

POLY(ETHYLENE OXIDE) ELECTROLYTES FOR OPERATION AT NEAR ROOM TEMPERATURE

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Summary

In an effort to improve the room temperature ionic conductivity of poly(ethylene oxide) doped with lithium salts, the effects of various additives were examined. Partial substitution of the high polymer by a poly(ethylene oxide) of low molecular weight had the effect of increasing the solubility of the crystalline polymer/salt complex in the liquid polymer as well as lowering the effective melting and glass transition temperatures of the polymer. An optimized composition had a much improved conductivity of $10^{-4} (\Omega \text{ cm})^{-1}$ at 40 °C.

Introduction

Many varieties of solid polymeric electrolyte can be obtained from suitable combinations of high molecular weight poly(ethylene oxide) (PEO) and alkali metal salts similar to those used in liquid organic solvents. A wide variation in conductive properties has been observed within this class of material [1]. Apart from the obvious variables of the salt composition and concentration, factors affecting the conductivity can be of a more subtle nature, such as molecular weight distribution, presence of impurities, or even the solvent from which the electrolyte film was cast [2]. In the light of recent theories regarding conduction in PEO [3], changes in conductivity can be attributed to variations in the polymer microstructure — particularly the fraction and connectivity of the amorphous phase, which provides the conduction path for the dissolved electroactive ions. A high degree of crystallinity due to the PEO/salt complex not only blocks the conduction path but also depletes the amorphous phase of dopant salt. Above the melting point of the undoped polymer, about 60 °C, the amount of crystalline complex salt can be reduced by reducing the dopant concentration, and the conductivity is correspondingly increased [4]. However, it will be shown below that the conductivity increase is at the expense of mechanical stability

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— as is also the case with another highly conductive variety of PEO [2]. Below 60 °C crystallization of undoped polymer occurs and the conductivity is blocked irrespective of salt content.

The aim of this work was to reduce the service temperature of poly-(ethylene oxide) electrolyte from about 100 °C to the near normal temperature region. In other, more traditional, applications of high polymers, improved properties at specified temperatures are often obtained by the addition of modifiers, *e.g.*, plasticizers. Such an approach was taken here, and a variety of modifications was tried in an attempt to improve the conductivity. It was expected that improved conductivity would probably be accompanied by increased fluidity, but that the latter disadvantage would not be prohibitive at low temperatures where the polymer should be more rigid anyway. An optimum combination of properties was considered to be a conductivity of at least $10^{-4} (\Omega \text{ cm})^{-1}$ and a fluidity too small to be monitored as a continuous deformation of the sample during operation.

Preliminary experiments

A series of polymer films was made from Polysciences PEO, M.W. 4×10^6 . All components desired in the final polymer film were dissolved in acetonitrile to form a 2% solution by volume. Each solution was poured into a glass Petri dish to a height of 1 cm such that evaporation of solvent in dry air left films of about 200 μm thickness. After vacuum drying at 120 °C for 24 h, tests included polarized light microscopy to reveal the microstructure, and extended period conductivity measurements at various temperatures to determine the stabilities of the products.

TABLE 1

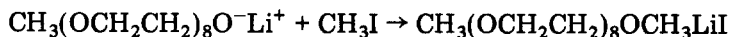
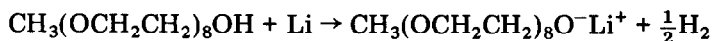
| Composition | Mode of failure |
|--|--|
| (PEO) ₈ LiClO ₄ | Slow crystallization at room temperature causing loss of conductivity |
| (PEO) ₈ LiCF ₃ SO ₃ with following plasticizers. . . Propylene carbonate | Slight volatility resulting in loss of substituents under vacuum |
| Dibutyl phthalate | Phase segregation, with liquid substituent being squeezed under pressure |
| PEG — a liquid form of PEO with molecular wt. 400 and hydroxyl end groups | Reaction with lithium shown by a large interfacial impedance with lithium electrodes |
| PEGDME — PEG with terminal hydroxyl groups methylated | None |

Table 1 shows the results of these preliminary investigations which led to the choice of $(\text{PEO})_8\text{LiCF}_3\text{SO}_3$ modified with $(\text{PEGDME})_8\text{LiI}$ as the system for detailed study.

