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Salt-Concentration Dependence of the Glass Transition Temperature in PEO–NaI and PEO–LiTFSI Polymer Electrolytes

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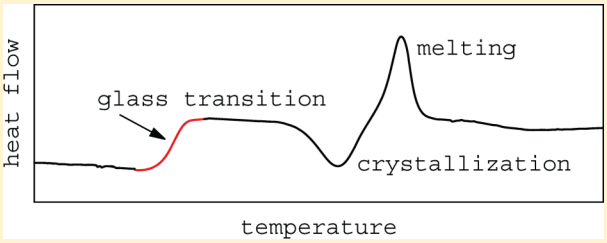
Supporting Information

ABSTRACT: We measured glass transition temperatures T_g as a function of the salt concentration in polymer electrolyte systems consisting of poly(ethylene oxide) (PEO) complexed either with sodium iodide (NaI) or lithium bis(trifluorosulfonylimide) (LiTFSI). At homologous compositions, T_g of PEO–NaI is found to be generally larger than that of LiTFSI. The present T_g values are markedly higher than previously reported reference data. Also the observed nonlinear concentration dependence differs from earlier studies. These findings are tentatively attributed to the more stringent preparation and measuring conditions maintained in the present work, thereby keeping organic solvent residues and water contamination at low levels. Also the high molecular weight of the polymer may have some influence. The measurements were performed by differential scanning calorimetry after quenching from the melt. We find that *ex situ* immersion quenching in liquid nitrogen leads to lower degrees of crystallinity than *in situ* quenching in the calorimeter environment. In addition, the strong decrease of the crystallinity with increasing salt content gives rise to pronounced steps in the heat capacity near T_g for the more concentrated electrolytes.



INTRODUCTION

Since their discovery in 1973,[1] solid-like polymer electrolytes (SPEs) have been extensively investigated. These complexes, consisting of a polar polymer matrix and a metal salt with sufficiently low lattice energy, exhibit a combination of properties which make them interesting for application in batteries and other electrochemical devices.[2] Most published studies deal with the easy-to-prepare polyether/alkali-metal complexes, which provide the technologically necessary mechanical flexibility as well as a fairly high ionic conductivity in the amorphous phase.[3,4]

In the case of polymer electrolytes, both the ionic mobility and the (microscopic) viscosity depend on the flexibility of the polymer chain segments, which is characterized by the glass transition temperature T_g. This renders it difficult to tailor/optimize the mechanical and ion-conduction properties separately. Rather it has been generally observed that an increase of the salt concentration to enhance the number of the charge carriers is counteracted by a decrease of the ionic mobility, which is due to the stiffening of the electrolyte material and accompanied by a significant increase of T_g.[5] However, despite the fact that the glass transition temperature may be viewed as a crucial parameter for polymer electrolytes, the number of systematic studies relating T_g to salt concentration (see, e.g., refs 6–10) is astonishingly small.

Previously published work at our laboratory dealt with ionic transport in PEO–NaI polymer electrolytes made up of poly(ethylene oxide) (PEO) complexed with sodium iodide.[11−14] For a series of compositions PEO_yNaI, specified by the EO/Na ratio y running from 10 to 1000, we measured the diffusivity of cations and anions with the radiotracers ^{22}Na and ^{125}I, respectively, over a wide temperature range (70–200 °C) in the (highly viscous) melt. Combining these data with the dc ionic conductivity σ_{dc} deduced from impedance spectroscopy, a virtually complete picture of mass and charge transport was obtained. To allow for a simultaneous evaluation of the three sets of experimental data for each composition, σ_{dc} was converted into the charge diffusivity D_σ with the aid of the Nernst–Einstein equation. On reasonable grounds, the employed transport model was assumed to rely on the occurrence of charged single ions (Na^+,I^-) which may associate to form neutral pairs (NaI^0). Specifically, the formal description was based on an expression for the pair fraction r_p, resulting from the mass action law, and on the "true" diffusivity of the individual mobile species given by

$$D_x = D_x^0 \exp[-B_x/(T - T_0)] \quad (1)$$

where the index "x" stands for Na^+, I^-, or p = NaI^0. This Vogel–Tammann–Fulcher- (VTF-) like equation depends on the particle-specific parameters B_x and D_x^0, subject to model-specific constraints,[11,15] as well as on the common parameter T_0 denoting the "zero mobility temperature" or "ideal" glass transition temperature.[16]

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In principle, T_0 can be assessed by fitting of the experimental data, as was done in earlier work at our laboratory.[11,12] However, the accurate determination of T_0 is not only affected by experimental error but also suffers from intercorrelations with the fitting of the VTF parameters B_x in a least-squares minimization procedure. The latter drawback is usually pronounced in ionic transport studies on polymer electrolytes because of the narrow T-ranges involved and the weak curvatures of the pertaining data when plotted in an Arrhenius diagram. Therefore, it would be beneficial to have an independent estimate of the T_0 value.

Both T_0 and T_g are indicative of the chain-segment flexibility of the amorphous polymeric substance under consideration. More specifically, in early studies of the shear viscosity and ion conductivity it was found that $T_0 \approx T_g - 50$ K may hold as an empirical rule for a broad spectrum of soft disordered materials.[17−19] In our recent work, we are dealing with different compositions within one and the same salt-in-polymer system, e.g., PEO_yNaI with varying y.[14] In this case, it seems even more justified to assume that T_0 and T_g are closely correlated, e.g., by the expression $T_0(y) \approx T_g(y) - \Delta_0$, where Δ_0 designates a constant T-shift independent of y. Thus, measuring $T_g(y)$ using thermal analysis would enable us to estimate T_0 (y) to a good approximation. This can be done either by taking a fixed value for Δ_0 (e.g., 50 K) or by adjusting Δ_0 in a overall fitting procedure that includes the transport data of all compositions.[14]

The present article reports the results of caloric T_g measurements on the systems PEO−NaI and PEO−LiTFSI (lithium bis(trifluorosulfonylimide)) upon quenching from the melt. PEO−NaI is a salt-in-polymer complex with model character and closely connected with the discovery of polymer electrolytes as a individual class of materials.[1] As indicated above, PEO_yNaI complexes reveal a pronounced ion-pairing tendency, which strongly depends on salt concentration in the dilute range ($y \geq 30$).[14] The PEO−LiTFSI system has attracted much attention because of some useful properties with regard to applications in lithium batteries. Specifically, $PEO_yLiTFSI$ complexes show little or no pair formation and a higher conductivity than PEO_yNaI complexes with the same composition parameter y, which relates to the bulky nature of the TFSI anion.[13] In general, polymer electrolytes of low salt concentration are of fundamental scientific interest, as complications due to phase separation and high ion densities are avoided.

