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Decoupling of Ionic Transport from Segmental Relaxation in Polymer Electrolytes

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Abstract

We present detailed studies of the relationship between ionic conductivity and segmental relaxation in polymer electrolytes. The analysis shows that the ionic conductivity can be decoupled from segmental dynamics and the strength of the decoupling correlates with the fragility, but not with the glass transition temperature. These results call for a revision of the current picture of ionic transport in polymer electrolytes. We relate the observed decoupling phenomenon to frustration in packing of rigid polymers, where the loose local structure is also responsible for the increase in their fragility.

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It is known that use of polymer electrolytes instead of traditional liquid electrolytes provides significant advantages for battery technologies [1, 2]. However, several decades of research did not identify a polymer with sufficient ionic conductivity, σ , around room temperature, and low σ remains the main obstacle for polymer electrolytes. According to the classical theory [3], ionic conductivity in a polymer is related to its segmental relaxation time, τ_s :

$$\sigma\tau_s T = \text{Const.} \quad (1)$$

The relationship (Eq.1) has been indeed observed for many flexible polymers, including the most studied polymer electrolyte poly(ethylene oxide) (PEO) [4]. The underlying physics is the coupling of ionic diffusion to the polymer segmental dynamics: ion motions are possible only when polymer segments undergo large amplitude rearrangements. As a result, the ionic conductivity drops to very low values when the polymer matrix slows down upon approaching glass transition temperature, T_g . Thus for many years the main direction of research has been focused on design of flexible polymers where shorter segmental relaxation time will lead to higher ionic conductivity.

However, studies of rigid polymers revealed that their ionic conductivity can be decoupled from their segmental relaxation [5-8]. This has challenged the conventional view of ionic transport in polymer electrolytes. Employing the decoupling of ionic conductivity from segmental dynamics might open a way to design of polymers with high ionic conductivity at ambient temperature, similar to the well-known “superionic glasses” [9]. This requires, however, understanding the microscopic mechanism controlling ionic conductivity in polymers and the role chain rigidity/flexibility plays in diffusion of ions. The authors of the earlier studies related the decoupling to extra free volume that exists in rigid polymers [6] and tried to correlate the decoupling to T_g of the polymers [5].

This letter is focused on detailed studies of the relationship between ionic conductivity and segmental relaxation for a set of polymers with variation in chain rigidity. We show that the classical picture for ionic transport indeed breaks down in rigid polymers, where the ionic conductivity exhibits much weaker temperature dependence than do segmental dynamics. The analysis demonstrates that the degree of decoupling correlates well with the steepness of the temperature dependence of the segmental dynamics (fragility), but not with T_g . We explain the observed decoupling phenomenon in terms of packing frustration in rigid polymers, where the loose local structure also leads to an increase in their fragility.

We synthesized five comb-like polymers [Poly(Polyethylene Oxide Styrene)-*b*-Polystyrene (PPEOST-*b*-PSt), Poly(Polyethylene Oxide Methacrylate) (PPEOMA), Poly(Polyethylene Oxide Caprolactone) (PPEOCL), Poly(Norbornene Carboxylic Ethoxymethyl Ester) (PNBCEM), and Poly(Polyethylene Oxide Styrene) (PPEOST)] by polymerizing macromonomers bearing PEO segments. The resulting polymers consist of linear backbones with different degree of rigidity and PEO side-chains that enhance the solvation of metal ions (detailed chemical structures are presented in the Supporting Information). Differential scanning calorimetric (DSC) measurements indicated all the polymers were in a single phase. Solid polymer electrolytes were prepared by dissolving polymers and 0.3-1.0wt% lithium perchlorate (LiClO₄) in tetrahydrofuran (THF), and subsequently removing the solvent in a vacuum oven at room temperature. For polymers with relatively high glass transition temperature, the mixtures were further dried at elevated temperature to completely remove the residual solvent. We specifically used low salt concentration (O:Li ratios in the range 220:1 – 540:1) to avoid possible problems due to salt solubility and microphase separation. The final samples were placed between two gold-plated electrodes with a Teflon spacer of 54 μm. To resolve both polymer segmental relaxation and ionic conductivity, dielectric measurements were performed at various temperatures using Concept 80 system (Novocontrol) in the frequency range of 10⁻²–10⁷ Hz.