Preparation of PEO/PEGDME samples

PEGDME was prepared as follows:

An excess amount of lithium foil was added to 15 ml of monomethoxy-poly(ethylene glycol) (Aldrich) dissolved in lithium-dried diethyl ether and the mixture was left for a few days under dry argon to convert all OH groups to alkoxide. On termination of hydrogen evolution (after about 1 day) the very light, golden-brown solution was filtered to remove lithium and side products. 20 ml of methyl iodide were added, whereupon the solution clouded initially, cleared, then a viscous, yellowish-solution separated after 1 h. The ether layer could be evaporated without residue and therefore the product was assumed to be $(\text{PEGDME})_8\text{LiI}$ according to the reactions:



Attempts to separate the lithium iodide side product led to severely decreased yield and quality of the PEGDME, so the product was used as prepared, accepting the iodide as a partial substituent for CF_3SO_3 . Films were then prepared as above.

Effects of composition on conductivity

A series of films was made with various mole fractions of $(\text{PEGDME})_8\text{LiI}$ in $(\text{PEO})_8\text{LiCF}_3\text{SO}_3$ and their conductivities were measured by the a.c. impedance method, using stainless steel or lithium electrodes where appropriate. The Arrhenius plot of Fig. 1 shows the conductivity enhancement due to the plasticizer. The main effects of the plasticizer were:

- (i) Generally higher conductivity, quantified in the Arrhenius phenomenology as a lower activation energy and a higher pre-exponential factor.
- (ii) An extension of the Arrhenius-like region to lower temperature.

A further series of films was made to investigate any improvement on increasing the O:Li ratio. Figure 2 shows increased conductivities in the Arrhenius region but not at the lower temperatures.

Lastly, in order to check for any effects of the anion substitution, a comparison was made between PEO plasticized with PEG containing pure LiCF_3SO_3 and 50% $\text{LiCF}_3\text{SO}_3/\text{LiI}$, respectively (Fig. 3). The result shows that LiI can have a significant effect, which is detrimental at low temperatures.

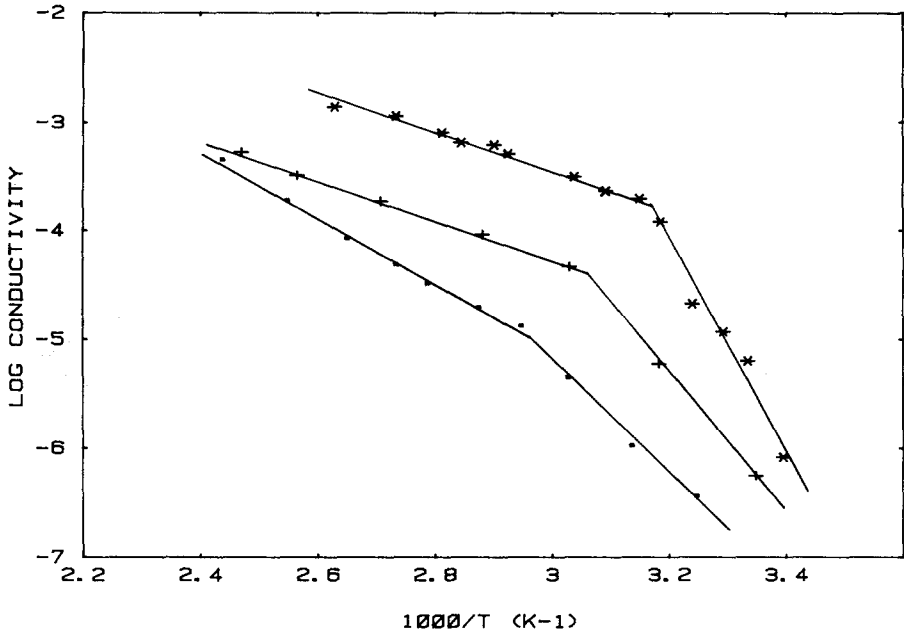


Fig. 1. Conductivity enhancement due to the plasticizer. •, 0 mole% PEGDME; +, 21 mole% PEGDME; *, 65 mole% PEGDME.

