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Some studies in the poly(ethylene oxide)–Zinc chloride system

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The $(PEO)_nZnCl_2$ system, in the range of concentrations $n = 4$–16 has been characterized by X-ray diffraction, TGA/DTA and electrochemical impedance spectroscopy (EIS). Considering these studies and some values reported in the literature a pseudo-equilibrium phase diagram has been drawn. An intermediate compound with a 4:1 composition appears to exist. The EIS conductivity measurements performed after rapid cooling of samples previously heated to above the transition temperature (T_t) indicated that retention of an amorphous phase below T_t is possible for short times.

1. Introduction

Since the initial reports about the ionic conductivity of complexes formed between poly(ethylene oxide), PEO and various alkali metal salts [1, 2], a continuously growing interest has been devoted to the properties and applications of polymeric solid electrolytes [3]. Although most of the work focused on the PEO–Li salts systems, because of their potential applicability in high-energy density batteries [4], several studies have been made with divalent cation complexes [5–12]. PEO electrolytes, particularly at room temperature are composed of crystalline phases owing to crystallites of PEO and polymer–salt complexes, which are dispersed in amorphous regions of solutions of salt in PEO. It is in the amorphous phase that ion conduction takes place. The temperature influences the amount of amorphous phase present, and the phase diagram of the system gives information about the nature, composition and proportions of existing phases in the electrolyte.

In previous studies [13], we have reported basic information on the properties of divalent polymer electrolyte films formed by complexes of PEO and nickel chloride. The study has been extended to PEO/NiI_2, $ZnCl_2$ and ZnI_2 systems. The PEO/$ZnCl_2$ system has been investigated and discussed in the past; nevertheless, it continues to intrigue us and must still be regarded as playing a central role in the divalent polymer electrolyte research and development. The appropriate definition of its phase diagram is clearly necessary. This paper reports thermogravimetry, differential thermal analysis (TGA/DTA), a.c. conductivity and X-ray diffraction studies carried out on $(PEO)_nZnCl_2$, with n varying between 4 and 16, thus leading to the establishment of a pseudo-equilibrium phase diagram that may be related to the system conductivity behaviour.

2. Experimental details

2.1. *Film preparation*

98% $ZnCl_2$ (BDH) and PEO (Aldrich), of 5 000 000 MW were used. The $(PEO)_nZnCl_2$ electrolytes were prepared from acetonitrile (Aldrich 99.9%) solutions by the casting procedure commonly used for the preparation of PEO-based complexes. Methanol (Merck 99.8%) was used too, as a solvent for the 4:1 composition. Appropriate amounts of powdered $ZnCl_2$ and PEO were dissolved in the solvent. Following dissolution of polymer and salt, the viscous solution was poured into 3.5 cm diameter glass cylinders placed on glass plates and into clean glass Petri dishes. The solvent was evaporated at room temperature in a desiccator containing molecular sieves. The final product was a film of thickness in the range 50–100 μm.

2.2. *X-Ray diffraction measurements*

X-Ray diffraction measurements were performed using a Kigaku model D/Max III C automated diffractometer with graphite monochromatized Co radiation. The films were mounted on an aluminium plate with a window for the exposure of X-rays. All measurements were made in air and at room temperature, and the scan speed and range were 2° min^{-1} and 5–50°, respectively.

2.3. *Thermogravimetric/differential thermal analysis (TGA/DTA)*

TGA/DTA curves were obtained using a Stanton Redcroft 706 temperature programmer and data acquisition system calibrated with Zn standard. The films were cut into pieces (typically 10 mg) and loa-