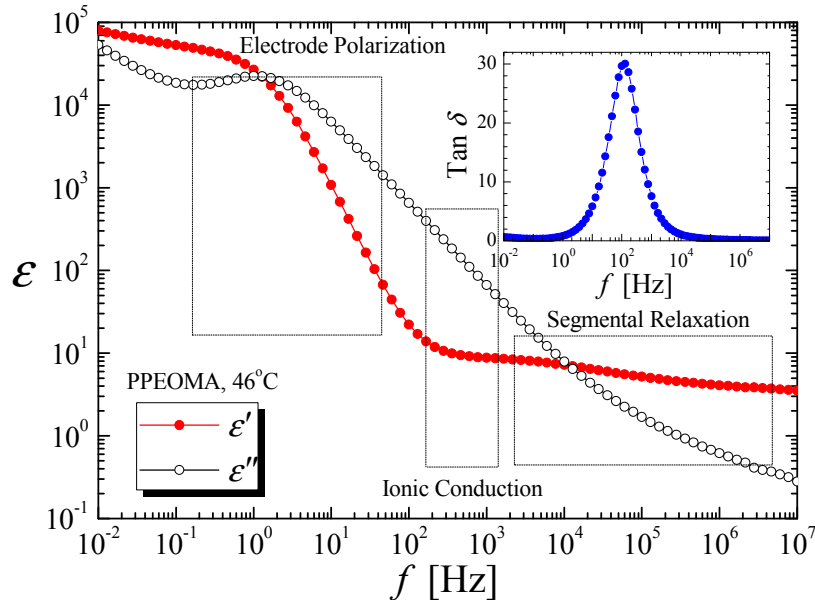


FIG. 1 (color online). Dielectric spectrum for PPEOMA at 46°C. The relaxation in the high-frequency region corresponds to the segmental motion of PPEOMA, whereas the low-frequency process is due to the electrode polarization effect. Inset: corresponding loss $\tan \delta$.

Dielectric spectroscopy can provide direct information about the segmental relaxation, and the ionic conductivity in polymer electrolytes. Figure 1 shows an example of the typical dielectric spectra, where three molecular processes — segmental relaxation, ionic conductivity and electrode polarization (EP) are all present. The segmental relaxation time τ_S can be estimated as the inverse frequency of the loss maximum from the derivative spectra [10, 11]: $\varepsilon_{\text{der}}'' = (-\pi/2)\partial\varepsilon'/\partial\ln\omega$, and the ionic conductivity can be calculated from the intermediate frequency region of ε'' as $\sigma = \varepsilon''/(2\pi f\varepsilon_0)$. The sharp rise of ε' and ε'' in the low frequency region is a result of the EP effect which arises from the accumulation of charges on the electrode surfaces.

If the ion transport is indeed coupled to the polymer segmental motion (Eq.1), then the inverse conductivity σ^{-1} and τ_S should have the same temperature dependence. Figure 2 (a) presents the temperature dependence of ionic conductivity σ and segmental relaxation time τ_S for two representative samples, PPEOS*t*-*b*-PSt and PPEOMA. The ionic conductivity of Li^+ and ClO_4^- in PPEOMA follows closely the segmental relaxation time (Fig.2a). In contrast, the ionic conductivity in PPEOS*t*-*b*-PSt shows much weaker temperature dependence than its segmental dynamics. At the glass transition temperature, the ionic conductivity is approximately 6 orders of magnitude higher than what is expected in the case of complete coupling (Eq.1). Such a decoupling phenomenon has also been observed in two other polymer electrolytes with rigid structures: PNBCEM and PPEOS*t*.

An alternative way to illustrate the decoupling between ionic conductivity and segmental dynamics is to present $\sigma T\tau_S$ as a function of τ_S , as shown in Figure 3(a). In such a plot, $\sigma T\tau_S$ should appear as a horizontal straight line if the ionic transport of Li^+ and ClO_4^- is closely coupled to the polymer segmental motion. This behavior is indeed observed in PPEOMA and PPEOCL which have flexible backbones, while the product $\sigma T\tau_S$ in PPEOS*t*-*b*-PSt, PNBCEM and PPEOS*t* changes approximately 4-6 orders, when τ_S varies from 10^{-7} to 10^2 s displaying a very significant decoupling.