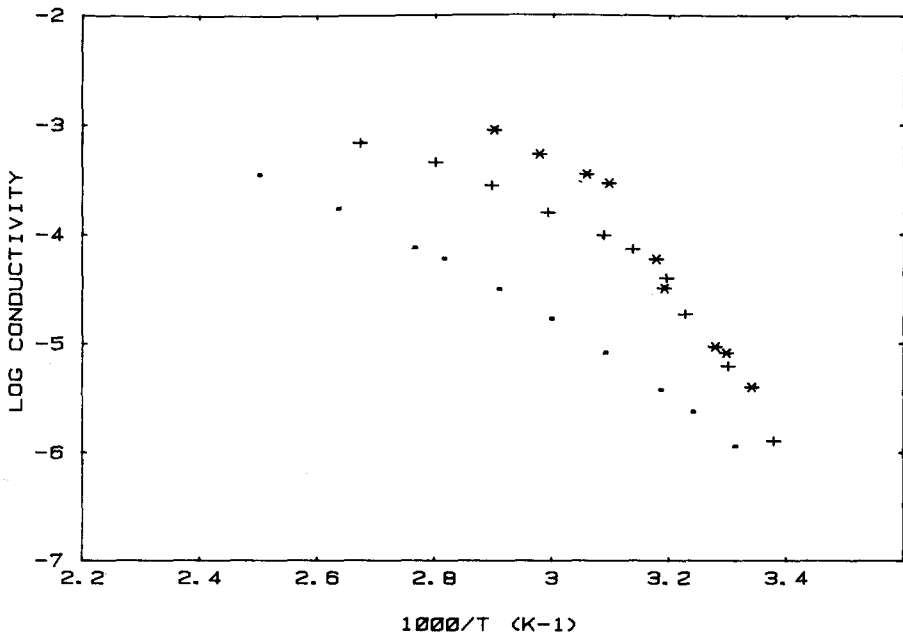


Fig. 2. Effect of O:Li ratio on the conductivity. •, 5.2:1; +, 8.3:1; *, 18.7:1.

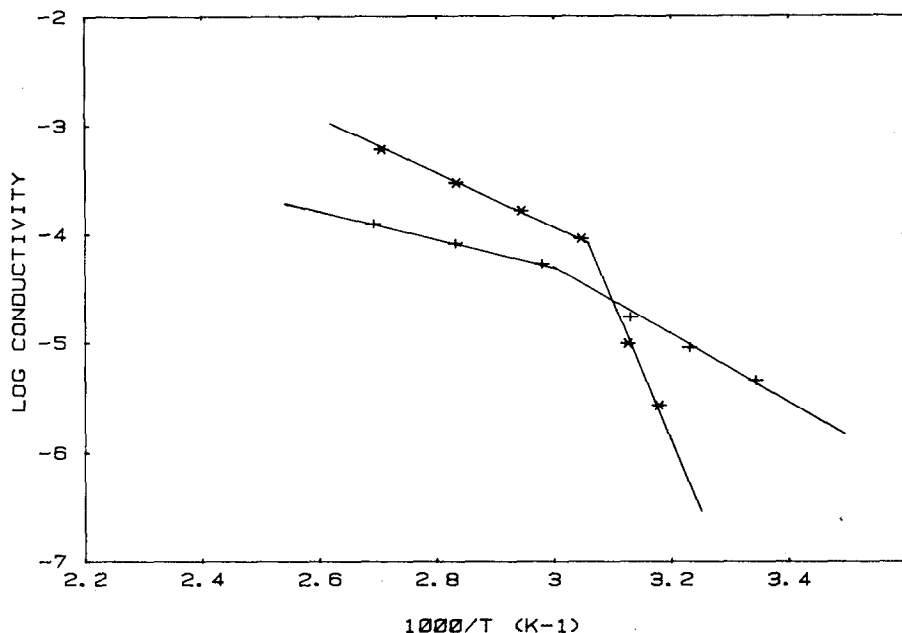


Fig. 3. Effect of LiI on the conductivity. +, 100% LiCF₃SO₃; *, 50% LiI/50% LiCF₃SO₃.

Effects of composition on the phase diagram

Hot stage microscopy in polarized light gave a rough indication of the phase changes occurring during temperature cycling, although the quantity plotted in Fig. 4, the visible (interspherulitic) amorphous fraction, does not include the amorphous material within the spherulites. The main observation was the temperature of complete dissolution of the complex crystals — this point decreased markedly on addition of plasticizer.

A more quantitative study of the phase diagram was made by differential scanning calorimetry (D.S.C.): In Fig. 5 we observe not only the lower temperature of complete dissolution (shown by the peak end), but also a decreased amount of crystalline material above the melting point of the PEO (shown by the smaller area of the dissolution peak). The melting point, or dissolution point of PEO, is also decreased with plasticizer addition. Finally, the low temperature scans of Fig. 6 show decreased glass transition temperatures for the remaining amorphous material.