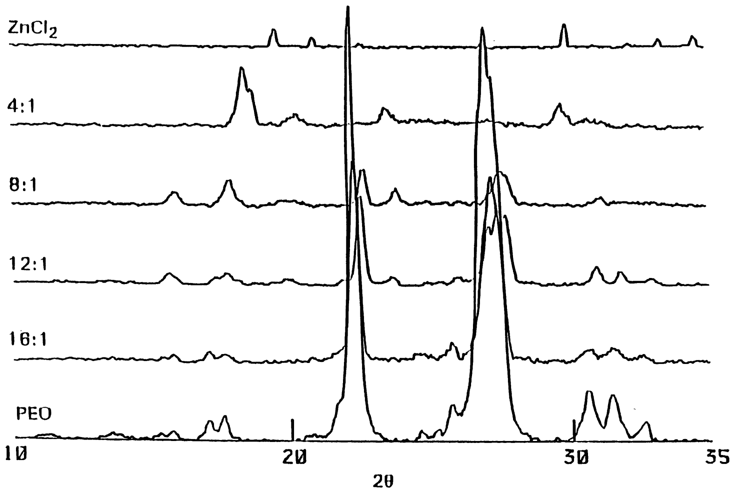

Fig. 1. X-ray diffraction patterns for the PEO/$ZnCl_2$ system. The ratios of PEO to $ZnCl_2$ are indicated.

ded to aluminium pans. An atmosphere of nitrogen was used and the heating rate was 10 °C min^{-1}.

In the majority of cases, thermal cycles (cooling after first heating and second heating) were performed. Cooling naturally took about 30 min.

2.4. *Conductivity measurements*

Polymer film conductivities were determined by sandwiching the zinc complex between two clean parallel symmetrical plane zinc electrodes. The contact area was 6.25 cm^2. The Zn/$(PEO)_nZnCl_2$/Zn sandwich was pressed between acrylic glass plates, allowing electrical contact to the measuring device. The cell assembly was kept in an oven, which enabled the control of the temperature in the range 20–200 °C, with a precision of ±1 °C. The conductivity was obtained by using a Solartron model 1250 frequency response analyser, controlled by a model 9000 HP microcomputer. The impedance response was measured in the temperature range 20–140 °C and in the frequency range 65 kHz–0.01 Hz, at 43 frequencies for each temperature.

3. Results and discussion

Results of the X-ray analysis at room temperature for the $(PEO)_nZnCl_2$ system are presented in Fig. 1. Comparison of the different patterns shows that adding salt to PEO produces peaks superimposed on the characteristics of the pure polymer. The relative intensity of this new pattern gradually increases with the concentration of the salt up to $(PEO)_4ZnCl_2$ electrolyte, whereas that of the PEO decreases, up to the 8:1 (molar ratio polymer to salt) composition. The absence of characteristics' reflections of the pure

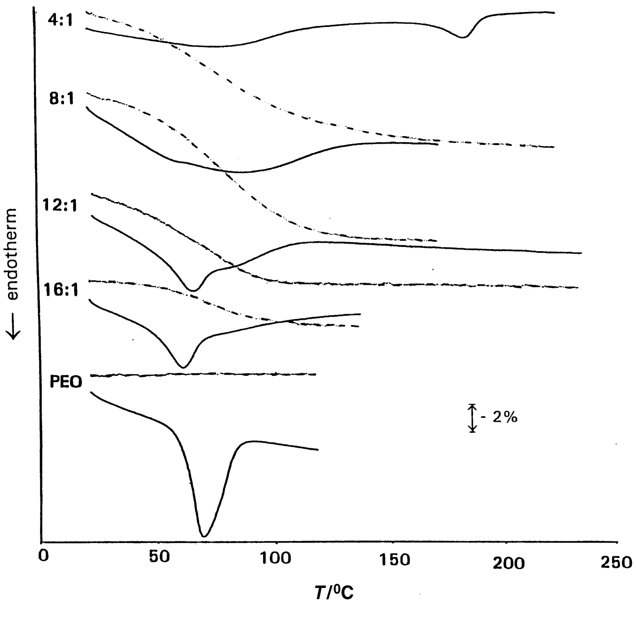

Fig. 2. TGA (dashed line)/DTA (continuous line) traces for the PEO/$ZnCl_2$ system. The ratios of polymer to salt and the scale of weight loss percentage are indicated. The heating rate was 10 °C min^{-1}. For the 16:1 composition, the TGA/DTA was conducted after heating at 120 °C for 4 h and allowing recrystallization for 60 h.

