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Decoupling Ionic Conductivity from Structural Relaxation: A Way to Solid Polymer Electrolytes?

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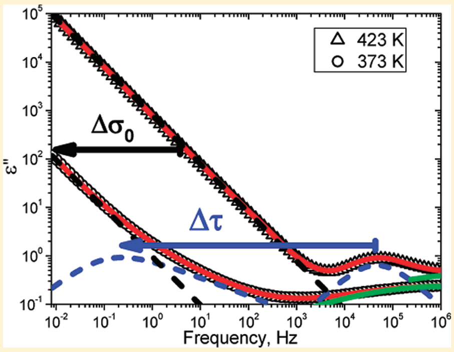
ABSTRACT: Using broadband dielectric spectroscopy, we studied the temperature dependence of ionic conductivity and structural relaxation in a number of polymers. We demonstrate that temperature dependence of ionic conductivity can be decoupled from structural relaxation in a material specific way. We show that the strength of the decoupling correlates with the steepness of the temperature dependence of structural relaxation in the polymer, i.e., with its fragility. We ascribe the observed result to stronger frustration in chain packing characteristic for more fragile polymers. We speculate that employment of more fragile polymers might lead to design of polymers with higher ionic conductivity.



I. INTRODUCTION

Use of solid polymer electrolyte (SPE) will improve performance of batteries by providing mechanical flexibility and stability, reducing weight, enhancing environmental and operational safety and many other advantages. Although this idea is known for several decades, its realization remains hindered by the low ionic conductivity of current SPEs at ambient temperature. Ionic conductivity σ is defined by diffusion of free ions D multiplied by their concentration N_{free}:[1−3]

$$\sigma = N_{\text{free}} q^2 D / T \tag{1}$$

(here q is the ion charge and T is temperature). The concentration of free ions is defined by salts solubility and energy of anion−cation dissociation in the electrolyte material. There are many polymers with rather high solubility of Li ions. For example poly(ethylene oxide) (PEO) can dissolve one Li-salt per less than ten monomers.[4,5] However, the main obstacle in achieving high conductivity in these polymers is low diffusivity of ions. According to the Stokes−Einstein relationship, the diffusnion coefficient is defined by the friction imposed on the ionic motion, i.e. by the characteristic relaxation time τ of the structural relaxation[6,7] (segmental relaxation in the case of polymers): $D \propto \tau^{-1}$. This leads to the well-known relationship between the ionic conductivity and structural relaxation time of the material:

$$\sigma \propto \frac{1}{\tau T} \tag{2}$$

Indeed this behavior (eq 2) is observed in PEO and many other similar polymers[2] and slowing down of structural relaxation time upon cooling close to the glass transition leads to significant decrease of ionic conductivity in these materials.

It is known, however, that in many glass-forming systems diffusion can be decoupled from structural relaxation. According to recent studies[8] this decoupling depends on the so-called fragility of the glass-forming systems, i.e. on steepness of their temperature dependence of τ at the glass transition temperature T_g. The fragility index m is traditionally defined as:[9]

$$m \propto \left. \frac{\mathrm{d}[\log \tau]}{\mathrm{d}\frac{T_g}{T}} \right|_{T = T_g} \tag{3}$$

It characterizes the deviation of the temperature dependence of τ from a simple Arrhenius behavior. It has been demonstrated in ref 8 that decoupling of diffusion-controlled motions in glass-forming systems and polymers from structural relaxation is stronger in more fragile systems and is not detectable in nonfragile ("strong") systems. Because the ionic conductivity is controlled by the ions diffusion, it is possible that σ can be also decoupled from structural relaxation, especially in strongly fragile polymers.