The T_g data obtained in this work cover a wide range of salt concentrations C_s which run from nominally zero to about 2.4 mol/L. The reliability of the data is sustained by comparative tests at different quenching rates and temperatures. We find a surprisingly strong increase of T_g with increasing C_s, which is much steeper than for published data on the same system.[6,20] The observed C_s -dependence is also stronger than reported for similar PEO-based systems with other alkali-metal salts. At higher salt concentrations T_g was found to be fairly constant. The results will be discussed with regard to phase separation, degree of crystallization, and contamination effects.

EXPERIMENTAL SECTION

Materials and Preparation. Appropriate amounts of PEO with a molecular weight of 8×10^6 g/mol (Aldrich[21]) and either NaI (>99 wt %, Grüssing) or $LiN(CF_3SO_2)_2$ (LiTFSI, 99.95%, Sigma-Aldrich) were dried under continuous vacuum pumping at elevated temperature and subsequently homogeneously dissolved in extra dry acetonitrile (Acros Organics, >99.95%, water content <0.01%, evaporation residue <0.001%). After evaporation of the solvent under high vacuum (HV, 10^{-5} hPa) at 100 °C using cryogenic traps, the already very dry and tough SPE material was cut in tiny pieces and again subjected to a HV treatment at 50 °C for 24 h. In this way, solvent-free complexes of different composition were obtained: PEO_yNaI with y = 10, 20, 30, 60, 120, 250, 500, or 1000 and $PEO_yLiTFSI$ with y = 20, 60, 250, or 1000. Great care was taken to avoid contact with ambient atmosphere. In analysis by pulsed-field-gradient nuclear magnetic resonance (PFG-NMR, not shown here), no ^1H resonance attributable to water or acetonitrile could be detected. Considering that all preparation steps were either carried out in a nitrogen-filled glovebox (H_2O < 1 ppm) or under continuous pumping in the HV range, the water contamination of the SPEs is assumed to be at the 10 ppm level or below.

Electrolyte Characterization. The prepared materials were generally characterized by Archimedes-type mass density measurements and differential scanning calorimetry (DSC) using PerkinElmer DSC-7 equipment. The mass density enters the calculation of the salt concentration per unit volume. In DSC analysis over the temperature range from room temperature to 200 °C, the only feature in second and multiple heating/cooling cycles was the endothermic peak near 67 °C due to the melting of PEO. We found no indications of precipitation, in agreement with literature data on PEO−NaI (see, e.g., Fauteux at al.[22]) and PEO−LiTFSI[23] but in contrast to observations for PEO−MI complexes with larger alkali metal cations (M = K, Rb, and Cs).[24] The reliable quality of all sample materials was confirmed by their systematic and reproducible behavior as a function of temperature and composition in conductivity measurements with electric impedance spectroscopy[13] and in diffusion experiments using radiotracers (PEO−NaI[14]) or PFG-NMR analysis (PEO−LiTFSI[25]).

Measurements of the Glass Transition Temperature. To determine T_g of amorphous PEO_yNaI and $PEO_yLiTFSI$ complexes, melt-quenched specimens were thermally analyzed by using a PerkinElmer Diamond DSC calorimeter with liquid nitrogen (LN_2) cooling. For *ex situ* quenching, approximately 10 mg of substance was encapsulated in a standard-type aluminum DSC pan under N_2 glovebox atmosphere and subsequently enclosed in a custom-built aluminum quenching capsule of low (thermal) mass. In the course of the experiments, the prototype capsule was replaced by an improved version of smaller size and mass. Following an annealing treatment in an oil-bath thermostat for 30 to 45 min at a preset quenching temperature (T_q) in the range 100−215 °C, the capsule was immersed in LN_2 under continuous agitation and finally left there at 77 K. Mean quenching rates were estimated to be in the range 1500−3000 K/min, depending on the mass of the employed capsule. Within 60 min after this *ex situ* quenching procedure, the DSC pan with the sample was mounted in the Diamond DSC calorimeter that was precooled at −80 °C, and kept at this temperature for typically 20 min. During mounting of the pan in the open measurement chamber a small temperature increase of 10−15 °C could not be avoided. Thus, *ex situ* quenching in conjunction with further *in situ* cooling constitutes the *first cooling* cycle. Then the glass transition was monitored by the occurrence of an endothermic event during heating across the melt transition up to 150 °C at a rate of 10 °C/min (*first heating* cycle). After application of a baseline correction, T_g was determined from the half-height point of the heat capacity change in the thermogram ("half-c_p method").

To check the reproducibility of T_g, the DSC measurement was repeated with a *second cooling* cycle from 150 to −80 °C inside the calorimeter followed by a stabilization time of typically 20 min and a *second heating* cycle. The second cooling cycle, also denoted as "*in situ* quenching", immediately followed the first heating cycle, i.e., without holding time at 150 °C. It was performed at a nominal rate of −20 °C/min, which at lower temperatures was close to or even exceeded the maximum cooling rate physically/technically achievable under the given conditions. Generally, the differences between the consecutive *ex situ* and *in situ* T_g values were about 1 °C or less. In most cases, the whole measurement including the quenching procedure was repeated with multiple samples of the same composition. The corresponding variations in T_g were typically 2 °C or less. In the case of PEO−NaI,

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the influence of the *ex situ* quenching temperature was investigated, i.e., by changing T_q for specimens of equal composition.