The ionic conductivity in polymer electrolytes can be described by the Nernst-Einstein relationship [12, 13], in terms of the free ion diffusion coefficient D , concentration p and the amount of charges q carried by the ion:

$$\sigma = \frac{pq^2D}{k_B T} \quad (2)$$

In the scenario of complete coupling between ionic translational diffusion and polymer segmental motion, the Stokes-Einstein relationship [14] indicates that the ionic diffusion coefficient D should be inversely proportional to the polymer segmental friction η_s and relaxation time τ_s :

$$D \propto \frac{T}{\eta_s} \propto \frac{1}{\tau_s}. \quad (3)$$

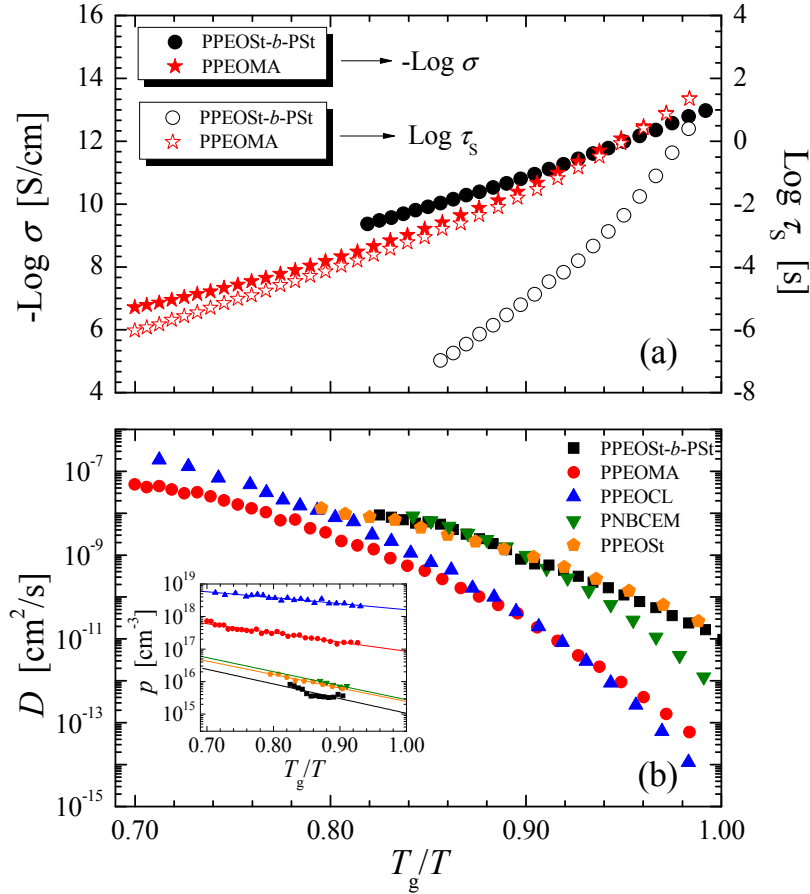


FIG. 2 (color online). (a) Temperature dependence of $-\log \sigma$ and $\log \tau_s$ for PPEOSt-*b*-PSt and PPEOMA. Solid symbols: $-\log \sigma$. Open symbols: $\log \tau_s$. (b) Temperature dependence of the ionic diffusion coefficient D obtained from σ and Arrhenius behavior of free ion concentration p . Inset: temperature variation of the free ions concentration (symbols), and its approximation by the Arrhenius fit (solid lines). The free ion concentration p has been corrected by certain constants such that p approaches its stoichiometric value in the high temperature limit, and D has also been adjusted accordingly. The T_g for the polymer electrolytes: PPEOSt-*b*-PSt, 338K; PPEOMA, 240K; PPEOCL, 210K; PNBCEM, 314K; PPEOSt, 265K. They are evaluated from the VFT equation as the temperature at which $\tau_s = 100$ s.

Combining Eq. (2) and (3) yields:

$$\sigma \propto \frac{p}{\eta_s} \propto \frac{p}{\tau_s T}. \quad (4)$$

It is easy to see that the traditional relationship (Eq.1) is a crude approximation to Eq.4, when the variation of free ion concentration can be neglected. Therefore, a more appropriate way to analyze the decoupling phenomenon is to directly examine the Stokes-Einstein relationship according to Eq.3, i.e., to determine if $D\tau_s$ stays a constant at different temperatures.

