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Materials Sciences Division

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Thermal Properties of the Polymer Electrolyte System P(EO)_nLiTFSI

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Abstract

A detailed study of the thermal and transport properties of the poly(ethylene oxide)-LiN(CF₃SO₂)₂ (PEO/LiTFSI) system indicates that T_m is heavily influenced by the thermal history of the sample. Melting transitions were observed for pristine samples for $n = 5-10$ in P(EO)_nLiTFSI, while pre-heated samples appeared amorphous in the DSC and conductivity experiments. Transport properties such as AC conductivity are heavily influenced by the physical state of the binary salt/polymer solution. For an accurate understanding of transport pertinent to the long-term operation of lithium batteries, it is important that the polymer electrolyte system be at thermal equilibrium, and that the kinetics of re-crystallization be well-characterized.

Keywords: polymer electrolyte, P(EO)/LiTFSI, thermal properties, transport properties, conductivity

Chemical Compounds: poly(ethylene oxide), LiN(CF₃SO₂)₂

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Introduction

Ion containing polymers, also known as polymer electrolytes, have been extensively studied during the last two decades, primarily for possible use in applications such as advanced batteries and electrochromic devices. [1] The original polymer in which ionic conduction was observed, poly(ethylene oxide) (PEO), is still an interesting host material due to its superior solvating ability,[2] and the relatively high conductivity that its salt solutions typically exhibit.[3] Unfortunately, the latter characteristic is only apparent at elevated temperatures, since significant ionic conduction in polymer-salt complexes only takes place through amorphous domains, as shown by NMR-measurements,[4] and PEO-based compounds are crystalline at room temperature.[5] In this context, the discovery of a new salt, $\text{Li}(\text{N}(\text{CF}_3\text{SO}_2)_2)$ (LiTFSI),[6] which, upon complexation with PEO, was reported to form a completely amorphous material for n values of 8 and 10 in $\text{P}(\text{EO})_n\text{LiTFSI}$ is significant.[7] A later report on a high molecular weight system confirmed this crystallinity gap using repeated differential scanning calorimetry (DSC) measurements. Although small endothermic peaks due to crystalline fractions did appear in the first heat cycle, all traces of non-conducting regions were gone in the second cycle.[8]

In this article, we report results showing the absence of a 'crystallinity gap'; i.e., no 'almost crystalline-free' concentrations exist near room temperature. Through extensive DSC measurements combined with AC impedance data, it is instead confirmed that the $\text{P}(\text{EO})_n\text{LiTFSI}$ system for all n values behaves in a similar manner to other PEO systems. At thermodynamic equilibrium, three phases are present in varying concentrations depending upon salt content and temperature; crystalline PEO, a crystalline stoichiometric compound and a minority salt-containing amorphous phase.[9]

Because transport properties such as AC conductivity are strongly affected by the physical state of the polymer electrolyte, it is important to understand the thermal properties before a more complete characterization can be carried out. Non-equilibrium behavior of polymer systems is often observed due to slow kinetics (e.g., of recrystallization),[10] but thermodynamic data is still relevant, particularly for long-term applications such as battery cycling.

Experimental

High molecular weight PEO (Aldrich, $M_v = 5 \times 10^6$ g/mol) was dissolved in acetone and recrystallized, to remove the butylhydroxytoluene (BHT) stabilizer. Lithium (bis)trifluoromethanesulfonate imide (LiTFSI), a gift from 3M Company, was dried at 180° C for at least 12 hours under vacuum. The $P(EO)_nLiTFSI$ electrolytes were fabricated in an inert atmosphere glovebox ($O_2 < 1$ ppm) under helium by dissolving pre-weighed amounts of polymer and salt in acetonitrile. The clear solutions were stirred, and then cast into glass rings before further drying for at least 24 hours under vacuum to remove the solvent took place. During this process, care was taken not to heat the electrolytes due to the slow kinetics of recrystallization.

Standard DSC aluminium capsules were prepared containing small amounts (20-30 mg) of electrolyte under helium atmosphere. Precautions were taken not to expose the hygroscopic samples to moisture before the measurements were carried out using a Perkin-Elmer DSC-7 differential scanning calorimeter. A DSC measurement consisted of an initial quenching (200°C/min) from room temperature to -100°C, followed by heating to +100°C at 10°C/min. This initial cycle was immediately followed by a second quench-heat cycle.

