

# Dynamics of Novel Polybutadiene Ionomers

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**ABSTRACT:** The dynamics of novel ionomers based on a low-molecular-weight polybutadiene with zinc acrylate moieties were investigated as a function of the number of ionic bonds by using a combination of calorimetry, dielectric broadband spectroscopy and rheology. We find that the ionic bonds have profound effects on the mechanical properties, including the introduction of a sol–gel transition. However, all techniques

consistently indicate that the segmental dynamics of the polymer chains remain largely unaffected, and only very small changes in the glass transition were observed. © 2019 Wiley Periodicals, Inc. *J. Polym. Sci., Part B: Polym. Phys.* **2019**

**KEYWORDS:** dielectric relaxation; glass transition; ionomers; segmental dynamics

**INTRODUCTION** Ionomers are polymers with a small fraction (few percent) of ionic groups covalently bonded to the polymer backbone as pendant moieties.<sup>1</sup> The presence of the ionic bonds can have profound effects on bulk properties and on the polymer dynamics in a manner similar to those systems containing covalent crosslinking. The main difference between these two crosslinking interactions is that the latter creates permanent chemical crosslinks, while the former creates physical bonds that are transitory in nature. Thus, for times shorter than the ionic bond lifetime ( $t \ll t_c$ ), the system behaves as if it was covalently bonded, while at longer times ( $t \gg t_c$ ), the polymer behaves like a free chain. The physics of ionomers tends to be much more complex than that of classical polymers because of added complications, namely that: (a) the ionic bond lifetime is dependent on the external conditions such a temperature or mechanical stress and (b) unlike covalent bonds ionic bonds are reversible.

In the literature, there is a considerable interest in ionomers due to their novel electrical and mechanical properties.<sup>2–6</sup> Similarly, to their chemical counterparts, above a certain level of association, physical bonds (i.e., ionic bonds) can induce sol–gel transitions. This is defined as a physical sol–gel transition to distinguish it from the chemical sol–gel transition induced by covalent bonds.<sup>7</sup> The chemical gel is a solid in which the chain can move only locally; conversely, owing to the transitory nature of the ionic bonds, the physical gel is a solid only for time shorter than the typical lifetime of the physical bond, and thus, large-scale rearrangements of the chains are possible at long times.<sup>8,9</sup> Moreover, the ability of physical bonds to break and reform

during different conditions of strain or temperature evidently complicates the physics of ionomers relative to that of covalent networks. The lifetime of an ionic bond is generally inversely proportional to the strength of the interaction; thus, it can be controlled by substituting anions and cations (e.g., different metal ligands).<sup>3,6,10</sup> In some cases, the lifetimes of the interactions can be hard to measure experimentally, because they can be longer than a typical experiment.

Zinc diacrylate/dimethacrylate is commonly used as an additive to reinforce butadiene rubbers. However, the zinc diacrylate in these systems is mixed in the solid state, and thus, it remains phase-separated from the polymer.<sup>11,12</sup> Herein, we investigate the physics of ionomers based on a low-molecular-weight polybutadiene (PB) modified by zinc acrylate moieties. The acrylate groups about the zinc ions are covalently reacted to the olefin groups in the polymer backbone in solution, and are thus presumably well dispersed. We find that the presence of the ionic bonds has a strong effect on the mechanical properties of the PB inducing a sol–gel transition, while surprisingly many thermodynamic and dynamic properties remain unchanged.

## EXPERIMENTAL

PB ionomers (iPBs) were synthesized by functionalizing a low-molecular-weight PB ( $M_w = 2800$ , 80% 1,4-PB, 20% 1,2-PB) with zinc acrylate (Sigma Aldrich 98% purity). The synthetic procedure was analogous to that used for the functionalization of PB by other authors.<sup>13</sup> The resulting acrylate-functionalized PB was isolated under vacuum and repeatedly precipitated to remove the (low) possibility of excess zinc

diacrylate, and any initiator. Unlike the starting polymer, iPBs have only limited solubility in methylene chloride or chloroform and have a higher viscosity than the starting material (Fig. 1). However, if a small amount of *p*-toluenesulfonic acid is added,<sup>14</sup> the polymers readily dissolve. This indicates that the increase in viscosity of iPBs is due to no covalent crosslinking but rather the presence of ionic crosslinks.