The diffusion coefficient of ions can be evaluated from the EP effect, according to the Trukhan model [15-17]:

$$D = \frac{2\pi f_{\max} L^2}{32(\tan \delta)_{\max}^2}, \quad (5)$$

where $(\tan \delta)_{\max}$ is the maximum value of $\varepsilon''/\varepsilon'$ in the frequency range of EP, f_{\max} is the frequency at which the $\tan \delta$ maximum occurs, and L is the sample thickness (see Fig.1). Here, it is assumed that both the cation (Li^+) and the anion (ClO_4^-) have equal diffusion coefficients. Strictly speaking, this assumption does not hold, as the diffusivities of cations and anions are generally different [18]. However, such a difference is typically less than an order of magnitude and therefore will not affect the basic conclusions of our analysis. In the earlier studies [11, 19], MacDonald's model [20, 21] was used to extract D and p from the EP effect. We stress that in the case of a Debye relaxation, the Trukhan model and the MacDonald model yield an identical expression (Eq.5) for the ion diffusion coefficient (details are presented in the Supporting Information). The free ion concentration p can be determined from the ion diffusion coefficient D and ionic conductivity σ :

$$p = \frac{\sigma k_B T}{q^2 D}. \quad (6)$$

The p estimated in this way follows the Arrhenius behavior: $p = p_0 \exp(-A/T)$, and decreases with decreasing temperature. Such a trend is in agreement with the previous investigations based on dielectric spectroscopy [11, 19], but at odds with the studies by radiotracer diffusion [22], Raman spectroscopy [23], pulsed field gradient NMR [24], and computer simulations [25, 26]. This apparent contradiction possibly arises from the fact that different experimental techniques are sensitive to only certain populations of ions [11]. This discussion is out of the scope of the current study and does not affect the main conclusion – decoupling of ionic conductivity from segmental dynamics. It is worth noting that the Trukhan model (eq.5) gives only qualitative

description, because it does not take into account the influence of electrode material on the EP phenomenon [27]. To compensate for that, we have normalized both D and p by certain constants, such that p approaches its stoichiometric value in the high temperature limit, i.e. p_0 is twice of the salt concentration. The temperature dependence of the diffusivity D and of the ion concentration p for all the five polymer electrolytes are summarized in Figure 2 (b), where D and p are presented as a function of T_g/T . The diffusion coefficients of different electrolytes have similar values at temperatures far above T_g . However, they differ by as much as 4 orders of magnitude near T_g . This is another manifestation of the decoupling between ionic transport and polymer segmental dynamics.

