

## **DSC STUDIES OF SOLID POLYMERIC ELECTROLYTES**

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Relations are demonstrated between the conductivity, phase structure and thermal history of some solid polymeric electrolytes. The results obtained for systems based on commercially available polymers, e.g. (ethylene oxide), and for specially synthesized materials are presented. Special emphasis is placed on the correlation between the crystallinity, glass transition temperature, melting temperature and conduction properties of the polymeric electrolytes.

**Keywords:** polymeric electrolytes, poly(ethylene oxide), phase structure, morphology, ionic conductivity, differential scanning calorimetry

### **Introduction**

Solid polymeric electrolytes based on complexes of alkali metal salts with electrodonor polymers have attracted considerable interest among research workers, due to the possibility of their application in various electrochemical devices working at ambient temperatures. It was recognized in an early stage of the investigations of these systems that their physical-chemical properties (mainly ionic conductivity) could be widely modified by changes of the structure and morphology of the polymer hosts [1, 2]. It should be stressed that the phase structure of most of the studied polymeric electrolytes is rather complex and they consist of amorphous as well as crystalline parts [3].

DSC was used for the characterization of polymeric electrolytes in order to establish the phase diagrams of the studied systems [4]. DSC experiments also reveal the degree of crystallinity of the electrolytes and the flexibility of their amorphous phases (by evaluation of the glass transition temperature,  $T_g$ ). DSC provides evidence of the phase separation of the studied systems and of their homogeneity. It has been shown that high values of the room-temperature ionic conductivity of polymeric electrolytes are usually related with a low degree of crystallinity and a high flexibility (low  $T_g$  value) of the polymer host [5]. Addition of alkali metal salts usually leads to an increase in stiffness of macromolecules, due to the cross-linking effect of the cations.

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The aim of the present paper is to show the role of DSC in studies of polymeric electrolytes. Several examples are given of studies on simple poly(ethylene oxide)-based electrolytes and on more complicated copolymer and blend hosts. The ionic conductivity values are compared in detail with DSC data obtained for various electrolytes.

## Experimental

Polymeric electrolytes were prepared by dissolution of a polymer and a salt in acetonitrile. Solid reagents were carefully dried in vacuum ( $10^{-6}$  Torr) at  $70^{\circ}$ – $100^{\circ}$ C for 4–6 hours prior to dissolution. Acetonitrile was vacuum-distilled twice over molecular sieves in order to remove traces of water. NaI, LiBF<sub>4</sub>, LiClO<sub>4</sub> (Fluka, reagent grade) and poly(ethylene oxide) (PEO;  $M_w = 5 \cdot 10^6$  g/mol, Polysciences) were used for electrolyte synthesis. Other polymeric systems (copolymers and blends) were prepared according to procedures described elsewhere [6, 7]. A homogeneous solution of dissolved reagents was poured onto a flat glass or Teflon substrate and the solvent was evaporated in an evacuated desiccator. Finally, polymeric electrolytes were prepared in the form of films 50–100  $\mu$ m thick. Samples were stored at room temperature in a vacuum desiccator for 2–4 weeks before experiments.

DSC investigations were performed in an inert nitrogen atmosphere, using a UNIPAN 605M microcalorimeter connected with an IBM PC AT microcomputer. Samples used for the DSC investigations were in the form of foils 50–100  $\mu$ m thick and their weights varied in the range 15–20 mg. DSC data were recorded in the temperature range from 140 K to 480 K. The heating rate was 2 or 3 deg/min. As a reference,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> or an empty pan was used. All the obtained data were analysed by a DSC analysing program on the microcomputer.  $T_g$  was calculated upon an endothermic shift of the baseline. However, since the obtained curves are usually complicated, the obtained glass transition temperatures were compared with those calculated from the changes in heat capacity of the electrolytes, analysed by a separate computer program. The resulting differences were negligible. As the inhomogeneity of almost all of the studied systems leads to distortion of the DSC curves, it was difficult to achieve full reproducibility of the shapes of the DSC curves, especially at temperatures lower than 273 K. However, the positions of transition temperature peaks and the thermal effects of transitions were reproducible for all of the studied systems. In order to confirm the DSC data, additional NMR and X-ray experiments were performed on some of the studied electrolytes.

Impedance spectroscopy experiments were carried out with a Tesla BM 507 impedance analyser. Samples were pressed between two stainless steel blocking electrodes. All experiments were run under vacuum. Impedance data were analysed by the NLSF program on an IBM PC XT microcomputer.