For AC conductivity measurements, symmetrical cells with blocking (stainless steel) electrodes, the electrolyte, and a polypropylene spacer 76 μm thick were assembled in the dry box. The whole "cell sandwich" was put into airtight SwagelokTM cells before being transferred to a convection oven with an estimated temperature stability of ± 0.5 $^{\circ}\text{C}$, for a 24 hour equilibration at 85 $^{\circ}\text{C}$. The impedances of the films were then measured over a frequency range of 65 kHz to 1 Hz, with a SolartronTM SI 1254 four-channel frequency response analyzer coupled to a 1286 electrochemical interface. The bulk resistance was taken as the touchdown point of the semi-circle or spur on the x-axis of the Nyquist plot. Measurements were performed at 10 $^{\circ}$ C intervals between 30 to 100 $^{\circ}\text{C}$; and the cells were allowed to equilibrate for at least one hour between measurements. To monitor the slow recrystallization process, a second identical measurement cycle was performed after a 72 hour storage period at -10 $^{\circ}\text{C}$.

Results and discussion

For n values ranging from 8 to 20 in $\text{P}(\text{EO})_n\text{LiTFSI}$, for samples with no thermal history, two melting transitions and one glass transition were observed in all initial DSC spectra. Figure 1a and b (bottom traces) show results for $\text{P}(\text{EO})_8\text{LiTFSI}$ and $\text{P}(\text{EO})_5\text{LiTFSI}$, respectively. This is consistent with previously published phase diagrams for other closely related PEO-salt systems, e.g., $\text{P}(\text{EO})_n\text{LiCF}_3\text{SO}_3$, for which the two melting transitions are attributed to the melting of a crystalline PEO phase and a crystalline stoichiometric complex, respectively, and the glass transition to the onset of polymeric vibrations in a minority amorphous phase.[11] In the second heating sequence, no melting transition whatsoever could be detected for n values ranging from 5 to 10 (middle traces in Figures 1a and b). A strong T_g -transition indicates that the samples are

completely amorphous, in good agreement with DSC measurements performed by Prud'homme et al. [7] and Armand et al. [8] on similar systems. A small melting transition is observed in samples stored at -10°C for 72 hours (Figure 1b, top trace), indicating that the recrystallization process is very sluggish. This propensity to remain amorphous after exposure to moderately elevated temperatures can most likely be attributed to the plasticizing effect of the large, flexible, TFSI-anion.

A further corroboration of the extremely slow recrystallization process in $\text{P(EO)}_n\text{LiTFSI}$ ($5 \leq n \leq 10$) complexes is shown in Figure 2, where an Arrhenius plot of the conductivity for $\text{P(EO)}_8\text{LiTFSI}$ is presented. Considerably lower conductivity for temperatures below the melting point of the crystalline compound ($T \approx 54^{\circ}\text{C}$) is seen in the pre-heated sample after it has been exposed to a "recrystallization treatment" (72 hours stored at -10°C). Ongoing DSC experiments indicate that the sample is still not completely recrystallized under these conditions, suggesting that the decrease in conductivity is most probably considerably underestimated. Slow recrystallization is likely to reduce the room temperature conductivity ($2.5 \times 10^{-5}\text{ S/cm}$) of completely amorphous $\text{P(EO)}_8\text{LiTFSI}$, if this polymer electrolyte is used as is in battery configurations. Thus, a more realistic appraisal of the conductivity and other transport properties is obtained for samples with no thermal history. Our present work is directed towards understanding the equilibrium transport properties of the P(EO)/LiTFSI system as well as the factors controlling the slow recrystallization kinetics.

Conclusions

The thermal properties of the P(EO)/LiTFSI polymer electrolyte films are dependent upon their thermal history. The re-crystallization kinetics is shown to be extremely slow for samples

that have previously been exposed to heat. The heat exposure affects transport properties beneficially, resulting in an elevated conductivity. Because of the proposed use of this polymer electrolyte system in long-term applications such as rechargeable lithium batteries, it is important to evaluate transport properties at equilibrium, because recrystallization is eventually expected to occur.