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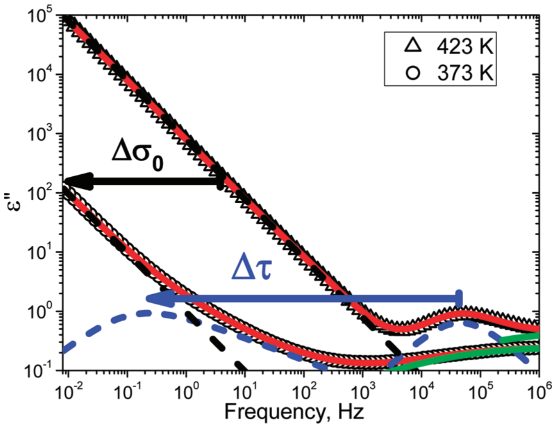

Figure 1. Example of dielectric relaxation spectra of poly(2-vinyl pyridine) at two temperatures (symbols). Segmental relaxation (loss peak) and conductivity shift differently with temperature. The lines present the following: (red line) total fit to the data; (blue dashes) structural (segmental) relaxation process; (green line) secondary relaxation; (black dashes) conductivity σ_o contribution.

This paper presents detailed studies of temperature dependences of ionic conductivity and segmental dynamics in a number of polymers. We demonstrate that the ionic conductivity indeed decouples from segmental relaxation in most of the polymers and the degree of decoupling is higher in more fragile polymers. Based on these results, we suggest that use of fragile polymers, i.e., polymers with relatively rigid structure, might be a better way to design advanced SPE. This direction is opposite to the dominating current approach in search for polymers with flexible structures, such as PEO and its derivatives.

II. EXPERIMENTAL SECTION

Poly(4-bromostyrene) (P4BrSt) with M_n = 32 000 g/mol (PDI = 1.7), poly(4-chlorostyrene) (P4ClSt) with M_n = 44 500 g/mol (PDI = 1.6), poly(2-vinylpyridine) (P2VP) with M_n = 50 000 g/mol (PDI = 1.04), and poly(4-vinylpyridine) (P4VP) M_n = 49 100 g/mol (PDI = 1.25) have been purchased from the Polymer Source, Inc. and were used as is. Poly(2-chlorostyrene) (P2ClSt), M_n = 49 500 g/mol (PDI = 1.7), and poly(3-chlorostyrene) (P3ClSt), M_n = 34 000 g/mol (PDI = 1.6), have been purchased from Scientific Polymer Products, Inc. and were used as is.

Dielectric measurements were performed with Novocontrol Concept 80 system which includes Alpha-A impedance analyzer, ZGS active sample cell interface, Quatro Cryosystem temperature control unit. Samples were placed between two gold plated electrodes separated by Teflon ring spacer. Measurements were performed in the frequency range 10^{-3}–10^{7} Hz. Dielectric spectra were fit by a sum of conductivity contribution and two (segmental and secondary relaxations) processes. Contribution of each relaxation process was fit to a Havriliak–Negami distribution function. The characteristic τ was estimated as the inverse of the frequency of the segmental loss maximum ν_{max}: $\tau = (2\pi\nu_{max})^{-1}$, while dc conductivity σ_o was estimated from the low-frequency tail of $\varepsilon''(\nu)$ as $\sigma_0/(2\pi\nu\varepsilon_0)$. Glass transition temperature T_g was defined as the temperature at which segmental τ = 100 s. The Vogel–Fulcher–Tamman (VFT) equation $\tau = \tau_o \exp[B/(T - T_0)]$ was used to fit the temperature dependence of τ and estimate the fragility.

Dielectric spectroscopy provides simultaneous measurements of dc conductivity and segmental relaxation at different temperatures (example is shown in Figure 1). The spectra in Figure 1 clearly show that conductivity shifts with temperature much slower than the segmental relaxation, in contradiction with traditional expectations (eq 2). Analysis of the data reveals significant difference in the temperature dependence of $(\sigma_o T)^{-1}$ and τ in all studied here polymers (Figure 2): conductivity varies with temperature much weaker than the structural relaxation. Moreover, it appears that change in the chemical structure of polymers affects significantly the temperature dependence of structural relaxation while has weak effect on temperature behavior of conductivity.