DSC was performed using a TA Instruments Q100 DSC with a standard cooling rate of 10 K/min. For TGA, the samples were heated in a TA Instruments Q500 up to a temperature of 970 K with a heating rate of 20 K/min in both nitrogen and air atmosphere.

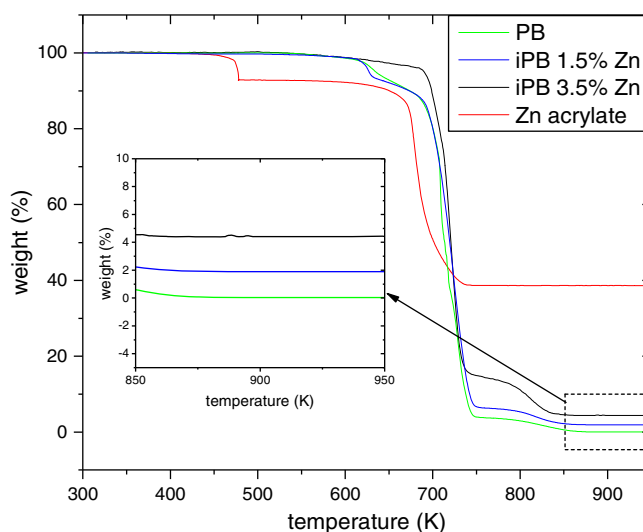
Dynamic mechanical measurement employed an Anton Paar MCR 502 rheometer, using a frequency range of  $10^{-2} \leq \omega(\text{rad/s}) \leq 10^2$ . Cone and plate geometries with different radii (8, 25, and 50 mm) and cone angles ( $1^\circ$ ,  $2^\circ$ , or  $4^\circ$ ) were used for the characterization of different dynamical ranges (smaller radius close to  $T_g$ ). Strain amplitude sweeps were measured for all samples to verify that the measurements were made in the linear response region, and a strain,  $\gamma$ ,  $0.5\% < \gamma < 1\%$  was used.

Dielectric relaxation spectroscopy was carried out using a Novocontrol Alpha analyzer. The electrode diameter was 16 mm, with a Teflon spacer of 50  $\mu\text{m}$ . During the measurements, the samples were held under vacuum in a closed cycle helium cryostat.

## RESULTS

### Thermogravimetric Analysis

Thermogravimetric measurements of the precursor polymer and of two representative ionomers are shown in Figure 2. The presence of the ionic crosslinks does not have any apparent effect on the thermal stability of the PB, which mostly degrades above 600 K. From the residual weight at high temperature ( $T > 900$  K), it is possible to determine the percentage content of zinc (and thus the average number of crosslinks per chain) in the iPBs, considering that the residual for neat PB (which is very close to 0%) and Zn oxide is stable to those temperatures. To determine more accurately the amount of Zn, the TGA measurements were performed in air to assure a full conversion of the zinc crosslinker into zinc oxide. This procedure was



**FIGURE 2** TGA of the neat PB, two Zn-crosslinked iPB, and zinc acrylate in air. The inset shows a detail of the high-temperature behavior evidencing the formation of Zn oxide. [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

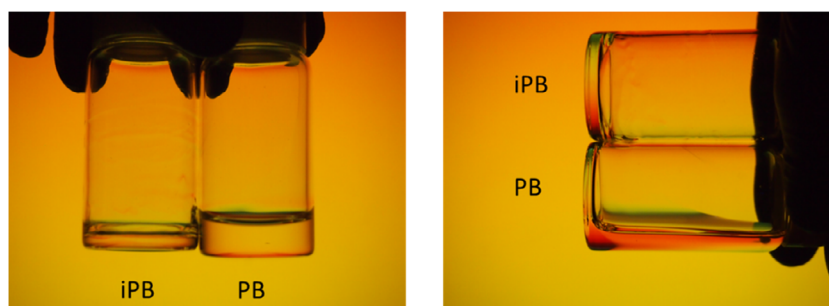
validated by heating the zinc acrylate monomer (Fig. 2). The percentage content of Zn is reported in Table 1.