Mechanical properties of plasticized samples

The impedance measurements with stainless steel electrodes sometimes showed decreasing resistance with time, especially at higher temperatures and with large amounts of plasticizer. The rate of decrease was shown to be

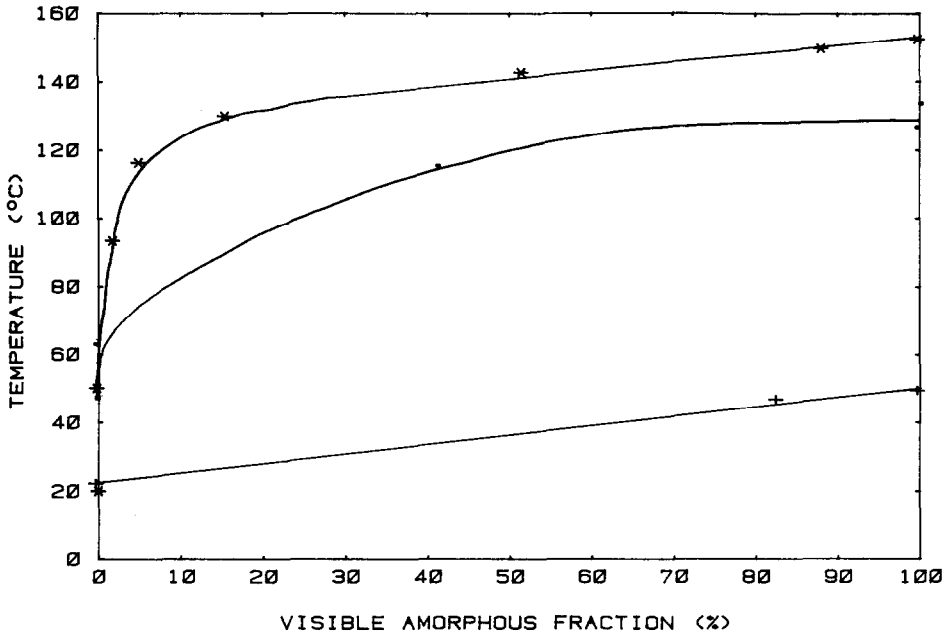


Fig. 4. Visible (interspherulitic) amorphous fraction as a function of temperature for: +, 65 mole% PEGDME; ·, 38 mole% PEGDME; *, 20 mole% PEGDME.

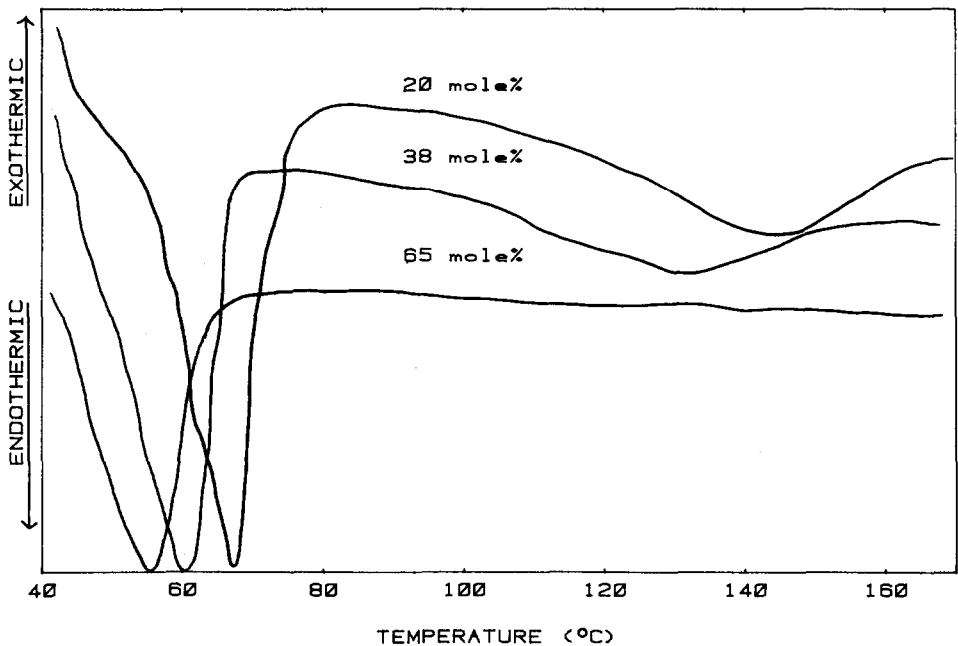


Fig. 5. D.S.C. traces for samples containing 20, 38 and 65 mole% PEGDME.