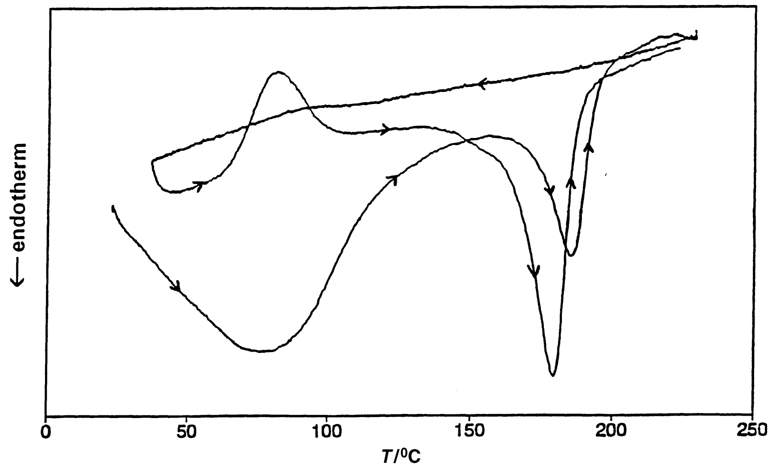

Fig. 3. DTA curve for $(PEO)_4ZnCl_2$ with the first heating, cooling and the second heating.

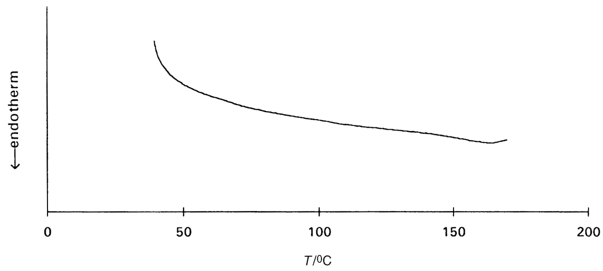

Fig. 4. DTA curve of the $(PEO)_8ZnCl_2$, second heating.

free $ZnCl_2$ salt, indicates that this compound is not present at any composition. All these observations suggest the presence in this system of an intermediate compound with the 4:1 composition.

In agreement with these results are the observations made from the TGA/DTA experiments, shown in Fig. 2. A crystalline phase at the 4:1 composition was identified giving rise to the sharp endotherm with an onset at 172.8 °C. The broad peak at lower temperatures is due only to loss of water and solvent that, in a second experiment (after cooling the sample), is no longer visible (Fig. 3). The endotherm appearing at 37.6 °C, which is almost overlapped by the peak due to loss of water/solvent for the 8:1 composition, is assigned to the eutectic melting of a mixture of the intermediate compound, $[(PEO)_4ZnCl_2]$ and the pure PEO. The melting of the $[(PEO)_4ZnCl_2]$ crystalline phase is better seen in the second heating of the sample, with an onset of ~143 °C (Fig. 4). For the 12:1 and 16:1 compositions only one melting peak is visible, probably because the amount of the intermediate compound is not sufficiently high to be detectable by DTA. This may be a consequence of the water remaining in the samples that provokes the production of larger regions of amorphous phase, reducing the relative amount of crystalline phase. In all compositions, the volatile matter, about 8 % in average and lost below 100 °C, is probably mainly due to the hygroscopic nature of the films.

