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THE USE OF THERMAL TECHNIQUES IN THE DETERMINATION OF THE PHASE DIAGRAM OF LANTHANIDE SALT BASED POLYMER ELECTROLYTES

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Differential thermal analysis, optical microscopy and ionic conductivity studies have been carried out on polymer electrolyte films prepared by deposition of solutions of neodymium trifluoromethanesulphonate and poly(ethylene oxide). A wide range of electrolyte concentrations were examined and a partial pseudo-equilibrium phase diagram of the system was determined. From the results obtained it is evident that the presence of relatively high concentrations of ionic guest species in the polymer host results in an inhibition of the growth of crystalline material (polymer spherulites or a polymer–salt coordination complex).

Keywords: neodymium trifluoromethanesulphonate, phase diagram, polymer electrolytes

Introduction

During the last two decades an intense international effort has been invested in the study of a promising class of conducting material designated by the term 'polymer electrolyte' [1]. The members of this class of material permit the migration of ionic species but differ dramatically in their physical and electrochemical properties from conventional liquid or solid electrolytes. The fact that the solvating species in polymer electrolytes is a polymeric medium means that the material is highly processable which is an important advantage in certain technological applications.

One of the most intriguing features of polymer electrolyte materials is their complicated phase behaviour and the effect this has on the electrical and mechanical properties of the material. In most poly(ethylene oxide), (PEO), based electrolytes there are at least three phases present within the temperature and composition ranges of normal operation of electrolyte based devices. The

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principal objective of this study was to use a combination of thermal and electrochemical techniques to determine the form of the pseudo-equilibrium phase diagram of the PEO-neodymium trifluoromethanesulphonate system.

Experimental

A sample of neodymium trifluoromethanesulphonate, (neodymium triflate), was prepared by the direct reaction of trifluoromethanesulphonic acid (Fluorochem 98%) on a slight excess of neodymium carbonate (J. Matthey 99.99%) in a stirred aqueous suspension. The unreacted carbonate was removed from the resulting mixture by filtration and the neodymium triflate was recovered from the clear solution by reducing the solution volume and filtering off the precipitated solid. The composition of the salt prepared in this manner was confirmed by microanalysis of the fully hydrated salt. The poly(ethylene oxide) (Aldrich, MW 5×10^6) used in the preparation of the electrolyte, was dried, at 55°C during one week, under moderate vacuum. As the lanthanide salt was known to be highly hygroscopic [2] the sample was dried at 180°C during 72 hours. This procedure resulted in the removal of the water molecules associated with the salt. All subsequent handling of the components and electrolytes was carried out in a glove box filled with dry argon.

Thin films of electrolytes of different compositions were prepared by the deposition, from acetonitrile (Aldrich HPLC grade) solutions of the components in appropriate proportions. The composition of the electrolytes prepared is conveniently designated by the ratio, n, of oxygen atoms in the polymer to salt cations, i. e. [O]/[Nd]. The solvent used in the preparation of the casting solutions was subjected to a drying procedure which involved prolonged contact with freshly regenerated molecular sieves. The casting solutions were decanted into teflon moulds which were located in an isolated chamber within a preparative glove box. The atmosphere of this chamber was recirculated through a column of molecular sieves by means of a low flow rate, oil-free pump to accelerate the removal of solvent. After solvent removal was complete the films were subjected to a final oven treatment, at 60°C under moderate vacuum for approximately 48 hours, to remove residual solvent. The electrolyte films produced by this process were typically 250 μm thick and of a homogeneous nature. This technique was used in the preparation of 26 compositions with n between 4 and 101.

Discs (10 mm diameter) of electrolyte for conductivity measurements were cut from the polymer films and located between gold electrodes in a purpose-built support which has been described in a previous publication [3]. The use of this design of support ensured that the separation of electrodes was effectively constant during heating cycles and invariant between experiments. The sample temperature was controlled by locating the support within a Buchi TO 50 oven (which was maintained inside a high integrity argon-filled glove-box) and measured with a type K thermocouple positioned close to the electrolyte disc. Total ionic conductivity of the electrolyte sample was obtained through complex impedance measurements using frequencies between 65 kHz and 500 mHz applied with a Solartron 1350 FRA and 1286 Electrochemical interface. Measurements of the conductivity were carried out at 5°C intervals between 25°C and 100°C.

Discs of 5 mm diameter were removed from electrolyte films for thermal analysis which was carried out using heat flux DTA (Mettler TC11 with a Mettler model DSC20 oven) calibrated with an indium standard. Samples were placed in 40 μl aluminium pans with perforated lids under the dry atmosphere of the glove box. The aluminium pans were then sealed and rapidly transferred to the oven where they were maintained in a flow of argon during the analysis.