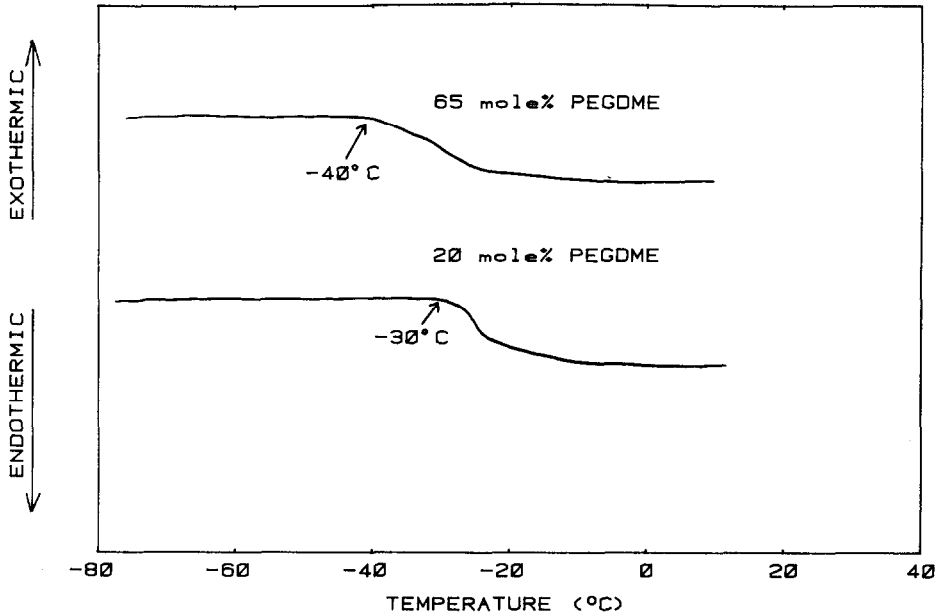


Fig. 6. Low temperature D.S.C. traces for samples containing 20 and 65 mole% PEGDME.

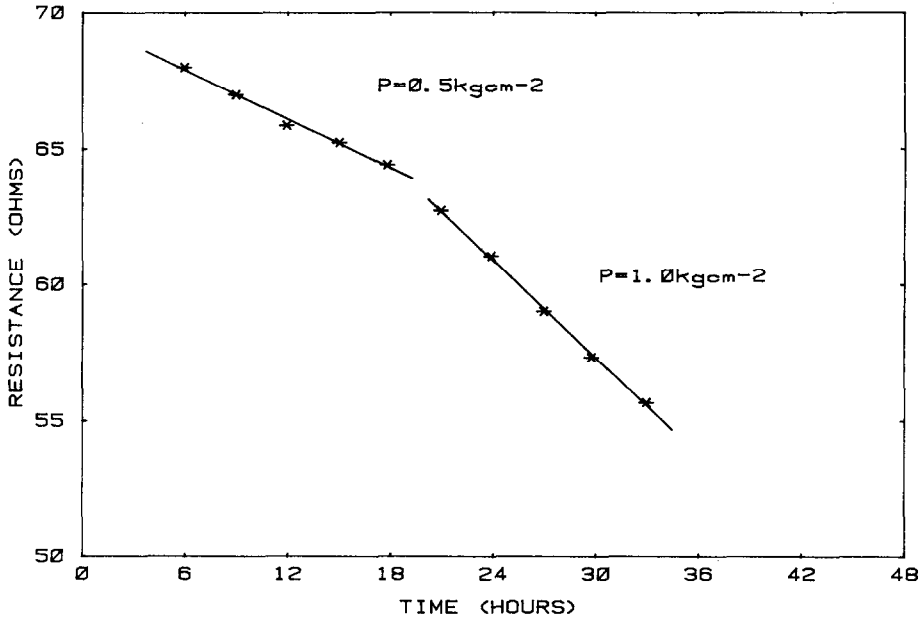


Fig. 7. Decrease in resistance of a plasticized sample due to creep, at two different loads.

proportional to the load applied, and the decrease attributed to slow creep of the sample (Fig. 7). It was initially believed that creep-rate measurements would yield viscosity values as a function of temperature (useful in the