X-ray diffraction analysis was done after heating the samples above the melting temperatures of the crystalline phases (Fig. 5). The observation that more

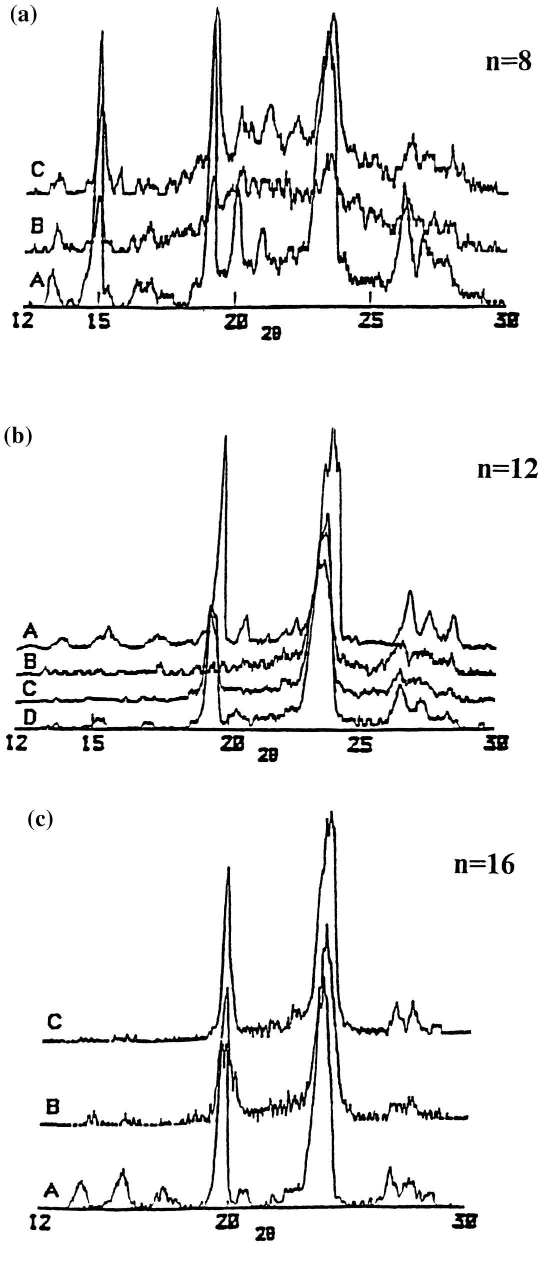

Fig. 5. X-ray diffractograms for $(PEO)_nZnCl_2$ at room temperature (A), and after heating with different cooling times (B, C, D): (a) Heated at 141 °C and cooled for 0.15 h (B) and 48 h (C). (b) Heated at 146 °C and cooled for 0.017 h (B), 0.1 h (C) and 288 h (D). (c) Heated at 75 °C and cooled for 0.2 h (B) and 168 h (C).

time is required for the PEO characteristic peaks to appear in the $(PEO)_8ZnCl_2$ electrolyte than in the more diluted samples, results from the increased difficulty of recrystallization of PEO when the salt is present in greater concentration. On the other hand, for the $(PEO)_8ZnCl_2$ material, the intermediate compound peaks appear after 2 days while for the $(PEO)_{12}ZnCl_2$ electrolyte these peaks are not well defined, even 12 days after heating, because the elastomeric phase is too dilute to allow the rapid recrystallization of the intermediate compound.

Based on the thermal transitions and crystallinities obtained from DTA and X-ray diffraction data presented in this work, and on some results obtained by Glasse *et al.* [14], a pseudo-equilibrium phase diagram has been devised and is presented in Fig. 6. The intermediate compound with the composition 4:1 forms a eutectic, (with PEO), whose melting temperature is about 50 °C and whose composition is near 16:1.

The diagram agrees with results obtained by other authors [14–16]. Wendsjö *et al.* have also found for the 4:1 composition electrolyte, a single crystalline phase due to the complex formed between $ZnCl_2$ and PEO [15]. Yang *et al.* have found the same result [16]. In spite of the different drying conditions used by Glasse *et al.*, the melting temperatures found [14] were little different from our values.