### Differential Scanning Calorimetry

DSC measurements for both the neat PB and ionomers with varying amounts of ionic groups are shown in Figure 3. The DSC scans show that the glass transition temperature (Table 1) varies little, only increasing slightly with the increasing number of ionic groups (about 0.4 K for the iPB with 3.5% Zn, a change barely larger than the experimental error). No additional glass transition or other type of transition (melting or crystallization) was observed at higher temperatures than in the reported scan. The presence of multiple glass transitions has been reported for other ionomers in the literature.<sup>15</sup> However, in this case, the clear increase in the viscosity is not accompanied by major changes to the DSC scan.

### Rheological Measurements

The shear modulus  $G^*(\omega) = G'(\omega) + iG''(\omega)$  of neat PB and iPB ionomers was measured as functions of the angular frequency

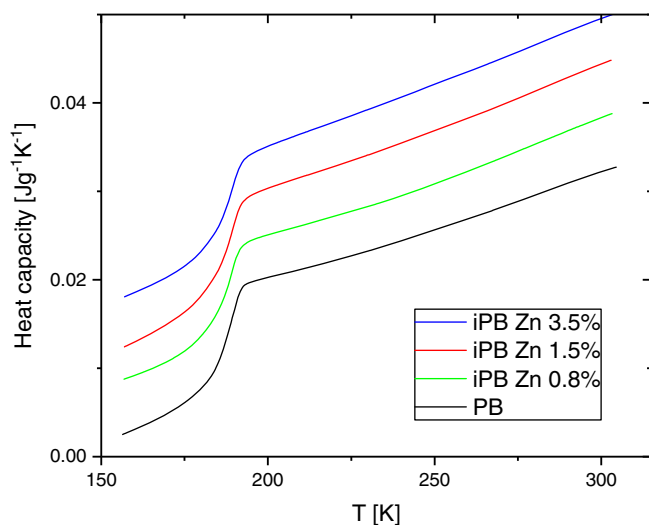


**FIGURE 1** Apparent high viscosity of the iPB ionomer with 1.5% Zn crosslinker with respect to the PB precursor. Noticable flow of the iPB required several minutes, while the uncrosslinked PB flowed immediately. [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

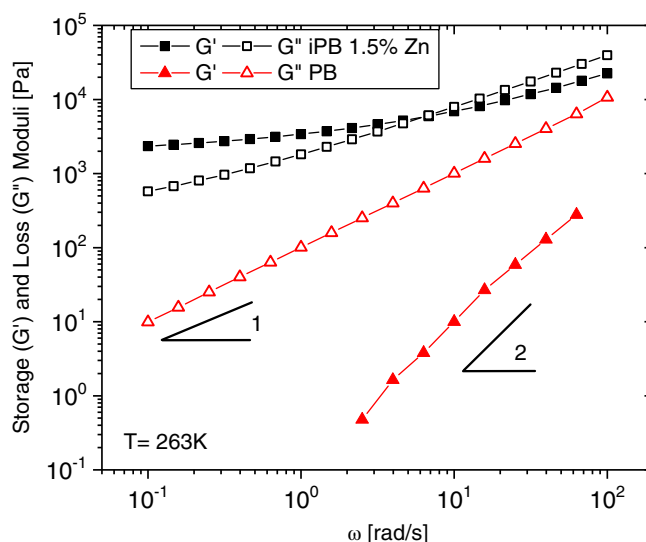
**TABLE 1**  $T_g$  from DSC and the Number of Ionic Crosslinks per Chain,  $n$ , versus % Zn