RESULTS

Phase Behavior. Figure 1 displays the DSC thermograms of a $PEO_{10}NaI$ sample (dashed line) and a $PEO_{20}LiTFSI$

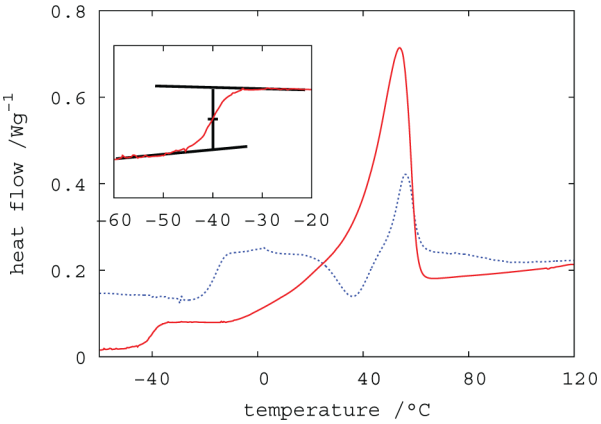

Figure 1. DSC thermograms of $PEO_{10}NaI$ (dashed line) and $PEO_{20}LiTFSI$ (solid line) electrolytes measured upon heating at 10 °C/min after *ex situ* quenching from 215 °C. T_g is determined by the half-c_p procedure, as schematically demonstrated by the inset.

sample (solid line) that were both monitored during the first heating after LN_2 immersion quenching from 215 °C. At this temperature the complexes are fully melted, in accordance with the corresponding locations in the respective phase diagrams. For $PEO_{10}NaI$ and the other compositions of this system, this is readily verified by the phase diagram in Figure 2 that was

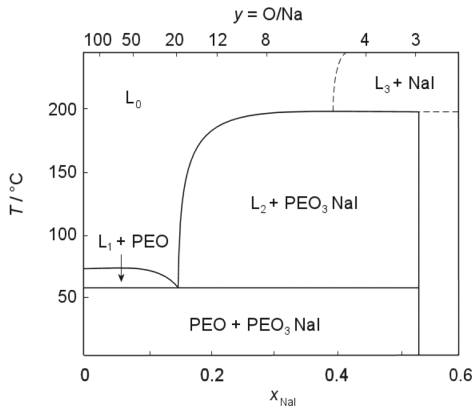

Figure 2. Phase diagram of the PEO−NaI system, as redrawn and adapted from the work of Fauteux et al.[3,22] The salt fraction x_{NaI} (lower *x*-axis) is based on weight ratios. The oxygen-to-sodium ratio O:Na (upper *x*-axis) equals the composition parameter *y*.

redrawn and adapted from the work of Fauteux et al.[3,22] Here, the single-phase melt region L_0 designates the equilibrium state of the electrolytes before quenching. A similar situation prevails for $PEO_{20}LiTFSI$ and the related, more dilute compositions, as may be checked with the PEO−LiTFSI phase diagrams found in the literature.[6,26]

In Figure 1, the $PEO_{20}LiTFSI$ thermogram (solid line) shows two endothermic events in the depicted *T*-range, i.e., a glass transition at −40 °C followed by a melt transition near 55 °C. Thus, there is no clear sign of incipient crystallization between these events. The distinct heat-flow step at the lower temperature allows for a reliable determination of T_g by the half-c_p procedure, as illustrated by the inset of Figure 1. From the area under the melt peak, the degree of crystallinity can be calculated (see below).

The dashed curve in Figure 1 is representative of $PEO_{10}NaI$. It exhibits a large step in the heat capacity (Δc_p) at −16 °C marking T_g. In this case, the maximum due to melting of the polymer at 55 °C is preceded by the exothermic crystallization event near 35 °C. Not only the large value of Δc_p but also the similar sizes of the crystallization and melting peak point to a low degree of crystallinity in the quenched state.

Crystallinity and Quenching Efficiency. The crystallinity χ_c of melt-quenched SPE samples is usually deduced from the DSC thermograms upon heating from the supercooled to the equilibrium melt phase. Specifically, χ_c was obtained by using the expression

$$\chi_c = \frac{\Delta H}{\Delta H_{PEO} f_{PEO}} \quad (2)$$

where ΔH in J/g denotes the difference between the melting endotherm and the crystallization endotherm (if observed). In addition, ΔH_{PEO} is the enthalpy of fusion of fully crystalline PEO (196.4 J/g[27]) and f_{PEO} is the PEO weight fraction of the sample.

Figure 3 shows the crystallinity as a function of the reduced salt concentration for both systems initially equilibrated at 215

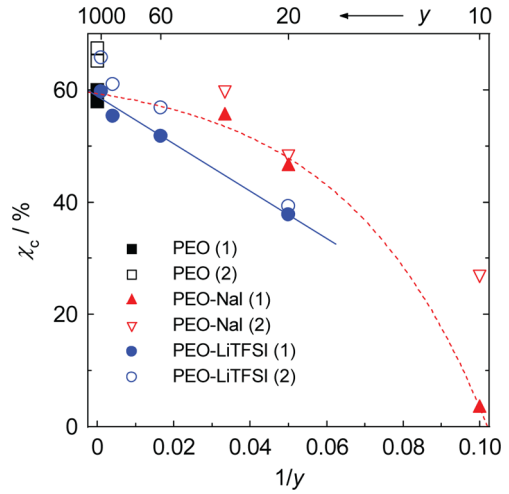

Figure 3. Crystallinity χ_c of PEO_yNaI and $PEO_yLiTFSI$ electrolytes as a function of the reduced salt concentration $1/y$. A distinction is made between data obtained during the first (closed symbols) and second (open symbols) heating cycle (i.e., after *ex situ* and *in situ* quenching, respectively). Solid and dashed line serve to guide the eye.