## Results and discussion

### PEO-alkali metal salt complexes

Figure 1 presents DSC curves obtained for pristine PEO and for PEO-NaI polymeric electrolyte. Two corresponding phase transitions (glass transition of polymer host and melting of crystalline PEO phase) are observed in both curves. Additionally, a melting peak for the crystalline PEO-NaI complex phase is present in the DSC curve of the polymeric electrolyte. The glass transition is shifted to a higher temperature range for the polymeric electrolyte in comparison with the undoped polymer. This effect is connected with the cross-linking tendency of sodium cations, leading to stiffening of the polymer host. The melting peak of the crystalline PEO phase is found at lower temperature in the case of the polymeric electrolyte. This results from the formation of a eutectic between the polymer and the salt. The DSC data also allow calculation of the amount of crystalline PEO phase from a comparison of the melting heat of crystalline phase with that measured for pure crystalline PEO (51 cal/g). The amount of crystalline PEO phase present in the PEO-NaI electrolyte found on the basis of these calculations was 70 mol%, i.e. slightly lower than for the undoped PEO (75–90%, depending on the molecular weight of the polymer and the polymerization procedure).

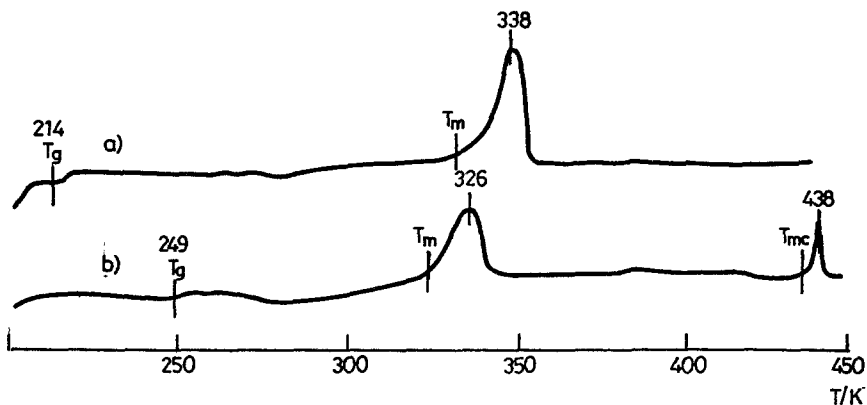


Fig. 1 DSC curves for pure PEO and PEO-NaI polymeric electrolyte containing 10 mol% of the added salt with respect to EO molecular unit concentration

The presented data are consistent with the NMR results [3]. Figure 2 shows the fraction of protons relating to particular phases of the  $(\text{PEO})_{10}\text{NaI}$  electrolyte. Protons were separated into fractions of different mobilities on the basis of the differences in spin-lattice relaxation times  $T_{1\rho}$ . As in the case of DSC experiments, three phases were found: a crystalline PEO phase, a crystalline PEO-NaI complex phase and an amorphous polymer phase. The molar fractions of protons relating to the particular phases vary with temperature. In the range 300–338 K, melting of the crystalline PEO phase is ob-

served. Above this temperature range, only the presence of an amorphous phase and the crystalline complex phase is evidenced. The amount of complex phase decreases, probably due to the dissolution of salt in the amorphous phase. The dissolution is completed at about 430–440 K, which corresponds to the melting temperature found for the crystalline complex phase from DSC experiments. It can be seen from Fig. 2 that the amount of the crystalline PEO phase calculated from NMR experiments is very similar to that found previously from DSC data.

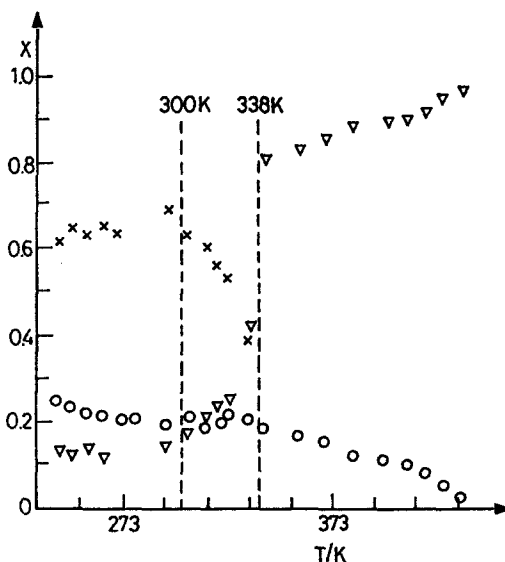


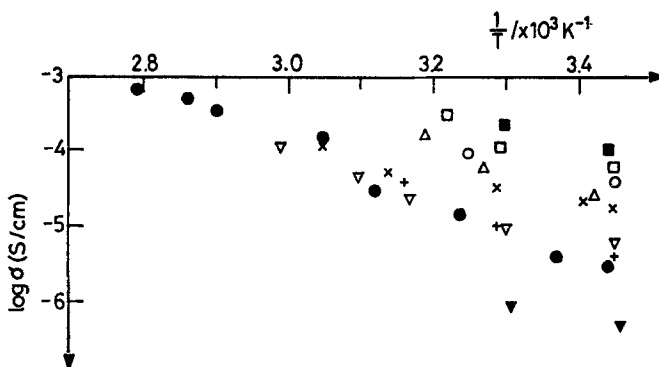
Fig. 2 Fractions of protons in:

[ ∇ ] – amorphous phase, [ o ] – crystalline complex phase, [ x ] – pure crystalline PEO phase, in  $(\text{PEO})_{10}\text{NaI}$  electrolyte

NMR experiments revealed [5] that an amorphous phase of polymeric electrolytes is responsible for fast ionic transport. Moreover, the motion of ions is correlated with the segmental motion of polymer chains. From the above observations, the presence of a highly flexible amorphous polymer phase should facilitate ionic transport in polymeric electrolytes. Unfortunately, as was shown by the above DSC and NMR results, PEO-based electrolytes are highly crystalline at temperatures lower than the melting point of the crystalline PEO phase. In order to improve the ambient-temperature conductivities, a number of methods were applied to obtain polymeric electrolytes in an amorphous form stable at ambient temperatures.

## Copolymer electrolytes

Among a number of methods leading to an improvement in ambient-temperature ionic conductivity of solid polymeric electrolytes, the preparation of ethylene oxide – EO copolymer-based systems seems to be one of the most prospective [8]. Figure 3 shows changes in ionic conductivity vs. reciprocal temperature for EO – propylene oxide (PO) copolymers (EO:PO molecular unit ratio equal to 84:16) doped with LiBF<sub>4</sub>. The salt concentration varied from 1 to 50 mol%. For some of the studied systems, the conductivity exceeded 10<sup>-5</sup> S/cm at room temperature, which is about 2 orders of magnitude higher than for the previously described system based on PEO-NaI complexes. The highest ambient-temperature conductivity was measured for the sample containing 5 mol% of the added salt, and exceeded 10<sup>-4</sup> S/cm at 30°C.



**Fig. 3** Changes in ionic conductivities vs. reciprocal temperature for EO-PO-LiBF<sub>4</sub> electrolytes (EO:PO = 84:16 molar ratio) with various LiBF<sub>4</sub> concentrations: [ o ] – 1 mol% LiBF<sub>4</sub>, [ x ] – 3 mol% LiBF<sub>4</sub>, [ □, ■ ] – 5 mol% LiBF<sub>4</sub>, [ Δ ] – 10 mol% LiBF<sub>4</sub>, [ + ] – 15 mol% LiBF<sub>4</sub>, [ ∇ ] – 20 mol% LiBF<sub>4</sub>, [ ● ] – 25 mol% LiBF<sub>4</sub>

The reasons for such a high increase in conductivity become evident after DSC investigation. DSC results on samples with various LiBF<sub>4</sub> concentrations are included in Table 1. It can be seen that the glass transition temperatures measured for the copolymer systems are about 30–40 deg lower than for the pristine PEO-NaI complex, and comparable to values measured for pristine undoped PEO. An increase in glass transition temperature after addition of alkali metal salt is noted, but it is not so pronounced as in the case of PEO-based electrolytes. The differences in glass transition temperature for samples doped with various amounts of LiBF<sub>4</sub> are small. All the studied electrolytes were X-ray-amorphous. Small melting peaks of the crystalline copolymer phase were observed in the DSC curves. However, due to the distortion of the curves, it was impossible to establish the crystallinity of the studied copolymer electrolytes, on the basis of the DSC results. The melting peaks are shifted to lower temperatures in comparison

with pristine PEO-based electrolytes. This is connected with an increase in amorphous phase content at ambient temperatures and hence with an increase in ionic conductivity. The lowest melting temperature found for the sample containing 5 mol% of LiBF<sub>4</sub> points to the presence of the eutectic near this composition.