Zn [%]	$T_g$ [K]	$n$
0	$188.9 \pm 0.5$	0
0.8	$188.9 \pm 0.5$	0.7
1.5	$189.1 \pm 0.5$	1.4
3.5	$189.3 \pm 0.5$	3.9

over a broad range of temperatures. The ionic crosslinks introduced by the zinc acrylate groups in the PB chain have a profound effect on the mechanical properties of PB, which is evident in the change of the frequency behavior of  $G'(\omega)$  and  $G''(\omega)$ . Because of the low molecular weight of the PB, there are no entanglements. At temperatures well above the glass transition temperature, the neat PB has the typical behavior of a Newtonian fluid with  $G'(\omega) \propto \omega$ ,  $G''(\omega) \propto \omega^2$ , and  $G''(\omega) < G'(\omega)$  (Fig. 4). In contrast, at the same temperature,  $G^*(\omega)$  of the iPB ionomer with 1.5% Zn (that corresponds to an average of 1.5 associated monomers per chain) shows a very different behavior, at low frequency  $G'(\omega) \approx G'_0$  and  $G''(\omega) \approx G''_0$ , where  $G'_0$  and  $G''_0$  are constants and  $G'_0 > G''_0$ . The behavior of the iPB ionomer with 1.5% Zn is typical of a polymer network even if no covalent crosslinks are present in this case because of the large association energy. When the average number of associated monomers per chain is larger than unity (which in this case corresponds to Zn % > 1.1%), almost all chains are connected to the network.<sup>8,16</sup>  $G'_0$  increases with the number of crosslinks per chain,  $n$ . To show this relationship, we plotted

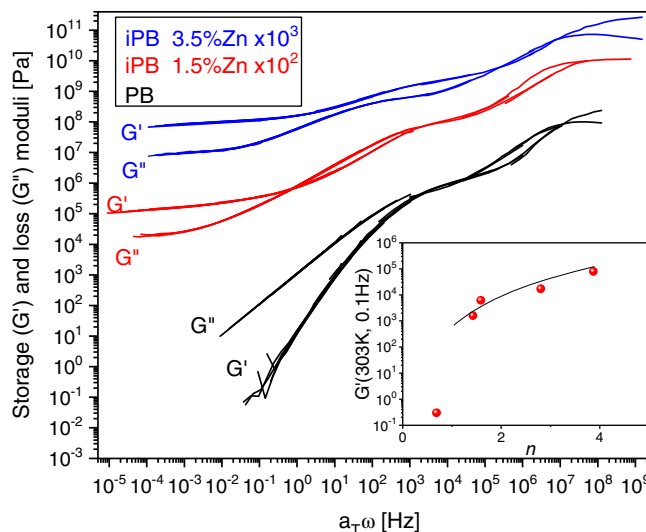


**FIGURE 3** DSC measurements of the neat PB and three iPB ionomers with different amounts of ionic groups. The measurements were done at a cooling rate of 10 K/min. The glass temperature,  $T_g$ , values determined from these scans are reported in Table 1. Little change to the  $T_g$  is observed in the PB functionalized with the ionic groups. A constant was added to the data to separate them along the Y axis. [Color figure can be viewed at wileyonlinelibrary.com]



**FIGURE 4** Storage ( $G'$ ) and loss ( $G''$ ) moduli versus angular frequency of neat PB (red) and iPB ionomer with 1.5% Zn (black) at  $T = 263$  K. [Color figure can be viewed at wileyonlinelibrary.com]

$G'(\omega = 0.1 \text{ Hz}, T = 303 \text{ K}) \approx G'_0$  versus  $n$  (insert Fig. 5). The point  $n = 1$  is the condition at which there is a network involving all the chains. In the plot of the plateau modulus  $G'_0$  versus  $n$ , a change in behavior in correspondence to  $n = 1$  is apparent. For  $n > 1$ , the behavior can be approximated with  $G'_0 \propto \epsilon^\nu$ , where  $\nu = 3.9 \pm 1$ . This behavior differs from what is