°C. In the case of $PEO_yLiTFSI$ we observe a virtual linear decrease of χ_c with $1/y$ from about 60% for pure PEO to about 40% for $1/y = 0.05$, as indicated by the straight line fitted to the data of the first cycle. For PEO_yNaI, χ_c of the first cycle falls from values near 60% for $1/y = 0$ down to about 3.5% for $1/y = 0.1$. Thus, the $PEO_{10}NaI$ complex was quenched to a predominantly glassy state with a frozen-in "amorphicity" of close to 100%. Apparently, the crystallization kinetics in salt-rich polymer electrolytes is much slower than in dilute ones. The dashed line fitted to the PEO_yNaI data is of exponential shape but only serves to guide the eye.

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The χ_c values obtained after LN_2 immersion quenching from 215 °C (1st heating) are generally lower than those resulting from DSC quenching from 150 °C (2nd heating). This is seen in Figure 3 by comparing the closed and open symbols for both electrolyte systems. For $1/y \leq 0.05$, the differences $\Delta\chi_c$ between the two quenching methods appear to *decrease* with *increasing* salt concentration and thus with *decreasing* crystallinity (see above), i.e., $\Delta\chi_c \approx 7\%$ for pure PEO and $\Delta\chi_c \approx 1.5\%$ for PEO_{20}LiTFSI. This demonstrates that the present *ex situ* quenching procedure is more effective than the *in situ* one. In addition, the findings for $\Delta\chi_c$ corroborate the preceding statement concerning the more rapid crystallization in salt-poor electrolytes. However, for PEO_{10}NaI there is a great disparity of 22% in χ_c between the two quenching methods. This relates to a substantial crystallization during the second cooling (directly following the first heating), as also found for all other electrolytes. It should be noted that PEO_{10}NaI is the only complex that exhibited a clear crystallization event during the first heating (cf. Figure 1).

Glass Transition Temperatures. Figure 4 shows the T_g data for PEO_yNaI obtained by quenching from different *ex situ*

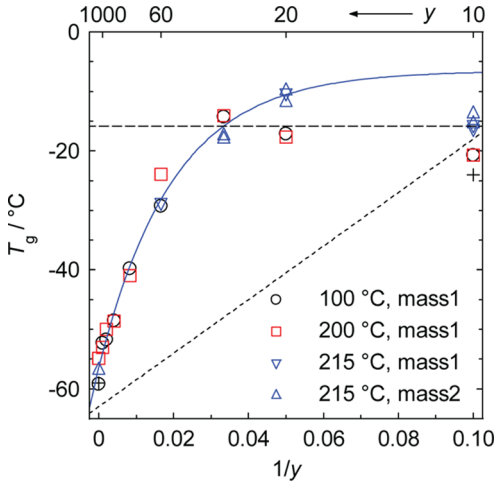

Figure 4. Glass transition temperature T_g of PEO_yNaI complexes as a function of the reduced salt concentration $1/y$ measured upon heating at 10 °C/min after quenching at different temperatures T_q, as indicated. The solid line represents the best fit by eq 3 to all data for $1/y \leq 0.033$ and those for $1/y = 0.05$ with $T_q = 215$ °C (triangles). The coarsely dashed line represents a constant value ($T_g = -15.8$ °C), as may be expected for quenching within the L_2 + PEO_3NaI phase region (cf. Figure 2). Previously published data are reproduced by the finely dashed line[20] and the crosses.[28,29]

equilibration temperatures T_q as a function of the reduced salt concentration $1/y$ (open and closed symbols). Every data point represents the mean value over multiple samples including in each case two heating cycles (*ex situ* and *in situ* quenching). The experimental error is typically given by ±2 °C.

Initially, a relatively low value of $T_q = 100$ °C within the melt phase region L_0 was chosen, in order to promote fast quenching (cf. Figure 2). It is seen that the data (open circles) exhibit a monotonic steep increase up to $1/y \approx 0.033$, beyond which T_g only varies within a limited range between about −15 and −20 °C. Qualitatively, this seems to comply with a crossover of the liquidus line in the phase diagram (L_2 in Figure 2), since it may be expected that T_g will be independent of y in the two-phase area between the eutectic and the line compound PEO_3NaI. However, a quantitative disparity becomes manifest because of the difference between the position of the kink in T_g ($y \approx 30$) and the location of the liquidus in the phase diagram ($y \approx 20$ at $T_q = 100$ °C).

To verify and supplement our initial results, we performed another series of experiments with a distinctly higher quenching temperature. Choosing $T_q = 200$ °C enables us to avoid the two-phase region L_2 + PEO_3NaI in Figure 2 also for the salt-rich compositions ($y \leq 20$), provided that the quenching procedure is rapid enough. The resulting T_g values are plotted in Figure 4 as open squares. For $y \geq 30$, circles and squares agree within experimental error, indicating that in this dilute composition range also quenching from a relatively high temperature (200 °C) proceeds sufficiently fast to avoid phase separation and the concomitant compositional changes in the two-phase regions L_1 + PEO and PEO + PEO_3NaI crossed and attained in the low-temperature regime, respectively. However, also these further T_g data for PEO_{20}NaI and PEO_{10}NaI (squares, $T_q = 200$ °C) agree with the initial ones (circles, T_q = 100 °C).

The reasons for this observation may be 2-fold. First, quenching may not be efficient enough to suppress the PEO_3NaI precipitation upon crossing the liquidus line L_2, i.e., entering the two-phase area (cf. Figure 2). Second, it seems conceivable that the liquidus line L_2 is rather inaccurate, so that a quenching temperature of 200 °C could still be within the "true" L_2 + PEO_3NaI region for the high salt concentrations of interest. The latter hypothesis was checked by further experiments, in which T_q was raised to 215 °C.

