curves are the fits to Eq. (1).

Both techniques are further confirmed by the fragility parameter $m$ shown in Table 3, which is quite similar to those reported for copolymers of poly(oxyethylene) and poly(oxypropylene).

Nevertheless, the DMTA technique leads to slightly different curves for the two copolymers and the homopolymer. The DMTA results indicate that the relaxation times of the $\alpha$-relaxation of PtBa are larger than those of the copolymers, which is unexpected because in the latter case the PtBa chains are linked to the glassy PS blocks.

Fig. 3. Imaginary part of the Young modulus $E''$ of the P305 copolymer as a function of temperature $T$ and angular frequency $\omega$ in the glass transition region of the PtBa blocks. The temperature difference between two consecutive curves is $2\,\text{K}$. Lines are aid for the eyes.

Fig. 4. Imaginary part of the Young modulus $E''$ as a function of temperature $T$ and angular frequency $\omega$ in the glass transition region of the PS blocks for the P305 copolymer. The temperature difference between two consecutive curves is $2\,\text{K}$. Lines are aid for the eyes.
temperature dependencies of $\tau_{a,a}$ obtained by both techniques, while the absolute values of $\tau_{a,M}$ obtained by DMTA are higher than those obtained by dielectric relaxation (around 10 times higher), which is the usual behaviour. This is more clearly pointed out in Fig. 7 which shows two examples of the relaxation function calculated from dielectric and DMTA experiments as

$$\phi(t) = \frac{\int_{-\infty}^{\infty} H(\ln \tau) \exp[-(t/\tau)] \, d\tau}{\int_{-\infty}^{\infty} H(\ln \tau) \, d\tau} \quad (4)$$

where $H(\ln \tau)$ is the relaxation spectra obtained from the $M^*$ and $\varepsilon^*$ data using a regularization algorithm. Contrary to the algorithm proposed by Weese the one described by Domínguez-Espínsola et al. allows one to include the low-frequency conductivity contribution in the kernel of the regularization method. Therefore, it is not necessary to extract such contribution from the raw $\varepsilon^*$ data before proceeding to calculate the retardation spectrum. As $T$ increases, the difference between the relaxation functions of PtBa and the copolymers increases, in accordance with Fig. 6. However, the differences between the $\phi(t)$ calculated from the electrical modulus remain almost constant over the whole temperature range. The discrepancies found between $\tau_c$ and $\tau_m$ are not new; similar differences were already reported by Havrilak and by Ngai. It must be stressed that in the work of Richert and coworkers the data of the mechanical moduli were compared to the corresponding compliances (or alternatively the electrical moduli to the corresponding permittivities), whereas in the present work electrical and mechanical moduli have been compared.

The results shown allow one to test an empirical relation proposed by Alvarez between the parameters of the Havrilak–Negami function and the exponent $\beta$ of the stretched-exponential relaxation function for the structural relaxation [19]: $\gamma^2 = \beta^{1.23}$. We have fitted the master curves of the DMTA experiments to the stretched-exponential function:

$$E'\left(2\pi f, T\right) - E_a = \int_0^\infty \frac{d\phi(t)}{dt} \exp\left[-i2\pi f \cdot t\right] \, dt \quad (5)$$

with $\phi(t) = A \exp\left[-(t/\gamma\Delta f)^{\gamma}\right]$, $E_a$ and $E_r$ being the unrelaxed and relaxed values of the real part of $E'$, respectively. The results lead to $\beta = 0.40, 0.36,$ and $0.35$ for PtBa, P305 and P307, respectively. Similar values have been reported for other poly(acrylate) polymers: 0.37 for poly(methyl acrylate) from DMTA measurements and 0.47 and 0.38 for poly(n-butyl acrylate) and poly(n-hexyl acrylate), respectively. The product $(\gamma\Delta f^{1/2})$ at 340 K takes the values $0.39$, $0.36$, and $0.33$, respectively, which is in agreement with the empirical relation proposed by Alvarez et al. However, there is an important difference between the description of the data using the $H$–$N$ and the stretched-exponential functions. In effect, the exponent $\beta$ controls both the width of the relaxation and the temperature dependence of the relaxation time whereas the parameters $\gamma$ and $\delta$ are only related to the width of the relaxation.