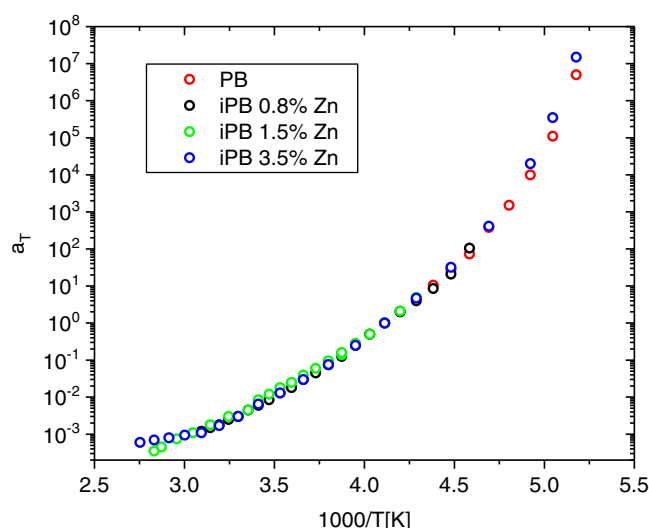
**FIGURE 5** Master curves of PB and of two iPB ionomers obtained from the  $G'$  and  $G''$  spectra at varying temperatures (data for the ionomers are rescaled to avoid superposition). In the insert, the storage modulus at 303 K and  $\omega = 0.1$  Hz is plotted versus the number of associated monomers per chain,  $n$  ( $G'(303 \text{ K})$  data for two additional ionomers with Zn = 1.7% and Zn = 2.7% are included in insert). The solid line is the fit with a power law behavior for the data with  $n > 1$ , which is above the gelation threshold. [Color figure can be viewed at wileyonlinelibrary.com]

expected for common networks in which  $G'_0$  is expected to scale with the inverse of the molecular weight of the strand between crosslinks,<sup>8,17</sup> and thus should be proportional to  $n$ . This deviation could be an indication that more than a single crosslink forms per each Zn ion, while in the calculation above to determine  $n$  from the weight percentage of Zn, we considered only a single crosslink between two chains. In other ionomers at high temperature, a decrease in  $G'$  is observed due to the dissociation of the ionic bonds (i.e., decrease of  $t_c$  at high  $T$ ). However, this behavior was not observed in the investigated range of  $T$  for the iPBs. Thus, the lifetime of the ionic bonds for the iPB was always longer than the experimental time, and for the investigated range of temperature (and strain), the crosslinks act as covalent crosslinks and not as “sticky” crosslinks.<sup>18</sup>

By introducing a shift factor  $a_T$  to renormalize the frequency of the storage and loss moduli spectra at different temperatures, we generated the master curves shown in Figure 5. The different behaviors of the neat PB and the modified iPB described above are even more evident at the lowest frequency (high temperature) sections of the master curves.

All  $G''(\omega)$  master curves in the limit of high frequency ( $a_T\omega \sim 10^7$ ) show a peak, which is related to the glass transition of the different materials. The fact that the peak is present at the same temperature for all master curves is consistent with the small change of  $T_g$  found by DSC measurements. The behavior of  $G'(\omega)$  in the glass is very similar for all materials with a glassy modulus  $G'(\omega) \simeq G_S \sim 200$  MPa.

Notwithstanding the large difference in  $G^*(\omega)$  for the iPB ionomers with respect to the neat PB, upon comparing the temperature dependence of the shift factor  $a_T$  for the different materials (Fig. 6), we find few differences between all materials. This is an indication that the ionic bonds have little effect on the dynamics of the polymer segments of PB, which