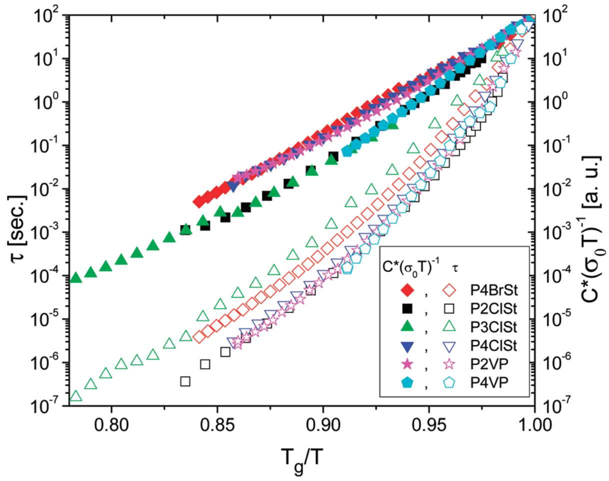

Figure 2. Inverse ionic conductivity $(\sigma_0 T)^{-1}$ (filled symbols), and segmental relaxation time τ (empty symbols) vs T_g/T for the polymers studied here: P4BrSt, T_g = 351 K; P2ClSt, T_g = 378 K; P3ClSt, T_g = 352 K; P4ClSt, T_g = 380 K; P2VP, T_g = 364 K; P4VP, T_g = 397 K.

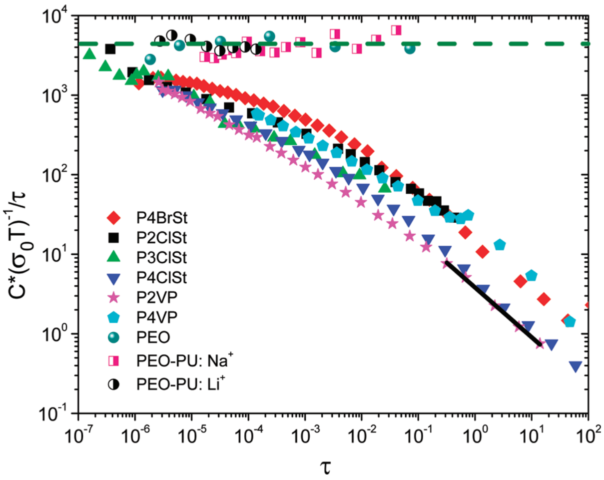

Figure 3. Ratio $(\sigma_0 T)^{-1}/\tau$ versus segmental relaxation time τ for the polymers studied here. We also add literature data: Data for PEO with EO:Li$^+$ ratio of 30 were taken from ref 5. Data for PEO-based polyurethane ionomers (PEO-PU) with either sodium (Na$^+$) or lithium (Li$^+$) ions are taken from ref 10. The rest of the symbols used here are the same as in the Figure 2. The dashed line presents the expected behavior when conductivity and structural relaxation are coupled (eq 2). The solid line presents the power law dependence according to the eq 4.

III. DISCUSSION

Decoupling phenomena in dynamics are best illustrated as a ratio of two parameters that are expected to have the same temperature dependence. In our case, we analyze the ratio of inverse conductivity and τ, i.e. $(\sigma_o T)^{-1}/\tau$ (Figure 3). According to classical models (eq 2) this parameter should be a constant