The intensity of the $\alpha$-relaxation $\Delta A_{\alpha}$ was found to increase slightly with $T$ for the two copolymers over the whole temperature range (see Fig. 8), while it decreases more strongly with increasing

Table 3

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$C_1$</th>
<th>$C_2$/K</th>
<th>$T_M$/K</th>
<th>$m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relaxation times from dielectric experiments</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PtBa</td>
<td>11.9 ± 0.2</td>
<td>42 ± 3</td>
<td>315.4 ± 0.7</td>
<td>69 ± 1</td>
</tr>
<tr>
<td>P305</td>
<td>15.7 ± 0.4</td>
<td>50 ± 4</td>
<td>308.5 ± 0.9</td>
<td>74 ± 2</td>
</tr>
<tr>
<td>P307</td>
<td>16.3 ± 0.3</td>
<td>37 ± 4</td>
<td>300.7 ± 0.8</td>
<td>71 ± 1</td>
</tr>
<tr>
<td>Relaxation times from DMTA experiments</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PtBa</td>
<td>11.3 ± 0.4</td>
<td>44 ± 1</td>
<td>315.4 ± 0.6</td>
<td>62 ± 1</td>
</tr>
<tr>
<td>P305</td>
<td>15.4 ± 0.2</td>
<td>66.4 ± 0.8</td>
<td>319.7 ± 0.4</td>
<td>69 ± 1</td>
</tr>
<tr>
<td>P307</td>
<td>17.5 ± 0.3</td>
<td>75 ± 1</td>
<td>313.6 ± 0.7</td>
<td>72 ± 2</td>
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</tbody>
</table>

Table 4

<table>
<thead>
<tr>
<th>Polymer</th>
<th>PtBa</th>
<th>P(307)</th>
<th>P(305)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-3}$ $E_A/R$</td>
<td>1.45 ± 0.04</td>
<td>1.32 ± 0.05</td>
<td>1.1 ± 0.1</td>
</tr>
<tr>
<td>$10^{-3}$ $\Delta G/R$</td>
<td>-1.6 ± 0.1</td>
<td>-1.9 ± 0.1</td>
<td>-2.2 ± 0.2</td>
</tr>
</tbody>
</table>

Fig. 5. Master curve obtained from the DMTA experiments for the P305 copolymer in the proximity of the $T_M$ of the PtBa block. Similar curves were obtained for the other polymers and also in the region close to the $T_g$ of the PS block. $\alpha_f$ is the shift factor.
T for the homopolymer as in most of the polymers. It must be stressed that the product $T_\alpha \Delta \varepsilon_\alpha$ for the homopolymer is 3–4 times larger than for the copolymers. Taking into account that the molecular weight of the PtBa blocks is similar, the big difference in the relaxation intensity must be due to the existence of frozen amorphous PtBa blocks due to the existence of glassy PS regions in the microphase separated copolymers. This has already been mentioned to explain that the size of the CRR is smaller in the block copolymers than in the homopolymers. One might expect that such constraints should be released as $T$ is increased. The intensity of the $\beta$-relaxation was found to slightly increase with $T$, although in this case the change for the PtBa homopolymers is less pronounced. Although the intensity of the $\beta$-relaxation is slightly larger for the homopolymers than for the copolymers, the differences never exceed 30%.

**Fig. 6.** Relaxation map obtained for the PtBa blocks in the different samples. The symbols correspond to relaxation times $T_R$ calculated according to $T_\alpha = \frac{q}{q_\alpha}$ from the retardation times $q_\alpha$ corresponding to the maximum of the loss dielectric curves. The two curves have been calculated from the shift factors of the DMTA experiments for PtBa and P307. The curve corresponding to P305 is intermediate to those shown and has not been plotted for the sake of clarity.

**Fig. 8.** Temperature dependence of the strength of the $\alpha$-transition obtained from the dielectric experiments. The uncertainty for the PtBa homopolymers is within the size of the symbols.

**Fig. 9.** Temperature dependence of the width $W_{H-N}$ of $\alpha$-relaxation of the PtBa blocks obtained from the dielectric experiments. $W_\text{Debye}$ refers to the width of a Debye relaxation (1.14 decades).

**Fig. 7.** Relaxation curves calculated from the dielectric and DMTA experiments for two samples at a temperature in which both experiments overlap: 333 K for PtBa and 331 K for P305. The curves corresponding to dielectric experiments were calculated from the dielectric modulus representation.

**Fig. 9.** Temperature dependence of the width $W_{H-N}$ of $\alpha$-relaxation of the PtBa blocks obtained from the dielectric experiments. $W_\text{Debye}$ refers to the width of a Debye relaxation (1.14 decades).
Moynihan and Schroeder have related the mean square deviation of \( \ln T \) from its average, \( \langle \Delta^2 \ln T \rangle \), to the volume of the CRR by

\[
\langle \Delta^2 \ln \tau \rangle = \left[ \frac{B T_2}{(T - T_2)^2} \right] \gamma k_B v_n \frac{\Delta C_p V}{\Delta \eta}
\]

(7)

where \( B \) and \( T_2 \) are the parameters that appear in the Vogel–Fulcher equation

\[
\ln \tau \approx \frac{B}{T - T_2}
\]

(8)

and \( v \) is the specific volume.