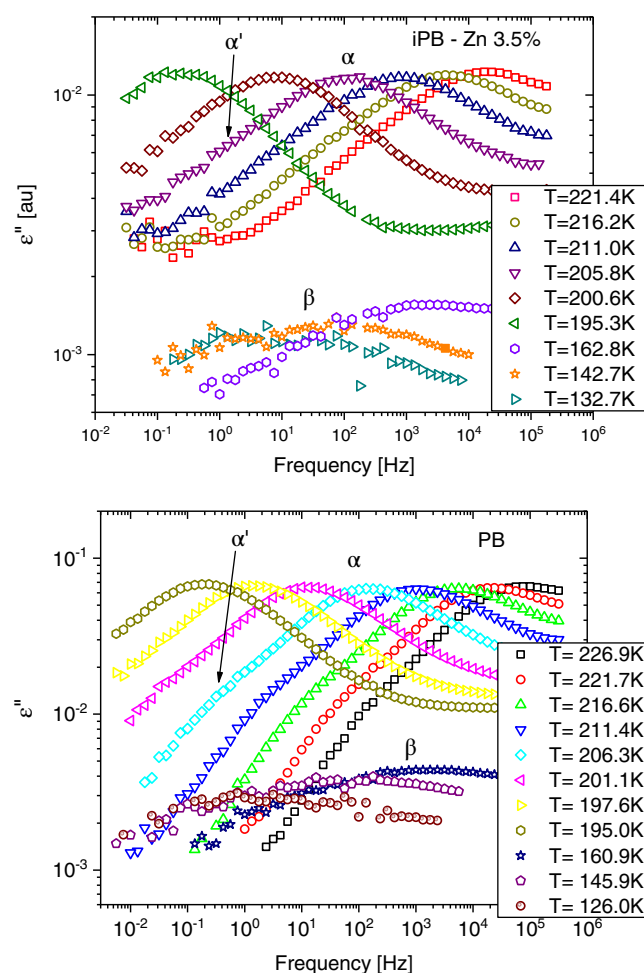


**FIGURE 6** Temperature dependence of the shift factor  $a_T$  from  $G'$  and  $G''$ . [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

is consistent with the very small change in  $T_g$ . Thus, the rheological measurements show that the ionic bonds do not alter the local chain dynamics (segmental dynamics) even if they block the chain diffusion, as evidenced in Figure 5.

### Broadband Dielectric Spectroscopy

The dielectric constant  $\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$  for neat PB and two iPB ionomers with 1.5% and 3.5% Zn was measured over a broad range of temperatures. The dielectric spectra (Fig. 7) above  $T_g$  show mainly the presence of the segmental relaxation (or  $\alpha$ -process). The  $\beta$ -process is evident mostly below  $T_g$ , because its intensity is much smaller than that of the  $\alpha$ -process. The  $\beta$ -process is generally attributed to the local noncooperative motions of the segments, and is often identified as a Johari–Goldstein relaxation. Less evident is a small shoulder in the low-frequency flank of the  $\alpha$ -process, which could be due to the presence of both 1,2 and 1,4 repeating units in the PB polymer. Because 1,2-PB and 1,4-PB have very different



**FIGURE 7** Dielectric loss spectra at various temperatures for neat PB (bottom) and iPB ionomer with 3.5% Zn (top). The temperatures of each spectra are reported in the legend. The spectra above the glass transition are dominated by the  $\alpha$ -process, and the  $\beta$ -process is evident well below the glass transition. [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

glass transitions (272 and 178 K, respectively<sup>19</sup>), their different dynamics could in principle be apparent in this case as a second glass transition. However, two glass transitions have been only being reported for block copolymers of 1,2-PB and 1,4-PB in the case of microphase separation.<sup>20</sup> This low-frequency shoulder cannot be attributed to the presence of the ionomer moiety, because it is also present in the neat PB. Another possible explanation of this shoulder at lower frequency is the presence of a normal mode (chain dynamics); however, this has not been reported to date. The presence of a normal mode in the dielectric spectra requires the presence of a dipole along the chain<sup>21–23</sup> that, in principle, is not present in PB, although the separation is not significantly different from what would be expected for the  $M_w$  of the investigated polymer. A dipole along the chain is not expected for neither the 1,2-PB or the 1,4-PB structure; however, a possible cause for the presence of a dipole along the chain could be the asymmetry of the two structures. A potential way to clarify the presence of a normal mode would be to verify whether for a higher  $M_w$  polymer, the two peaks will be more separated in the frequency domain. In other ionomers, an additional peak at low frequency attributed to the ionic bond has been observed<sup>24</sup> (amplitude increase with the number of ionic bonds); however, no additional relaxation peaks due to the ionic bonds were observed in our measurements. At high temperatures, the spectra were dominated by DC conductivity of impurities, with the conductivity being smaller in the ionomers than in the initial PB.