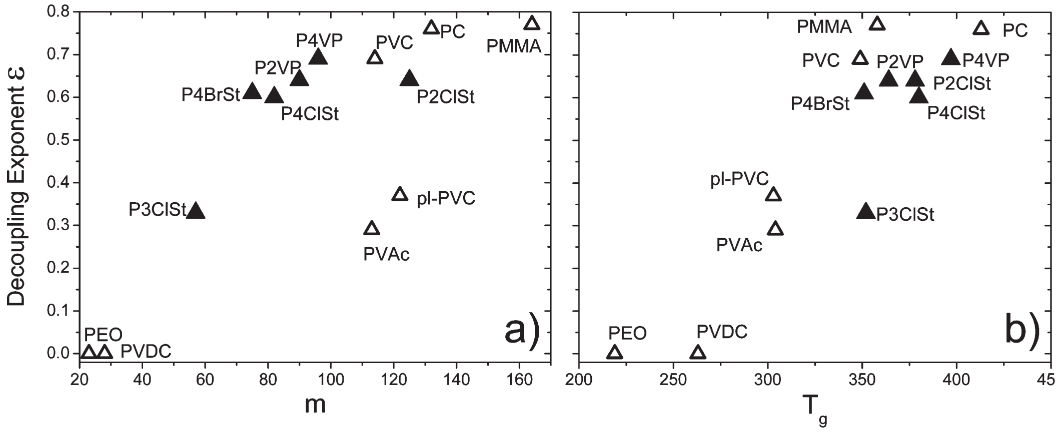

Figure 4. Correlation between the decoupling exponent ε and (a) fragility index *m*, and (b) glass transition temperature T_g. For the polymers studied here (▲) the decoupling exponent was estimated using the last 2 decades of data closest to the polymers' T_g. Decoupling exponent for the literature data (Δ) is taken directly from the source. Data on PEO are from [ref [5]] and data for poly(vinylidene chloride) (PVDC), poly(vinyl acetate) (PVAc), poly(vinyl chloride) (PVC), plasticized poly(vinyl chloride) (pl-PVC), polycarbonate (PC), and poly(methyl methacrylate) (PMMA) are from ref 15.

number that is independent of temperature and structural relaxation time. This is clearly observed for PEO[5] and PEO-based polyurethane ionomers.[10] However, the rest of the polymers show strong deviation from the expected behavior, i.e., exhibit strong decoupling of ionic conductivity from the structural relaxation (Figure 3). This decoupling becomes stronger as the material approaches its glass transition temperature T_g.

We want to emphasize that the eq 2 does not take into account possible temperature variations of the concentration of free ions N_{free}. The latter depends on energy of anion–cation dissociation and decreases with decrease in temperature.[11] So, it can only increase the temperature dependence of conductivity. Because we are analyzing the opposite behavior—weaker temperature dependence of σ_0 relative to segmental dynamics—we will neglect a possible temperature dependence of N_{free} in the following discussion.

Usually, the decoupling behavior can be approximated by a power law[12] (the so-called fractional Stokes–Einstein relationship). The degree of decoupling[8] can be quantified by the decoupling exponent ε estimated from the power-law behavior close to T_g (Figure 3):

$$(\sigma_o T)^{-1}/\tau \propto \tau^{-\varepsilon} \qquad (4)$$

The exponent ε is zero when there is no decoupling (e.g., example of PEO in the Figure 3) and increases with increasing the difference in temperature dependence of ionic conductivity and structural relaxation.

Earlier studies of molecular and polymeric liquids suggested that the decoupling between different dynamic processes correlates with fragility of the material.[8,13,14] Analysis of our data also reveals a correlation between the degree of decoupling (the decoupling exponent ε) and fragility m (Figure 4a): Polymers with higher fragility exhibit stronger decoupling of the ionic conductivity from segmental relaxation. Thus, the observed decoupling of the ionic conductivity from segmental dynamics in polymers is consistent with other decoupling phenomena in dynamics of soft materials. Decoupling of ionic conductivity from segmental dynamics in polymers has been reported previously.[15] The authors of ref 15 related the degree of decoupling to the glass transition temperature of the polymers. Our analysis (Figure 4b) also reveals the correlation of the decoupling strength to T_g (Figure 4b). Due to known correlation between T_g and fragility in polymers[16,17] it is difficult to disentangle influence of these two variables on the degree of decoupling. However, analysis of the diffusion–structural relaxation decoupling in nonpolymeric systems provides clear evidence that fragility is the major parameter influencing the decoupling phenomena:[8,13,18] silica glass has $T_g \sim 1500$ K and fragility m~20, but shows no decoupling; tris-naphthylbenzene (TNB) has $T_g \sim 337$ K and $m \sim 66$ and exhibits the decoupling with $\varepsilon \sim 0.13$, while *o*-terphenyl (OTP) has the lowest $T_g \sim 246$ K and highest fragility $m \sim 81$ among these materials and also exhibits the highest decoupling exponent $\varepsilon \sim 0.23$. Thus, decoupling of diffusion from structural relaxation in nonpolymeric systems obviously does not correlate with T_g, but correlates with fragility. Assuming that similar underlying mechanism is responsible for the decoupling between ionic diffusion and segmental dynamics, we suggest that fragility is the main parameter influencing the strength of the decoupling. Trend observed between exponent ε and T_g (Figure 4b) is thus a consequence of trivial correlation between glass transition temperature and fragility in polymers.[16,17]