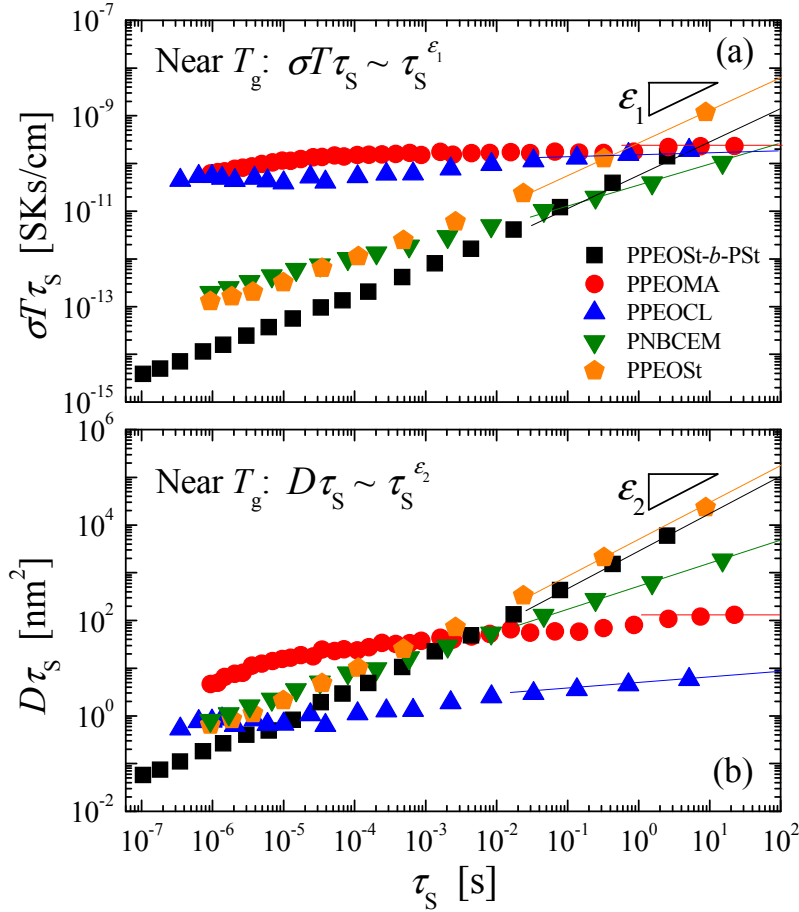


FIG. 3 (color online). (a) $\sigma T \tau_S$ and (b) $D \tau_S$ versus τ_S for the polymer electrolytes in this study. The dependence of $\sigma T \tau_S$ and $D \tau_S$ on τ_S near T_g can be fit by a power law (solid lines): $\sigma T \tau_S \sim \tau_S^\epsilon$ and $D \tau_S \sim \tau_S^\epsilon$. The exponent ϵ , which is the slope of each curve near T_g , reflects the degree of decoupling.

To examine the validity of the Stokes-Einstein relationship, $D \tau_S$ is plotted as a function of τ_S in Figure 3(b). Similar to the behavior of ionic conductivity, $D \tau_S$ of flexible PPEOMA and

PPEOCL remains roughly a constant, when τ_S varies from 10^{-7} to 10^2 s, indicating a close relationship between the ion diffusion and the polymer segmental motion. On the other hand, the Stokes-Einstein relationship clearly breaks down in rigid PPEOSt-*b*-PSt, PNBCEM, and PPEOSt. The decoupling behavior near the glass transition temperature can be approximated by a power law: $\sigma T\tau_S \sim \tau_S^\varepsilon$ and $D\tau_S \sim \tau_S^\varepsilon$, which reduces to the classical Stokes-Einstein relationship in the case of $\varepsilon = 0$. As has been suggested earlier [17], the exponent ε can be used to quantify the degree of decoupling. It can be seen from Figure 3 that, among these samples, PPEOMA behaves like the classical PEO system, showing a decoupling exponent $\varepsilon \approx 0$. All the other samples exhibit different degree of decoupling between the ionic transport and the segmental dynamics. The strongest decoupling is observed in PPEOSt-*b*-PSt and PPEOSt, where ε for $D\tau_S$ can be as large as 0.78.

Having confirmed our initial conjecture that ionic transport in polymer electrolytes can be decoupled from segmental relaxation, we now would like to examine the correlation between the degree of decoupling and the properties of the polymer. While earlier report [5] suggests the degree of decoupling correlates with T_g of the polymer, our recent study [8] suggests that the fragility index m [28, 29], defined as:

$$m = \left. \frac{d \log \tau_S}{d(T_g / T)} \right|_{T=T_g}, \quad (7)$$

might be the key factor. In Figure 4, the decoupling exponents (ε_1 and ε_2) for both $\sigma T\tau_S$ and $D\tau_S$ are compared with the fragility index m and the glass transition temperature T_g of the polymer electrolytes studied here. Indeed, the degree of decoupling between ionic transport and segmental relaxation shows a strong correlation with the fragility index, a trend that closely resembles other decoupling phenomena in a wide variety of polymeric and non-polymeric glass-forming liquids [8, 30]. The decoupling exponent ε increases with increasing fragility index m , with a coefficient of determination $R^2 \sim 0.8$. In contrast, the R^2 for ε and T_g is only around 0.3. In particular, PPEOSt and PPEOMA have similar T_g (265K for PPEOSt and 240K for PPEOMA), but show a huge difference in decoupling (PPEOSt, $\varepsilon_2 = 0.76$; PPEOMA, $\varepsilon_2 = 0.05$). On the other hand, PPEOSt and PPEOSt-*b*-PSt exhibit the same degree of decoupling ($\varepsilon_2 = 0.76$), but their glass transition temperatures differ by 73K. This result suggests that fragility, rather than the glass transition temperature, is the key factor that governs the decoupling between ionic transport and segmental relaxation in polymer electrolytes. It is known [31, 32] that in many polymers T_g and

fragility correlates, and this apparently leads to the observed weak correlation of the decoupling exponent ε and T_g (Fig.4b).