To analyze the spectra, a linear superposition of two Kohlrausch–Williams–Watts (KWW) and one Cole–Cole (CC) function<sup>25</sup> was used

$$\epsilon^*(\omega) = \Delta\epsilon_{\alpha'} L_{i\omega} \left[ -\frac{d\varphi_{\alpha'}(t, \tau_{\alpha'})}{dt} \right] + \Delta\epsilon_{\alpha} L_{i\omega} \left[ -\frac{d\varphi_{\alpha}(t, \tau_{\alpha})}{dt} \right] + \frac{\Delta\epsilon_{\beta}}{1 + (i\omega\tau_{\beta})^{1-\alpha_{cc}}} + \epsilon_{\infty} \quad (1)$$

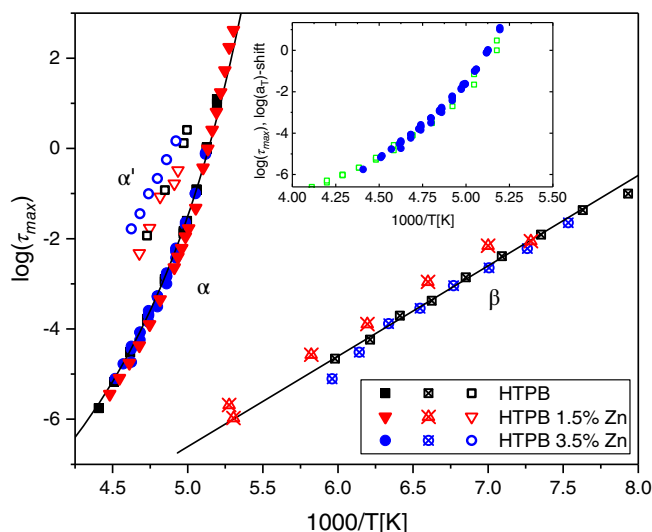
where  $\Delta\epsilon$  is the dielectric strength,  $\tau$  is the relaxation time,  $\alpha_{cc}$  is the shape parameter of the CC function,  $\epsilon_{\infty}$  is the relaxed dielectric constant, and  $\varphi(t)$  is the KWW function

$$\varphi(t) = \exp \left[ - (t/\tau)^{\beta_{KWW}} \right] \quad (2)$$

where  $\beta_{KWW}$  is the stretching parameter ( $0 < \beta_{KWW} \leq 1$ ).

The relaxation times  $\tau_{\alpha'}$ ,  $\tau_{\alpha}$  and  $\tau_{\beta}$  determined from the best fit to the spectra are reported in Figure 8.<sup>26</sup> We find that the dynamics of the  $\alpha$ -process remains unaltered by the introduction of the ionic moiety, which is consistent with the mechanical measurements and the DSC measurements of  $T_g$ . Additionally, dielectric measurements also show that the dynamics of the  $\alpha'$  and secondary  $\beta$ -process remain unchanged within the experimental error.