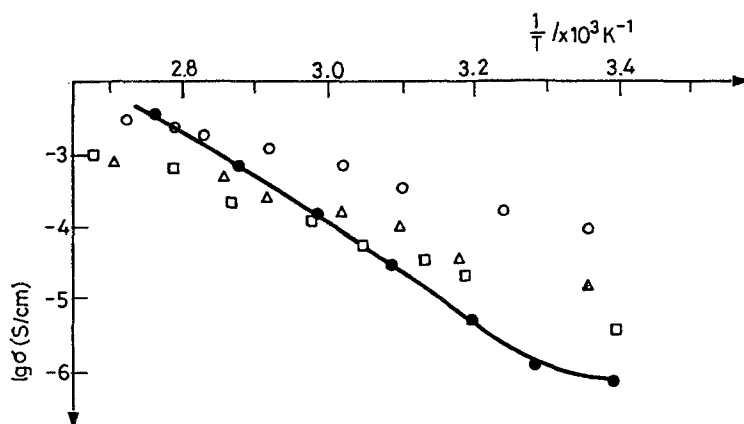
**Table 1** DSC data obtained for EO – PO copolymer solid electrolytes doped with various alkali metal salts (EO : PO molecular unit ratio is equal 84 : 16)

Kind of salt	Salt concentration / % mol	$T_g$ / K	$T_m$ / K
undoped sample	0	200	311
LiBF <sub>4</sub>	1	216	314
LiBF <sub>4</sub>	3	216	311
LiBF <sub>4</sub>	5	208	306
LiBF <sub>4</sub>	10	208	309
LiBF <sub>4</sub>	15	217	–
LiBF <sub>4</sub>	20	214	–
LiBF <sub>4</sub>	25	215	–

salt concentration in respect to copolymer molecular unit concentration.  $T_g$  — glass transition temperature,  $T_m$  — melting temperature of crystalline phase

#### Blend-based polymeric electrolytes

The preparation of blend-based polymeric electrolytes containing PEO as one of blend components seems to be a very simple method leading to the preparation of highly conductive polymeric electrolytes [7]. The conductivity of PEO-PMMA (poly(methyl methacrylate)) blends depends on the molecular weight, the tacticity of



**Fig. 4** Changes in conductivity vs. reciprocal temperature for PEO-PMMA blends (30 wt% of PMMA) doped with LiClO<sub>4</sub> (10 mol%); PMMA of various tacticity: [○] – IPMMA, [Δ] – SPMMA, [□] – APMMA, [●] – PEO-LiClO<sub>4</sub> polymeric

PMMA and the mode of sample preparation [9]. Especially the tacticity of PMMA plays an important role in the conductivity of blend-based electrolytes (Fig. 4). The highest values of conductivity are measured for blends of isotactic PMMA-IPMMA. This is connected with the lowest  $T_g$  values found for these systems (Table 2, Fig. 5) from DSC experiments. The glass transition temperatures measured from PEO-IPMMA blend-based electrolytes are only slightly higher than that for undoped PEO, and are lower than the  $T_g$  values calculated for undoped blends from the Fox equation. This corresponds to the specific morphology of PEO-IPMMA blends found from the experiments of Silvestre *et al.* [10]. IPMMA is situated inside the crystalline structure of PEO fibrils and hence the conducting PEO phase is separated by methacrylic polymer. Such a microstructure leads to a lowering of the cross-linking effect of the added salt, and hence to an increasing segmental motion of the polymer host and electrolyte conductivity. The DSC curves also show broad endothermic peaks in the range 320–420 K. These peaks seem to be attributable to melting of the crystalline PEO phase and the PEO-LiClO<sub>4</sub> complex phase. However, the peaks corresponding to particular phenomena cannot be separated on the basis of the presented results. The obtained data permit only a rough estimate of the content of the PEO crystalline phase, which varied in the range 20–40 mol%.

**Table 2** DSC data for PEO – PMMA – LiClO<sub>4</sub> blend based polymeric electrolytes. PMMA of different tacticity: APMMA – atactic PMMA, IPMMA – isotactic PMMA, SPMMA – syndiotactic PMMA

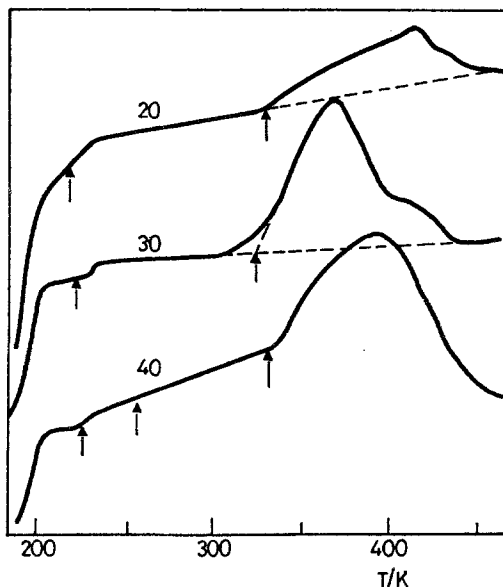
Type of PMMA host	Concentration of PMMA weight %	$T_g$ / K	$T_g^*$ / K
APMMA	20	240	232
APMMA	30	248	247
APMMA	40	260	261
IPMMA	20	216	230
IPMMA	30	220	240
IPMMA	40	228	250
SPMMA	20	246	236
SPMMA	30	249	249
SPMMA	40	252	263

LiClO<sub>4</sub> concentration is equal to 10 mol% – mol in respect to ethylene oxide molecular units concentration.  $T_g$  – glass transition temperature,  $T_g^*$  – glass transition temperature calculated for undoped blends from the Fox equation.