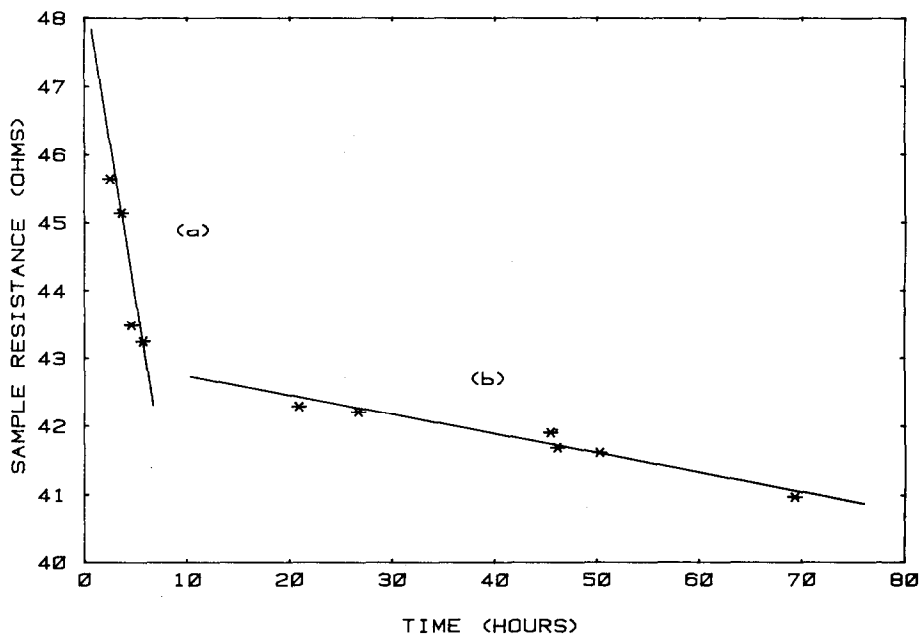


Fig. 8. Time dependent creep behaviour of a partially crystalline sample containing 20 mole% PEGDME. (a) $\eta = 1.9 \times 10^{10}$ Pascal s, (b) $\eta = 5.9 \times 10^{11}$ Pascal s.

application of transport theories to the conduction process) for each polymer. This was the case for some samples in the totally amorphous regime where viscosities were calculated to be in the region $10^{10} - 10^{11}$ Pascal s. However, a meaningful correlation with conductivity proved difficult because of a peculiar time dependence observed in partially crystalline samples, as in the example of Fig. 8. In some cases, *e.g.*, the one giving 10^{-4} at 40°C , the creep rate initially corresponded to about 10^{10} Pascal s, but after a period of 1 - 10 h, varying according to the sample and its thermal history, the creep rate decreased beyond the detection limit of about 10^{12} Pascal s. This result may be taken as evidence of partial crystallinity providing mechanical stability.

Discussion

Previous work has shown that LiCF_3SO_3 -doped PEO exists as a composite material containing the amorphous solution as well as a crystalline complex within the normal temperature range of operation as a solid electrolyte. However, its macroscopic properties are more solid-like than usual for a liquid/solid composite, and the tendency toward phase separation less than usual for a solvent-swelled polymer, even in the case where a large amount of low molecular weight material is present as plasticizer. The reason for this may lie in the spherulitic microstructure, which as yet is not known but is probably similar to that of polydisperse, undoped PEO.

In the latter case, a large fraction of amorphous material is accommodated in layers of fixed thickness between regularly stacked, lamellar crystals of microscopic dimensions [5] and impossible to separate from the crystalline phase. Such a microstructure would explain the smaller amorphous fraction observed by microscopy than that indicated by D.S.C. in this work.

Regardless of the structural reasons, an acceptable mechanical stability of highly plasticized, doped PEO has been demonstrated at temperatures at which the conductivity is high.

The conductivity of non-plasticized PEO at low temperatures is largely due to a very low solubility of the salt in the amorphous phase. This work has shown that the addition of PEGDME to the amorphous PEO substantially increases its solvating power towards the dopant at low temperatures, and in this way dramatically improves the conductivity. The slope of the Arrhenius plot is characteristic of PEGDME rather than PEO; indeed, extrapolation of the conductivity results gives a similar result to the measured conductivity value for the PEGDME solution. Therefore it seems that once diluted into the plasticizer, the PEO plays little part in the conduction process. However, this may be of little importance from a device point of view, and suitably plasticized PEO should be regarded as worthy of long term stability testing as an acceptable solid electrolyte for use at temperatures down to 40 °C.

References

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