A similar equation was found for \( \langle \Delta^2 \ln \tau \rangle \) in terms of the Free-Volume theory:

\[
\langle \Delta^2 \ln \tau \rangle = \left[ \frac{B T_2}{(T - T_2)^2} \right] \gamma k_B T \Delta \eta
\]

\[
\frac{\Delta C_p V}{\Delta \eta}
\]

(9)

where \( \Delta \eta \) and \( \Delta \eta \) are the changes in isothermal compressibility and isobaric expansivity at the glass transition, respectively. \( T_2 \) is now the temperature at which the free-volume of the equilibrium liquid would vanish. Taking into consideration typical values of the Priogine–Defay ratio \( T_2 = \frac{\Delta C_p \Delta \eta}{T} \), Moynihan and Schroeder [36] found that \( \frac{V_N}{V} = 1.8 - 2.4 \).

Using MSA techniques, a conformational analysis using MDS and the dihedral angles \( \phi_1 \) and \( \phi_2 \) for the model PtBa block, was evaluated through the Boltzmann equation

\[
\Delta G = R T \ln \frac{f \phi_1}{f \phi_2}
\]

(10)

where \( f \phi_i \) is the frequency at which a given value of \( \phi_i \) appears.

Ngai has proposed an empirical correlation between the \( \beta \) parameter and the value of the relaxation time of the \( \beta \) transition at \( T = T_\beta \), with \( T_\beta \) defined as the temperature at which the relaxation time of the \( \alpha \)-transition is \( 10^4 \) s. We have found that the correlation leads to values which are almost 3 decades higher than the values shown in Fig. 6. In an analysis of random copolymers of PS and poly(n-butyl acrylate) Ngai has indicated that these kinds of discrepancies may arise from the concentration fluctuations in the copolymers. Furthermore, it must be considered that Ngai’s correlation was proposed for the so-called Johari–Goldstein (J–G) secondary relaxations. It is not straightforward to test whether the \( \beta \)-transition of the present samples fulfill the conditions for the J-G relaxations pointed out by Ngai and Paluch because the \( \alpha \)-and \( \beta \)-relaxations cannot be measured at the same temperature within the experimental frequency regime. This would be important because one of the conditions of the J-G relaxations is that they do not follow an Arrhenius-like temperature dependence above \( T_\beta \).

The relaxation maps obtained from dielectric relaxation experiments show that for the \( \beta \)-transition the characteristic time for the PtBa blocks is faster in the homopolymer than in the copolymers, see Fig. 6. This is an unexpected result because the \( \beta \)-relaxations have a more local character. We assume that the relaxations times for PtBa blocks of the P(307) and P(305) are being affected by the P307 block. The free energy (\( \Delta G \)) for the conformational change of the dihedral angles \( \phi_1 \) and \( \phi_2 \) of the PtBa block, was evaluated through the Boltzmann equation.

Fig. 10. Distribution of frequencies of the dihedral angles \( \phi_1 \) and \( \phi_2 \) for the model PtBa homopolymer at 1700 K.
Acknowledgments

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5. Conclusions

A calorimetric, dielectric, and the dynamic-mechanical study of PtBa and two diblock copolymers of PS and PtBa has been carried out around the glass transition temperature of the systems. Two separate $T_g$ are present in each of the copolymer which are very close to those of the corresponding homopolymers. The size of the cooperative rearranging regions for each type of block has been calculated from the $C_p$ vs. $T$ curves, and it shows no significant differences between the samples.

The relaxation map for the PtBa blocks has been calculated from the dielectric relaxation curves. While no significant differences have been found between the results of the different samples for the $\alpha$-relaxation, the relaxation times corresponding to the $\beta$-relaxation are smaller for the PtBa homopolymer than for the copolymers. This is a surprising result because the motions corresponding to the $\beta$-relaxation have a more local character than those of the $\alpha$-one. The temperature dependence of the relaxation time obtained from the DMTA experiments for the $\alpha$-relaxation is very similar to the one obtained from dielectric relaxation. However, the magnitude of the relaxation times is different, the values from DMTA being larger than those from dielectric relaxation. Moreover, the DMTA experiments show that there are some differences between the temperature dependence of the relaxation times of the three samples. The width of the dielectric relaxation curves increases with $T$, which is unusual.

Conformational analysis seems to be a powerful tool to describe the differences in the mobility of the ester group. The results point out that the mobility of the t-butyl acrylate group is strongly influenced by its molecular surrounding, thus leading to different activation energies in the homopolymer than in the copolymers. This is in qualitative agreement with the fact that the relaxation times of the $\beta$ transitions are different in both types of chains.

The temperature dependence of the relaxation time $\tau$ of the $\alpha$-relaxation, the relaxation times corresponding to the $\beta$-relaxation have a more local character than those of the $\alpha$-one. The temperature dependence of the relaxation time obtained from the DMTA experiments for the $\alpha$-relaxation is very similar to the one obtained from dielectric relaxation. However, the magnitude of the relaxation times is different, the values from DMTA being larger than those from dielectric relaxation. Moreover, the DMTA experiments show that there are some differences between the temperature dependence of the relaxation times of the three samples. The width of the dielectric relaxation curves increases with $T$, which is unusual.

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