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Figure Captions

Figure 1

DSC thermograms for a) a P(EO)₈LiTFSI sample with no pre-heat treatment in the first heating cycle (lower graph) and in the second heating cycle (upper graph), and b) for a P(EO)₅LiTFSI sample with no pre-heat treatment during the first heating cycle (bottom) and the second heating cycle (middle), and after storage at -10 °C for 72 hours (top).

Figure 2

The logarithm of the conductivity as a function of reciprocal temperature for a P(EO)₈LiTFSI sample after a 24 hour equilibration at 85° C (open squares) and after a 72 hour subsequent exposure to - 10° C (filled circles).

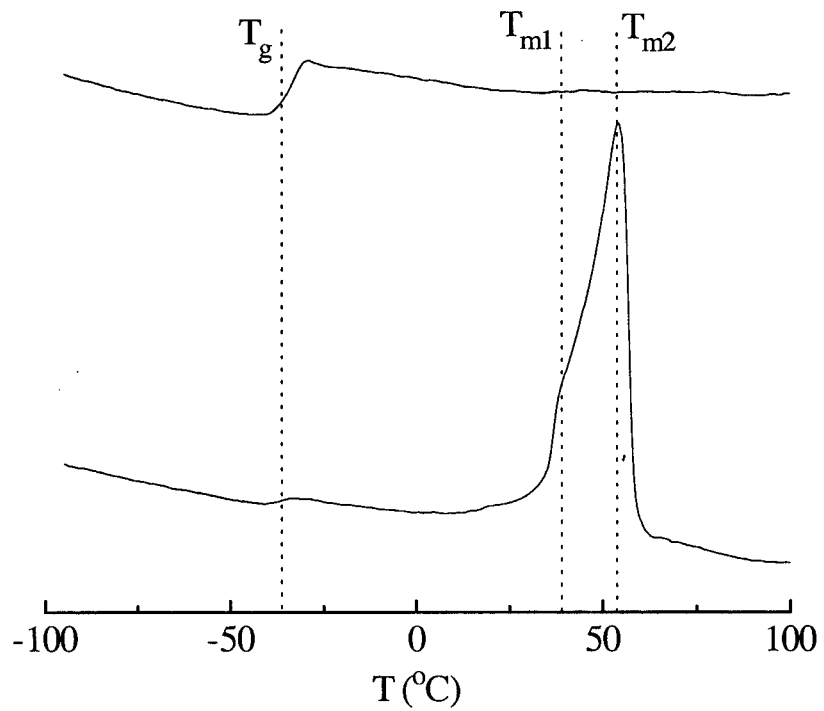


Figure 1a

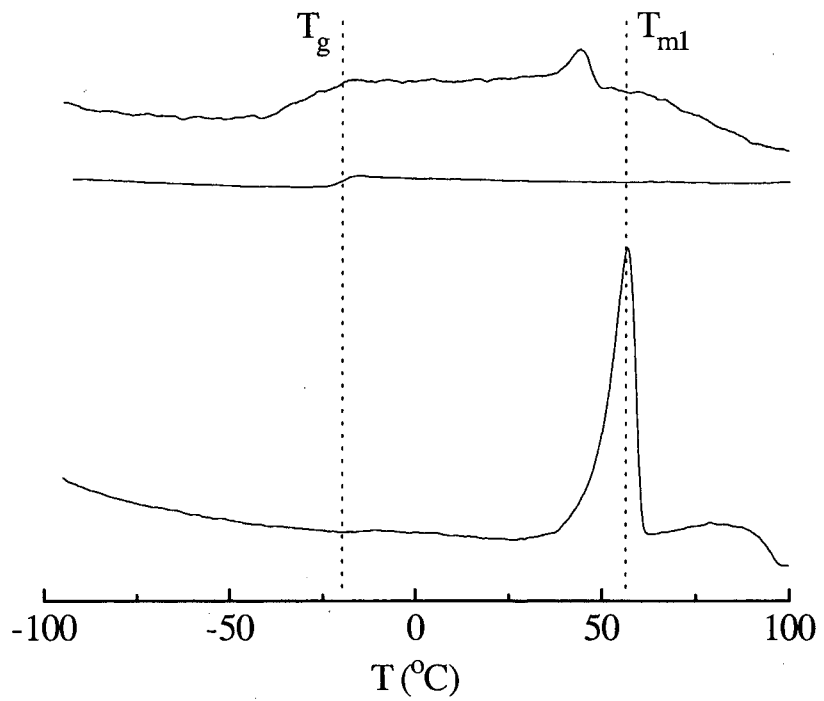


Figure 1b

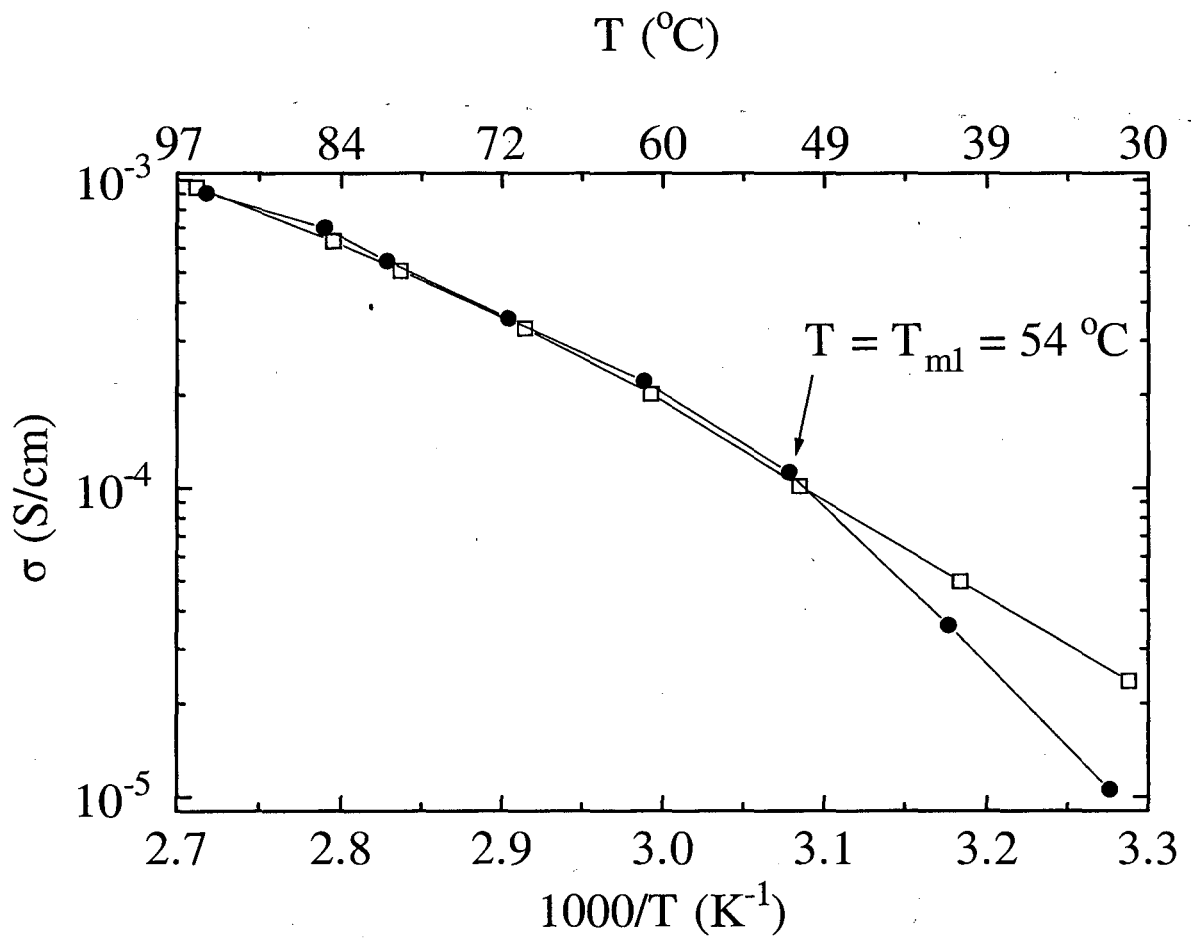


Figure 2

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