The mechanism of decoupling of diffusion from structural relaxation even in simple molecular systems remains a subject of active discussions,[8,13,14,18–21] although most models relate it to dynamic heterogeneities. However, the relationship between dynamic heterogeneity and fragility is not clear.[22,23] Moreover, most of the models analyze decoupling of self-diffusion (i.e., diffusion of the same structural units that forms the liquid) from the structural relaxation. These models might be not applicable in our case because we study diffusion of guest entities – ions. The decoupling of ionic motions in that case might depend strongly on the size of ions. This might explain why the observed decoupling of ionic diffusion in polymers (Figure 4a) is even stronger than the predicted by the model[8] decoupling of diffusion from structural relaxation. Thus, for explanation of our observations (Figure 4a), we turn to the recent theoretical and experimental studies,[24–28] which provide convincing evidence that polymer fragility depends on relative rigidity of chain structure. This includes rigidity of the backbone and of the side groups.[26,28] According to these ideas, flexible chains can pack well, form rather dense structure and show almost Arrhenius temperature dependence of the segmental dynamics (i.e., are least fragile). In contrast, rigid chains have frustrated packing, form rather loose structure and exhibit strongly non-Arrhenius temperature variations of segmental dynamics, i.e., are very fragile.

Based on this picture, we speculate that in polymers with higher fragility ions can move easily through the loose structure even when segmental relaxation is very slow, while in dense structure of less fragile polymers ions can only move when segments are moving. For example, PEO is the least fragile polymer,[16] has extreme chain flexibility (low energy barriers for intrachain rotations, conformational changes) and should have extremely well-packed structure. As a result, ions can diffuse through the PEO structure only when segments are moving. This scenario provides simple qualitative explanation for the observed correlations of the decoupling of ionic conductivity with fragility of polymers (Figure 4a).

If it is correct, it suggests interesting approach for the choice of polymers for solid electrolytes. Based on the classical picture (eq 2), traditional approach for decades was a search for flexible polymers with relatively fast segmental dynamics (e.g., low T_g) in the temperature range of interest. A good example that glass transition temperature is not the single most important parameter for ion conduction comes from the field of superionic glasses that have rather high T_g, but at the same time exhibit high conductivity. At room temperature these superionic glasses are already well below their glass transition temperature, but still show remarkable conductivity[29] on the order of 10^{-2} S/cm. Such unique properties of superionic glasses are thought to come from excess free volume present in their structure.[30] It is not possible to achieve significant decoupling of ionic diffusion (conductivity) from segmental dynamics in flexible polymers, such as PEO and its derivatives. So, approaching T_g of these polymers will always lead to significant slowing down of ionic diffusion and, as a consequence, sharp decrease in conductivity. This scenario also emphasizes that PEO might be a bad choice for SPE: despite extremely high solubility of Li salts, ionic motion will be always coupled to segmental dynamics in amorphous phase of this polymer. As a result, one should not expect high ionic conductivity in PEO even if crystallization will be completely suppressed. In contrast, polymers with more rigid chains, such as, e.g., PMMA and PC, form less dense structure where ions might diffuse when segmental dynamics is very slow or even completely frozen. Thus, the results presented here suggest an alternative approach: one might look for relatively rigid polymeric structures with significant frustration in packing where ionic diffusion might be strongly decoupled from segmental dynamics. Strong enough decoupling might provide sufficient ionic conductivity, of course, if the polymer also has high solubility of the ions.

IV. CONCLUSIONS

The presented analysis demonstrates that ionic conductivity in polymers can be decoupled from structural (segmental) relaxation and the degree of decoupling increases strongly with increase in fragility (the steepness of the temperature dependence of structural relaxation). We speculate that the observed decoupling might be related to the frustration in packing of rigid polymeric chains that increases in more fragile systems. In this sense, ionic diffusion in materials with flexible chains (e.g., PEO and its derivatives) will be strongly coupled to structural relaxation. As the result, ionic conductivity in such materials will essentially disappear when segmental motions freeze upon approaching T_g. In contrast, the loose structure of the rigid chains leads to significant ionic diffusion even when segmental relaxation is very slow. We suggest that employing this alternative approach it might be possible to develop *solid* polymer electrolytes with sufficient ionic conductivity around room temperature.

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