Small rectangular sections (approximately 4x4 mm) for optical microscopy (OM) analysis were cut from the electrolyte films and located on a glass microscope slide which was placed in a recess in an aluminium heating block. A cover slip was located on top of the sample and a further glass microscope slide was held in place over the cover slip by two spring clips, ensuring that a good thermal contact was maintained between the polymer sample and the heating block. All the samples prepared for OM analysis were subjected to an annealing process at 90°C for 12 hours and then cooled to room temperature in a 3 h interval. The sample, now in the form of a thin translucent film, conveniently spread between the slide and the cover slip, was sealed by applying a trace of rapid curing epoxy resin round the edge of the cover slip. The entire OM sample preparation was completed under a dry argon atmosphere.

Results and discussion

Since the introduction of polymer electrolytes based on PEO in the mid seventies a large number of publications have been produced reporting results obtained with a remarkable variety of guest ionic species [4–6]. In the majority of electrolytes based on commercially available semi-crystalline PEO, the pseudo-equilibrium phase diagram of the systems are fairly simple and, within the composition range of *n* between 100 and 7, have the form of a two component solid–liquid diagram where the components are pure PEO and a complex formed between the PEO and the added salt (Fig. 1). The composition of the complex is partly determined by the physical size of the cation and normally *n* lies between 4 and 10. The form of the log conductivity *vs.* $1/T$ graph is dependent on the crystallinity of the sample of electrolyte studied. Highly crystalline samples of electrolyte normally show linear Arrhenius-type behaviour with an inflexion near the melting point of PEO, while amorphous polymers produce non-linear behaviour. Examples of both these types of graphs are found with the neodymium triflate based PEO electrolyte. Of particular interest is the indication, deduced from conductivity measurements, that the crystallinity of the electrolyte is dramatically altered by the addition of the neodymium salt, and that the kinetics of crystallization of uncomplexed PEO is also retarded as the concentration of salt is increased. This effect was studied by the application of thermal methods.

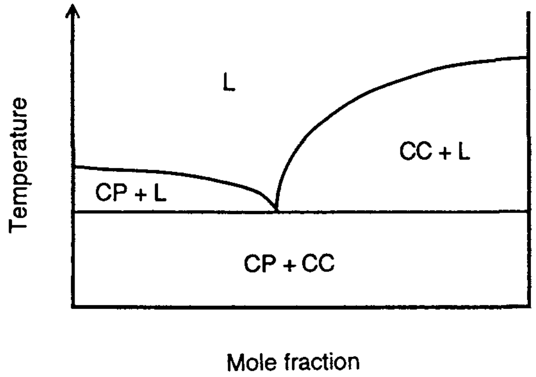

Fig. 1 Schematic phase diagram for a typical polymer electrolyte (L–amorphous melt or liquid phase, CP–crystalline polymer, CC–crystalline polymer–salt complex)

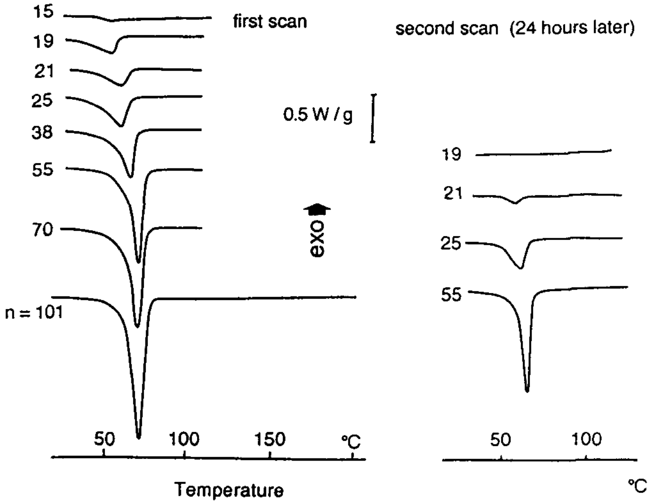

Fig. 2 DTA results for selected electrolyte compositions (*n* refers to the oxygen/neodymium ratio)

Results of DTA experiments are shown in Fig. 2 and demonstrate that a single endotherm is registered between 25° and 200°C and that the onset temperature varies slightly with composition in the range of *n* between 101 and 16. The endset temperature of the endotherm also decreases slightly over this range of compositions. The crystallinity of the samples is significantly reduced as the salt concentration in the polymer is increased and *n* is decreased, and indeed certain samples of *n* less than about 15 have not crystallized during the first year of storage under dry conditions. As a result thermal analysis of electrolyte samples in the composition range of *n* between 15 and 5 show no thermal events between 25° and 200°C, confirming their amorphous character. The analysis of samples by means of hot stage microscopy with crossed polaroids confirms the variation of the melting range quantified by DTA and shows a marked influence of the electrolyte composition on the diameter of the spherulites produced. While in the low salt concentration region of the phase diagram the spherulites are large, as the concentration is increased the spherulite diameter decreases. At low salt concentrations the formation of spherulites is complete within an hour when the sample is maintained a few degrees below its melting point. At higher concentrations of added salt however, the electrolyte shows no indication of spherulite formation even after several hours. This result is qualitatively explained in terms of the presence of the relatively large quantities of added salt impeding the growth of polymer fibrils by restricting access to regions of uncomplexed amorphous polymer.