The temperature dependence of the  $\tau_{\beta}$  is well described with an Arrhenius equation,



**FIGURE 8** Temperature dependence of the relaxation time for the  $\alpha'$  (open symbols),  $\alpha$  (solid symbols), and  $\beta$ -process (open symbols with cross) determined from the fit to the dielectric spectra of the neat PB (black symbols) iPB ionomer with 1.5% Zn (red symbols) and the iPB ionomer with 3.5% Zn (blue symbols). The solid lines are the best fit to the data with a VFT equation and an Arrhenius equation. Inset: comparison of the temperature dependence of the  $\alpha$ -process with the shift factor  $a_T$  from the mechanical measurements. Note that to determine  $a_T$ , the reference temperature was 243.15 K and the  $a_T$  data were shifted by the value of  $\tau_{\alpha}$  at that temperature. [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

$$\tau_{\beta}(T) = \tau_{\beta}^{\infty} \exp \left( \frac{E_{\beta}}{kT} \right) \quad (3)$$

with a constant activation energy  $E_{\beta}$ , where  $k$  is the Boltzmann constant and  $\tau_{\beta}^{\infty}$  is the high temperature limit of  $\tau_{\beta}$ . In the best fit to the  $\tau_{\beta}(T)$  (solid line in Fig. 8), we find  $E_{\beta} = 35.6 \pm 0.8$  kJmol<sup>-1</sup> and  $\log(\tau_{\beta}^{\infty}) = -15.7 \pm 0.3$ .

The temperature behavior of  $\tau_{\alpha}$  is characterized by an activation energy increasing with decreasing temperature, which is well described by a Vogel–Fulcher–Tamman (VFT) function

$$\tau_{\alpha}(T) = \tau_{\alpha}^{\infty} \exp \left( \frac{B}{T - T_0} \right) \quad (4)$$

where  $\tau_{\alpha}^{\infty}$  is the high temperature limit of  $\tau_{\alpha}$ ,  $B$  is a constant, and  $T_0$  is the Vogel temperature. According to the VFT equation at the temperature  $T_0$ ,  $\tau_{\alpha}$  is supposed to diverge. However, this divergence cannot be observed, because below  $T_g$ , the system cannot reach equilibrium, and often a deviation from the VFT is observed (see ref. 27 and references therein). From the best fit of the VFT (solid line in Fig. 8) to the  $\tau_{\alpha}$  data above  $T_g$ , we find  $\log(\tau_{\alpha}^{\infty}) = -13.0 \pm 0.1$ ,  $B = 1260 \pm 10$  K, and  $T_0 = 153 \pm 1$  K.

The temperature dependence of  $\tau_{\alpha}$  is in a very good agreement with that of the shift factor from mechanical measurement  $a_T$ ,



as shown in the insert of Figure 8. Thus, both dielectric and mechanical measurements indicate that the temperature dependence of the mechanical measurements is controlled by the segmental dynamics of PB, which in turn is largely uninfluenced by the ionic bonds between the chains. This “lack” of effect can be attributed to the high flexibility of the PB chain and of the side chains. Thus, the formation of ionic bonds prevents chain diffusion (increase of viscosity), but it does not hinder the local rearrangements of the chain segments as evidenced by the absence of a change observed for both  $\tau_\alpha$  and  $\tau_\beta$ . This behavior is different from that of covalent PB networks in which the temperature dependence of  $\tau_\alpha$  was found to change with increasing crosslinking density, probably due to the higher rigidity of the covalent crosslinks.<sup>28–30</sup>

## CONCLUSIONS

The dynamics of new elastomeric ionomers based on low-molecular-weight PB were investigated using a combination of DSC, rheology, and broadband dielectric measurements. We found that the introduction of the zinc-based ionic bonds has a large effect on the rheological properties of the PB, which are comparable with those expected in the case of covalent crosslinks. However, the presence of the ionic bonds has only minute effects on the segmental dynamics of the iPB, with small changes of the glass transition (<0.5 K) and no evident changes in the steepness index of PB. Thus, even if the long range motions of the chains are blocked by the presence of the ionic crosslinks, the local segmental (and secondary) dynamics remain unaffected. Owing to the high strength of the ionic interactions, the lifetimes of the ionic bonds are so large that dissociation was not observed in the investigated range of the frequency even at high temperatures. This absence is consistent with the low-temperature sensitivity of the zinc-oxygen coordination observed for similar zinc ionomers.<sup>31</sup>

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