In Figure 4, the data representing $T_q = 215$ °C are plotted as open and closed triangles. These symbols discriminate between two versions of the quenching capsule, having either a higher (downward-triangle) or a lower (upward-triangle) mass. However, no significant dependence on the capsule mass (size) is observed. For dilute compositions ($1/y \leq 1/30$), the T_g data from $T_q = 215$ °C agree with those from the lower quenching temperatures within experimental error (cf. Figure 4). For PEO_{20}NaI, however, the new T_g values (close to −10 °C; triangles) are higher than the initial ones (ca. −17 °C; circle and square). Apparently, the T_g data obtained by quenching from 215 °C follow the course of T_g with $1/y$ for the lower salt concentrations, as indicated by the solid line in Figure 4. In fact, all these data are well described by the empirical expression (solid line)

$$T_g = T_{g0} + \Delta_T[1 - \exp(-a/y)] \quad (3)$$

where the parameters $T_{g0} = -56.5 \pm 0.7$ °C, $\Delta_T = 49.7 \pm 1.9$ °C, and $a = 51.7 \pm 5.1$ result from least-squares fitting. In this equation, T_{g0} denotes the glass transition temperature of pristine PEO ($1/y = 0$), while Δ_T and a characterize the amplitude and the relative change rate of $T_g - T_{g0}$ with salt concentration.

For PEO_{10}NaI, the T_g values upon quenching from 215 °C fall below those of PEO_{20}NaI and they are on the same level as the PEO_{30}NaI value (see closed triangles in Figure 4). This may indicate that even with the capsule of low mass quenching was not fast enough to suppress the PEO_3NaI precipitation upon crossing the two-phase region between about 200 and 60 °C. Nevertheless, choosing 215 °C for T_q instead of 200 or 100 °C obviously leads to higher glass transition temperatures for compositions with $1/y \geq 1/30$.

The T_g data of PEO_yLiTFSI are displayed in Figure 5. All data result from $T_q = 215$ °C as initial quenching temperature.

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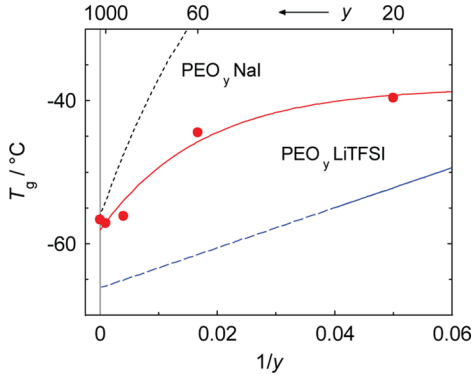

Figure 5. Glass transition temperature T_g of $PEO_yLiTFSI$ complexes as a function of the reduced salt concentration $1/y$ measured upon heating at 10 °C/min after quenching from T_q = 215 °C. The solid line represents the best fit by eq 3 to all data. Previously published data are reproduced by the low straight line,[6,30] of which the dashed part indicates an extrapolated range. The finely dashed line represents the T_g data of PEO_yNaI (cf. Figure 4).

As indicated before, subsequent *ex situ* and *in situ* experiments agree within experimental error. In fact, the plotted data represent averages of multiple samples with two heating cycles each. The data are fitted by eq 3 (solid line) yielding the following best parameter values: $T_{g0} = -58.1 \pm 1.4$ °C, $\Delta_T = 20.0 \pm 3.2$ °C, and $a = 57.8 \pm 26.9$.

DISCUSSION

Comparison with Literature Data. Previous T_g data for the PEO−NaI system have been reported by Minier et al.[20,31] Their data are described by the linear equation $T_g = T_{g0} + 450(1/y)$,[20] which includes the value of pure PEO, $T_{g0} = -63$ °C, for which the original paper refers to the literature.[32] Figure 4 shows that these early data, represented by the finely dashed line, differ considerably from the present ones, both quantitatively and qualitatively. We observe in our work not only markedly higher T_g values, with a maximum difference of about 32 °C near $1/y = 0.04$, but also a pronounced nonlinear dependence on the salt concentration in the dilute range.

It should be mentioned, however, that only two compositions of Minier et al.[31] (y = 10, 24) fall into the range depicted in Figure 3. Furthermore, their T_g value of $PEO_{10}NaI$ was found to vary from −3 to −23 °C upon changes in T_q from 127 to 172 °C, however, in a nonmonotonic manner. For the composition with y = 24, the T_g value differed by 25 °C between slow and fast cooling.[31] Other publications on PEO−NaI report $T_g = -24$ °C for y = 10 and $T_g = -59$ °C for pure PEO.[28,29] These data are shown by the crosses in Figure 4. Obviously, the value for $PEO_{10}NaI$ (cross) is even smaller than that of Minier et al.[31] (dashed line).

Also for PEO−LiTFSI, the previously published T_g data fall distinctly below the present results. This is obvious from the position of the lowest line in Figure 5 reproducing the results of Lascaud et al.[6,30] Only their compositions with $10 \le y \le 24$ represented by the solid line segment with slope 2.8 °C/mol %[6,30] are in the range of the present study. The dashed line segment is a mere extrapolation to zero salt concentration and thus not supported by experimental data. Altogether, the data constellation for PEO−LiTFSI in Figure 5 is similar to that of PEO−NaI in Figure 4. Specifically, the largest difference between the old and new T_g data amounts to about 16 °C near $1/y = 0.03$.

Lascaud et al. also measured T_g for more concentrated PEO−LiTFSI complexes, i.e., up to the very salt-rich composition with y = 0.5.[6,30] They observed a monotonic increase with increasing molar fraction of salt, $x_{salt} = 1/(1 + y)$, up to a (near-)liquidus composition ($x_{salt} \approx 0.4$, y = 1.5) followed by a constant T_g of 14 °C indicative of a two-phase region (liquid complex plus pure salt).[6] However, quenching temperatures are not mentioned in their work and the dependence of T_g on T_q was apparently not explored.

Other PEO−salt systems investigated for their phase behavior and glass transitions include $LiCF_3SO_3$,[33,34] MSCN (with M = Li, Na, K, and Cs),[35,36] $LiClO_4$,[33] $LiBPh_4$,[36] and MTFSI (with M = Na and K).[30] All these studies were carried out by Prud'homme and co-workers like that on PEO−LiTFSI.[6,30] The range of examined compositions typically extended from y = 24 to y = 1.5, similar to PEO−LiTFSI, so that the extreme low-concentration regime including pristine PEO was not covered by these early data. In the dilute range of all these electrolytes, the increase of T_g with salt concentration was rather modest, of linear type, and never exceeded a slope of 6.7 °C/mol %.[6] This figure has to be compared with the slope S_g of the T_g -versus-$1/y$ plots in Figures 4 and 5, containing the aforementioned literature values for PEO−LiTFSI (2.8 °C/mol %[6]) and PEO−NaI (4.5 °C/mol %[20]).