A further thermal feature of some interest appears in compositions between $n = 30$ and $n = 5$ and is located at temperatures between 100° and 180°C. Expansion of the calorimetric scale of curves registered within this range of compositions shows an extremely broad, low intensity peak. This rather poorly defined peak may be due to either the fusion of the PEO–salt complex or a cooperative, progressive loss of crystalline structure of the PEO spherulites. PEO is known to have an extremely high melt viscosity [7], even at more than one hundred degrees above the melting temperature of spherulites. The fact that the position and intensity of the peak in question is apparently only slightly affected by electrolyte composition leads us to believe that the latter explanation is more correct.

The ionic conductivity behaviour indicates that the complex composition probably lies between 7 and 8, and that the eutectic is located near $n = 15$. The approximate composition of the complex can be identified from the variation of the total ionic conductivity with electrolyte composition as a significant reduction in this parameter is expected when the motion of the polymer chains is restricted through ionic crosslinks. The eutectic composition of the phase diagram is expected to coincide with the location of a maximum in the log conductivity versus composition data as the transport of ions in the polymeric medium is very sensitive to the freedom of polymer chain motion. As the eutectic represents the lowest temperature at which fusion of the solid solution of PEO and polymer–salt complex occurs, a low temperature maximum of total conductivity would be predicted. The structure of the resulting system phase diagram is not very different from that tentatively proposed for other salts of the lanthanide series [8], and similar slow kinetics of crystallization have also been encountered in these systems. Combining the results obtained from conductivity and thermal measurements, it is possible to determine the form of a region of the electrolyte pseudo-equilibrium phase diagram as shown in Fig. 3.

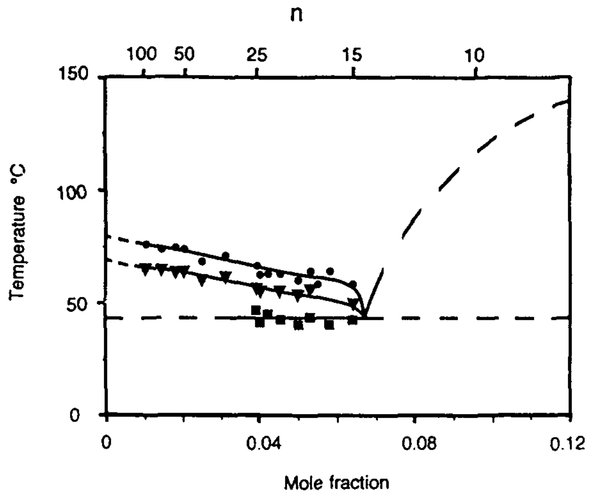

Fig. 3 Partial pseudo-equilibrium phase diagram (DTA onset ■,DTA endset •, and OM ▼)

Conclusion

The most remarkable aspect of the results reported for this polymer system is the width of the amorphous window which extends from $n = 15$ to the composition of the complex at $n = 7$. The total ionic conductivity of the electrolyte is comparable with that reported for other multi-valent salt based electrolytes [8–10] and the location of the eutectic coordinates are not notably different from other electrolytes based on other lanthanide salts [10–12].

Ionic conduction in electrolytes based on PEO, or modified polymers with similar structural elements, is now accepted as occurring within the amorphous phase. As a result, several chemical and physical modifications (such as the use of radiation-induced and chemical crosslinking, the addition of plasticizers, etc.) have been applied to maximize the portion of the amorphous phase. From the results reported in this paper it would appear that the addition of substantial quantities of certain salts can have a similar effect on the crystallinity of the electrolyte produced. Unfortunately the presence of large amounts of added salts also reduces the ionic conductivity of the electrolyte by immobilization of the polymer chains. The usefulness of this means of reducing the crystallinity of electrolytes is thus very limited.

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Zusammenfassung — Durch Abscheidung der Lösungen von Neodymtrifluormethansulfonat und Poly(ethylenoxid) wurden Polymer-Elektrolytfilme hergestellt, die als Untersuchungsobjekt für DTA-, Lichtmikroskopie- und Ionenleitfähigkeitsuntersuchungen dienten. Dabei wurde ein breiter Bereich für die Elektrolytkonzentration untersucht und ein partielles Pseudogleichgewichts-Phasendiagramm des Systemes erstellt. Aus den Resultaten ist ersichtlich, daß die Gegen- wart von relativ hohen Konzentrationen von ionischen Gastspezies in den polymeren Wirtspezies zu einer Hemmung des Wachstumes des kristallinen Materiales (polymere Sphärolithe oder ein Polymer–Salz Koordinationskomplex) führt.