The Fox equation:

$$\frac{1}{T_g^*} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}$$

where  $w_i$ ,  $T_{gi}$  weight ratios and glass transition temperatures of blend components



**Fig. 5** DSC curves for PEO-IPMMA-LiClO<sub>4</sub> electrolytes (concentration of LiClO<sub>4</sub> 10 mol% with respect to ethylene oxide molecular unit concentration). Samples with various concentrations of IPMMA

### *Mixed-phase polymeric electrolytes*

Mixed-phase systems consist of PEO-NaI polymeric electrolyte and SiO<sub>2</sub> powder with grain sizes lower than 5 μm dispersed in the electrolyte structure [11]. The powder is added together with other solid components during preparation of an electrolyte.

Mixed-phase systems exhibit good mechanical properties and a wider temperature range of stability than those of pristine PEO-NaI electrolytes. Addition of an inert ceramic powder leads to serious changes in phase structure and morphology of the polymer host, as can be observed from the DSC results (Table 3). The glass transition temperature shifts to a higher temperature range with increasing SiO<sub>2</sub> concentration. This is connected with the influence of small ceramic particles on the segmental motion of the polymer chains. The small melting peaks of the PEO crystalline phase indicate the low degree of crystallinity of the studied electrolytes. The decrease in melting temperature with increasing SiO<sub>2</sub> concentration is connected with changes in spherulite size. A high concentration of nucleation centres leads to the crystallization of small crystallites, which melt at lower temperatures than high molecular PEO systems. A decrease in crystallinity and changes in the morphology of the polymer host lead to an increase in electrolyte conductivity up to 10<sup>-6</sup> S/cm at room temperature. The DSC results were confirmed by X-ray diffractometry. The decreasing area under the diffraction peaks corresponds to the changes in electrolyte crystallinity. On the other hand, the



increase in half-width of the peaks is related to the decrease in spherulite size. Changes in structure of the mixed-phase systems in comparison with pristine PEO-based electrolytes were additionally confirmed by NMR experiments [11–13]. The NMR data showed an increase in the amorphous phase content [13], which is connected, however, with stiffening of the polymer hosts. The glass transition temperatures calculated from NMR experiments were in the range 260–270 K, i.e. slightly higher than those measured from DSC investigations.

**Table 3** DSC data for PEO – NaI (10 mol% in respect to EO molecular unit concentration) – SiO<sub>2</sub> system

Inorganic powder concentration / wt %	$T_g$ / k	$T_m$ / K
0	214	341
5	251	338
10	259	326
20	264	322

$T_g$  – glass transition temperature,  $T_m$  – melting temperature of crystalline phase

## Conclusions

It was shown that DSC is a powerful tool in investigations of solid polymeric electrolytes. The DSC results support the conductivity and structural data as concerns the explanation of ionic transport phenomena. Some examples of the modification of PEO-based electrolytes demonstrate the crucial role of DSC in the investigations. The DSC data confirmed that a high ambient-temperature ionic conductivity of polymeric electrolytes is usually connected with a low degree of crystallinity of the polymer hosts and their high flexibility (low glass transition temperature). On the basis of the DSC results, some changes in morphology of the studied systems can also be explained. However, it should be stressed that the obtained DSC curves are usually difficult to analyse, mainly because of the complex structure of the studied materials. Accordingly, the presented data are of a qualitative rather than a quantitative character.

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**Zusammenfassung** — Es soll der Zusammenhang zwischen der Leitfähigkeit, der Phasenstruktur und der Thermohistorie einiger fester polymerer Elektrolyte gezeigt werden. Dazu werden Resultate von Systemen auf der Basis im Handel erhältlicher Polymere (z.B. Polyethylenoxid) als auch gesondert hergestellter Materialien dargelegt. Dabei findet die Beziehung zwischen Kristallinität, Glasumwandlungstemperatur und Schmelzpunkt der polymeren Elektrolyten und deren Leitfähigkeitseigenschaften besondere Betonung.