How can we explain the observed correlation of the decoupling and fragility? Recent theoretical and experimental studies [30, 33-35] have revealed that polymer fragility depends on relative rigidity of chain structure. Chains with rigid backbones suffer an appreciable amount of packing frustration, which results in a loose local structure and strong non-Arrhenius temperature dependence of segmental dynamics. Ions may utilize the loose packing structure of fragile (rigid) polymers and diffuse through the polymer matrix even when segmental dynamics is slow or frozen. On the other hand, the ionic transport in PEO (one of the least fragile polymers [31]) is strongly coupled to the segmental relaxation, due to its well packed structure of flexible and symmetric chains. This scenario provides a simple explanation to the observed strong correlation between the decoupling of ionic transport and the fragility of the polymer electrolytes. No strong correlation of the decoupling to the glass transition temperature suggests that we might find a polymer with significant frustration in packing (high fragility) and not very high T_g . As a result, the desired conductivity level ($\sim 10^{-3}$ S/cm) can be achieved in the polymer at room temperature.

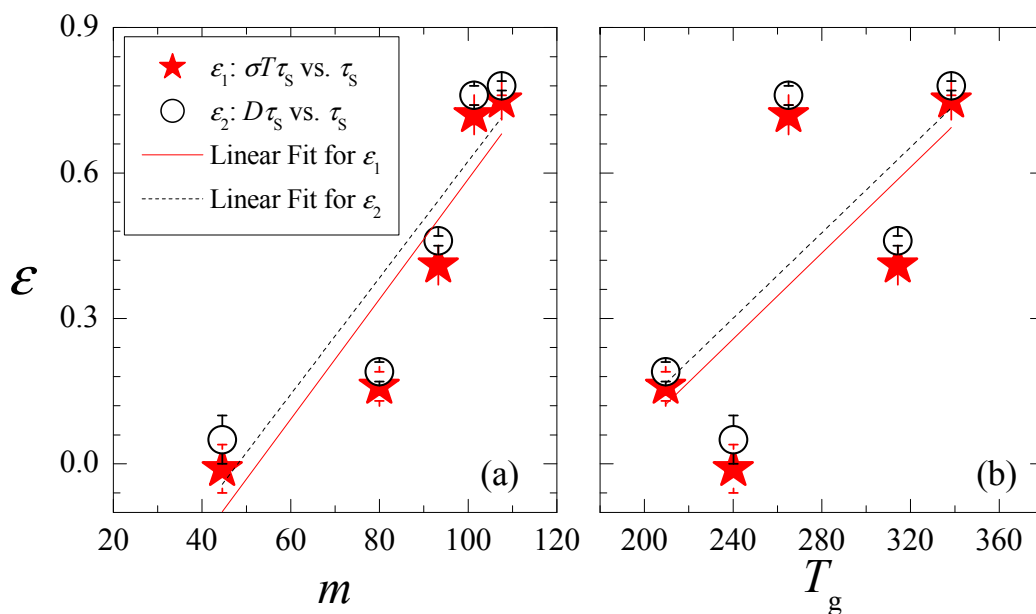


FIG. 4 (color online). Correlation between the decoupling exponent ε and (a) the fragility index m , and (b) the glass transition temperature T_g . The fragility index is estimated from the VFT fittings parameters: $m = (\ln 100 - \ln \tau_0)[T_\tau(\ln 100 - \ln \tau_0) + B_\tau]/(2.303B_\tau)$. Solid lines: linear fits for ε_1 ($\sigma T \tau_S$ vs. τ_S) vs m (a), and vs T_g (b). The coefficient of determinations R^2 for m and T_g are 0.80 and 0.31, respectively. Dashed lines: linear fits for ε_2 ($D \tau_S$ vs. τ_S) vs m (a), and vs T_g (b). The corresponding R^2 for m and T_g are 0.78 and 0.33, respectively.

In conclusion, we have measured the ionic conductivity, ion diffusivity, and segmental relaxation time for polymer electrolytes with different chain rigidity. We have demonstrated that contrary to the widespread belief that segmental motion controls ionic transport in polymers, ion diffusion and conductivity can be strongly decoupled from segmental relaxation. The reported decoupling phenomenon calls for a revision of the current picture of ion transport in polymer electrolytes. We found that the degree of decoupling increases with increasing fragility index of the polymer. This trend can be understood in terms of the recent theoretical ideas that relate the fragility of polymers to frustration in their packing. The observed correlation between decoupling and fragility may provide an alternative approach to design of highly conductive materials: by incorporating relatively rigid chain structures, it is possible to develop a new class of solid polymer electrolytes with strongly decoupled ionic conductivity.

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