Obviously, distinctly higher T_g increase rates are observed for the present strongly diluted PEO−NaI and PEO−LiTFSI complexes. For PEO−NaI, this is quantitatively confirmed by calculating the slope of eq 3 as $S_g \equiv dT_g/d(1/y) = a\Delta_T \exp(-a/y)$, where for dilute compositions $1/y$ does not significantly differ from $x_{salt} = 1/(1 + y)$. Indeed, in the low-concentration limit we have S_g = 25.7 °C/mol % while for $1/y$ = 0.02 our data yield S_g = 9.1 °C/ mol %. However, for $1/y$ = 0.033 and 0.05 the present increase rate reduces to 4.6 and 1.9 °C/mol %, respectively. The latter S_g values comply with the increase rates reported in the literature for comparable composition domains. Yet a disparity remains, since PEO−NaI exhibits the "common" low T_g increase for T_g values only in the range from −20 to −10 °C (Figure 4), whereas the related systems mentioned above show a similar behavior over longer T_g intervals extending to temperatures down to about −55 °C.

Comparison of PEO−NaI with PEO−LiTFSI. For the two systems examined, the actual T_g data are generally higher than the previously published ones. However, what remains in both cases is that T_g of PEO−NaI exceeds that of PEO−LiTFSI for the same salt concentration over fairly wide composition ranges. It is known that the alkali metal ions Na and Li similarly coordinate to the oxygen atoms in the polymer chains leading to conformational constraints of the PEO segments involved in cation binding. The concomitant reduction of polymer flexibility is accompanied by an increase of T_g. Probably, the differences in T_g induced by Na and Li coordination are small, since it was observed that the ion conductivity of $PEO_{30}MI$ electrolytes with M = Li, Na, K, Rb, or Cs coincides over broad temperature ranges in the amorphous phases[24] (cf. L_0 region in Figure 2). Consequently, the disparity in T_g between PEO−NaI and PEO−LiTFSI essentially arises from the distinct anions involved. Specifically, the bulky TFSI ions may more efficiently prevent dense packing of polymer segments than the comparatively small iodine ions and thus have a stronger plasticizing effect.[33]

The present glass transition temperatures of PEO−NaI and PEO−LiTFSI exhibit similar behavior as a function of salt

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concentration, which is empirically described by eq 3. The relative change per unit of reduced concentration, $(T_g - T_{g0})^{-1}d(T_g - T_{g0})/d(1/y) = a/(\exp(a/y)-1)$, is given by the dimensionless parameter "a" in eq 3. It is found by fitting that the numerical values of this parameter for PEO−NaI (a = 51.7) and PEO−LiTFSI (a = 57.8) are not too different. By contrast, the difference in Δ_T is quite large, 49.7 °C versus 20.0 °C, which, according to the discussion above, mainly reflects the dissimilar properties of the anions. Altogether, this quantitative analysis seems more reliable for PEO−NaI than for PEO−LiTFSI, i.e., because of the larger body of experimental data and the wider composition range of the former system.

Composition Dependence of T_g. The present fitting result for PEO−NaI (cf. eq 3) only slightly differs from a similar expression previously used for the evaluation of ion transport data.[14] As indicated in the Introduction, we utilized the experimental T-dependence of T_g for a simultaneous fit of all PEO_yNaI transport data (diffusivity of Na and I as well as the charge diffusivity D_σ) comprising six compositions in the y-range from 30 to 1000. Thus, based on the empirical rule[17−19] that T_g and the VTF parameter T_0 only differ by a y-independent constant, i.e., $T_0(y) \approx T_g(y) - \Delta_0$, all measured diffusion coefficients were well reproduced with the adjusted best value $\Delta_0 = 44 \pm 3$ K.[14] This finding supports the reliability of the T_g data obtained in the present work. In particular, the steep increase of T_g with increasing salt concentration for PEO−NaI (cf. Figure 4) appears to be reflected by corresponding changes in the ionic diffusivity (cf. eq 1).

For polymer electrolytes, diverse T_g behavior as a function composition has been reported in the literature. A simple linear dependence on the salt concentration was mentioned before regarding the work of Minier et al.[20,31] and the Prud'homme group.[6] On the other hand, LeNest et al.[5] observe for PEO of low molecular weight (1050, 2100, and 3800 g/mol) complexed with $LiClO_4$ a linear decrease of the *inverse* glass transition temperature, i.e., $1/T_g = 1/T_{g0} - 2.7 \times 10^{-4}\ C_s$ with C_s given in mol/L. Similar behavior was found for the same PEO materials without salt as a function of the urethane cross-link density. On the basis of their quantitative results, LeNest et al.[3,5] conclude that cations bound to the ether groups of PEO act as cross-links of reduced effectivity. It is noteworthy that these authors used *ex situ* quenching in LN_2, like in the present work, with T_q = 100 °C. We checked the above relationship by plotting our PEO−NaI and PEO−LiTFSI data as $1/T_g$ versus $1/y$. However, for both systems a pronounced nonlinear behavior was observed, which does not agree with the findings on PEO−$LiClO_4$.[5]

Kim et al.[10,37] have provided an equation for the composition dependence of T_g in polymer−salt systems which is based on changes in configurational entropy, using the ideas of DiMarzio and Gibbs[38] as well as Flory−Huggins theory.[39] This equation is nonlinear in x_{salt} and it predicts a T_g behavior globally similar to that observed in the present study. However, the use of Kim's equation for the description of our data proved to be less successful, since it was not able to reproduce the strong curvature in T_g for small $x_{salt} \approx 1/y$ values. This may not surprise, as the model of Kim et al.[10,37] involves several strong assumptions, e.g., (1) ion association is neglected, and (2) differences in the solvation of cations and anions are not taken into account. Both assumptions are questionable, since first, the impact of pair formation on ion transport, particularly in PEO−NaI, is found to be strong,[13,14] and second, the binding situation for cations and anions within the polymer matrix is crucially different (see above). The development of an improved physical model is beyond the scope of the present article. We believe, however, that future evaluations should separately include the T_g-enhancing (stiffening) effect of cations, the T_g-lowering (plasticizing) effect of anions, and a possible influence of ion pairing.

For completeness it should be mentioned that exponential T_g behavior has been observed in polymers. Specifically, this concerns the dependence of T_g on the *n*-alkyl side chain length for a series of comblike structures, as reported by Reimschuessel.[40] In these cases, T_g decreases exponentially with increasing n up to a critical side chain length indicated by n_c. The expression given by Reimschuessel[40] bears resemblance to eq 3

Possible Causes of Discrepancies in T_g. *General Considerations.* Although the present glass transition temperatures of dilute polymer electrolytes are consistently higher than those reported in the literature, we can only speculate about the reasons for this finding. It is obvious that residual solvent and moisture in the samples may contribute to a lowering of T_g, as such contaminations act as plasticizer for the nominally solvent-free polymer-salt systems.[41−43] Also ineffective quenching caused by too low cooling rates may give rise to seemingly low T_g values, since then the precipitation of salt-rich crystalline phases cannot be prevented. In that case, the measured glass transition temperature has to be attributed to an amorphous phase which is more dilute in salt than the nominal composition of the quenched specimen. On the contrary, it is hard to conceive of preparative or experimental artifacts that would lead to a significant *increase* of T_g.

Small differences among T_g data on nominally identical samples may arise from experimental error including variations in composition and temperature within common tolerances. In addition, some scatter among the results from different studies may be due to differences in heating rate (10−40 °C/min) and the applied T_g evaluation method, i.e, as denoted by "half-c_p", "point of inflection", "onset value", or some other keyword. However, the overall uncertainty from such sources may be estimated to be on the order of ±5 °C in worst cases, which is still far below the discrepancies of up to 32 °C (PEO−NaI) and 16 °C (PEO−LiTFSI) between present and previous T_g data disclosed in this work.

Effect of Polymer Specifications. Differences in T_g may also be due to distinct specifications of the employed materials. In particular, molecular weight and purity of the polymer may be relevant features of the polymer-salt complexes. The PEO material in our work is characterized by a very high molecular weight (8×10^6 g/mol) and a production-related fraction of oxide particles (1.7 wt %).[21,44] In principle, this might explain that the present result for T_{g0} (−57 ± 1 °C) is slightly higher than some of the literature values (e.g., −60 to −65 °C[3,45]). However, Wu et al.[46] report experimental T_g values for semicrystalline PEO to be in the range from −45 to −60 °C, which is based on the results of nine different original publications (for references, see Wu et al.[46]).

Also many other studies on polymer electrolytes are based on purchased PEO materials of high molecular weight, which always contains a small fraction of oxide particles.[44] This contamination is inherent to the manufacturing process but it is rarely mentioned in the experimental sections of published work.[44] However, several recent investigations show that the impact of added oxide particles on the glass transition and crystallinity of salt-in-PEO electrolytes is not significant.[47,48]

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Data reported for $PEO_{50}AgCF_3SO_3$ with varying amounts of MgO nanoparticles in the range from 1 wt % to 10 wt % show that T_g and χ_c are essentially constant.[47] A similar result is obtained from a study on $PEO_{15}KI$ for additions of nanosized CeO_2 particles of up to 15 wt %.[48] Furthermore, also the particle size tends to be uncritical for T_g and χ_c, as indicated by the data on $PEO_{25}NaClO_4$ with ZrO_2.[48]

Indirect evidence for the weak interaction between oxide nanofillers and the salt in SPE systems is obtained from ionic conductivity and diffusivity measurements. Several recent studies show that the admixture of different types and amounts of nanosized oxide particles changes the ion conductivity in the melt only to extents that are comparable with experimental error (e.g., 20%).[44,49,50] Similar is true for the diffusion coefficients of cations and anions as determined by PFG-NMR[44] or radiotracer techniques.[50] These studies include PEO_{20}LiBETI with 10 wt % SiO_2 particles[44] and PEO_{60}NaI with 5 wt % TiO_2 or 10 wt % Al_2O_3 particles.[50] Altogether, the effect of 1.7 wt % oxide particles in the PEO material employed in this work seems negligible.

The early studies on PEO−NaI also used high-molecular-weight PEO, i.e., specified as 9×10^5 g/mol[31] or 5×10^6 g/mol.[28] Of the cited literature on polymer electrolytes, a direct measurement of T_g for pristine PEO is only reported by Przylusky and Wieczorek.[28] Their result, −59 °C (cf. Figure 4), is close to the present data. Therefore, it seems less plausible that the disparity in T_g from distinct studies on PEO−NaI is due to different material specifications. By contrast, the previous PEO−LiTFSI data are based on purified polymer material of relatively low molecular weight ($\sim 4 \times 10^3$ g/mol[6]) like the other results of the Prud'homme group.[30,33−36] In these cases, a lowering of T_g with regard to high-molecular-weight material is in principle predicted by the Flory−Fox equation.[51,52] This effect is based on the relatively large number of chain end units in short-chain polymer matrices, which in turn leads to more free volume and higher segmental flexibility. Using quantitative data for other polymers,[52] also the magnitude of the T_g -difference for PEO−LiTFSI between present and previous[6] data could be rationalized by the differences in molecular weight. In addition, it has been observed for related PEO/Li-salt systems that the partial substitution of high-molecular-weight PEO with low-molecular-weight PEO leads to a lowering of T_g.[53] However, the question remains whether the chain length effect is able to explain the qualitative change in the T_g composition dependence as well, i.e., from linear to exponential-type (cf. Figures 4 and 5).

Effect of Solvent and Water Residues. To prepare their PEO−NaI complexes, Minier et al.[31] used the "solution and cast" procedure, after which the electrolyte film was outgassed under partial vacuum followed by a treatment in flowing argon. No information is given about sample handling. For similarly prepared PEO−NaSCN complexes, Lee and Christ[54] observed a T_g-dependence on salt concentration which is within a few percent of the Minier result. Interestingly, it is explicitly stated in their article[54] that "no precautions were taken to prevent contact with water vapor". Thus, it seems plausible that the similarly low literature data reported for PEO−NaI and PEO−NaSCN have been influenced by the plasticizing effect of H_2O molecules.[41] By contrast, the preparation procedure for PEO−LiTFSI electrolytes by Lascaud et al.[6] is described in considerable detail. The reported use of high vacuum and elevated temperatures for solvent evaporation make it plausible that their polymer-salt mixtures were of high purity in the as-prepared state. However, the authors provide little information about the avoidance of water contamination during sample handling.

The effect of solvent and water contamination was exemplarily monitored by rheological investigations on a related polyether-based system.[55] To this aim, a test sample prepared by the "solution and cast" method in air ambient was compared regarding its mechanical properties with reference material prepared by the standard high vacuum and glovebox procedures (see Experimental Section). After 3 days of ambient exposure, the storage modulus G' of the test sample at 40 °C was found to be only about 60% of the reference value G'_0.[55] Gradually smaller and smaller decreases down to about 50% of G'_0 were determined after 6 and 14 days of ambient exposure. A similar behavior was revealed by the zero shear viscosity.[55] These observations may be explained by the presence of residual acetonitrile in the test sample in conjunction with a continuous uptake of moisture from the air. We note that water absorption as a function of exposure time has been previously studied for PEO-based polymer electrolyte systems.[56] Our test experiment indicates that solvent and water contamination may lead to lower viscosities, which is closely connected to a decrease of T_g. Specifying the water or solvent content of polymer electrolytes (based on PEO of extremely high molecular weight) is not an easy task. At least no ^{1}H signal related to water or acetonitrile was detected during PFG-NMR analysis (cf. Materials and Preparation). However, this point is not as critical as it seems, i.e., for the following reasons: (1) Quite high concentrations of water (0.05 molar fraction[41]) or organic solvent (several wt %[42,43]) are necessary to have a significant effect on T_g. Such concentrations are far beyond state-of-the-art contamination levels and thus certainly not contained in our samples. (2) The effect of water or organic solvents in noticeable amounts would lead to a *decrease* of T_g.[41−43] However, the main result of the present paper is a substantial *increase* of T_g compared to previous work. Therefore, our observations cannot be rationalized by artifacts due to solvent residues in our samples.

Effect of Quenching Rate and Temperature. In principle, the quenching temperature T_q and the quenching rate R_q are important parameters in measurements of T_g. T_q determines the equilibrium state of the sample at the onset of quenching, whereas R_q controls to which extent this initial state can be frozen in and thus to which extent phase separation can be avoided during the cooling-down procedure. It may be expected that R_q is more critical in the high-T region where the ions are more mobile than at lower temperatures. In the case of PEO−salt complexes, a special feature is the (partial) crystallization of PEO. Usually, this phase transformation cannot be suppressed by *in situ* quenching, as also reported by others.[6] In our measurements, the corresponding exothermic events commonly occurred in the range from 40 °C down to 20 °C.

It should be emphasized that the present results for T_g do not critically depend on the quenching method. The data gained by *ex situ* and *in situ* quenching mutually agree in all cases (cf. Figures 4 and 5). There are only differences in the degree of crystallization χ_c, which are generally small, except for PEO_{10}NaI (cf. Figures 3). Consequently, the disparity between our T_g values and the literature data cannot be explained by differences in the quenching rate.

By contrast, a dependence on the *ex situ* quenching temperature is found for PEO_yNaI with $y \leq 20$ (cf. Figure

4), while it was not examined for $PEO_yLiTFSI$. This dependence for concentrated PEO−NaI may relate to the position of the liquidus line L_2 in Figure 2, as discussed in the section Glass Transition Temperatures. It is remarkable, however, that also for $PEO_{10}NaI$ and $PEO_{20}NaI$ the differences in T_g after consecutive *ex situ* (T_q = 215 °C) and *in situ* (T_q = 150 °C) quenching are within 2 °C. Apparently, the short time of residence in the melt phase between about 60 and 150 °C of roughly 14 min (first heating immediately followed by second cooling) is too short to establish a corresponding equilibrium state. This indicates that equilibration times may play a crucial role at moderate and lower quenching temperatures.

CONCLUSIONS

The results of this study on the glass transition in the polymer-electrolyte systems PEO_yNaI and $PEO_yLiTFSI$ can be summarized as follows:

(i) The present T_g values for salt concentrations below about 2.4 mol/L (y > 10) are distinctly higher than comparable data reported in the literature.
(ii) T_g shows an exponential increase with increasing salt concentration in the highly diluted composition range. This clearly deviates from a linear dependence, as previously reported for PEO−NaI, PEO−LiTFSI, and other SPE systems.
(iii) *Ex situ* quenching using liquid nitrogen may lead to lower degrees of crystallinity than *in situ* quenching inside the calorimeter. As a result, bigger steps in the heat capacity at the glass transition are obtained, which facilitates the measurement of T_g.
(iv) Upon quenching, the crystallinity of SPEs decreases with increasing salt concentration.

The reasons for the higher T_g data obtained in this work are not clear. In the case of PEO−NaI, the low levels of residual organic solvent and water contamination in our samples may be responsible for the determination of "true" T_g values representative of the pure binary salt-in-polymer complexes. For PEO−LiTFSI, the high molecular weight of the employed PEO material could at least partly explain the T_g increase with respect to the literature data. Further studies are needed to elucidate the composition dependence of the glass transition in polymer electrolytes.

ASSOCIATED CONTENT

Supporting Information

Additional DSC thermographs of PEO−NaI and PEO−LiTFSI complexes after melt quenching showing glass transitions and a table of storage module data on a related polyether-based electrolyte with solvent residues revealing effects of exposure to air ambient as a function of time. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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