The conductivity of the polymer electrolytes was determined by complex impedance analysis, using nonblocking zinc electrodes. Non ion-impermeable passivating layers on the zinc electrodes were identified by evaluation of the zinc/polymer capacities, which simplified the analysis of the results. Figure 7 shows typical impedance plots obtained at two selected temperatures for the $Zn/(PEO)_8ZnCl_2/Zn$ cell. At 45 °C, two semicircles are displayed and, according to the commonly accepted equivalent circuit, the high frequency semicircle corresponds to the electrolyte impedance and the other, is assigned to the interfacial impedance. At 99 °C, an arc with a 45 ° branch, curving towards the real axis appears at low frequencies, corresponding to the diffusion impedance. The high frequency semicircle almost disappears, but the bulk resistance of the electrolyte may be easily evaluated and the conductivity value determined.

The a.c. conductivity results, obtained during the initial temperature rise are summarized in Fig. 8. The

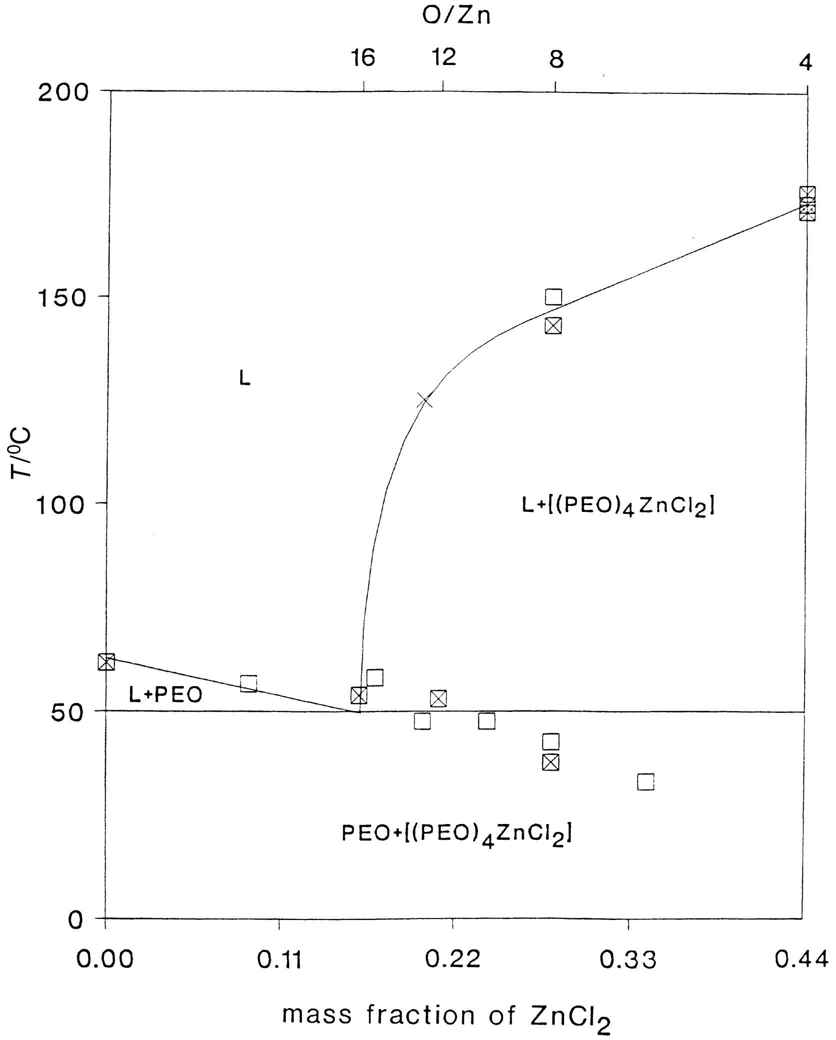

Fig. 6. Pseudo-equilibrium phase diagram of the $PEO/ZnCl_2$ system. L stands for the liquid-like amorphous phase and $[(PEO)_4ZnCl_2]$ is the intermediate compound suggested by the obtained results. Transition temperatures were observed by DTA (our results) ⊠, VTPM ([14]) ×; DSC ([14]) □.

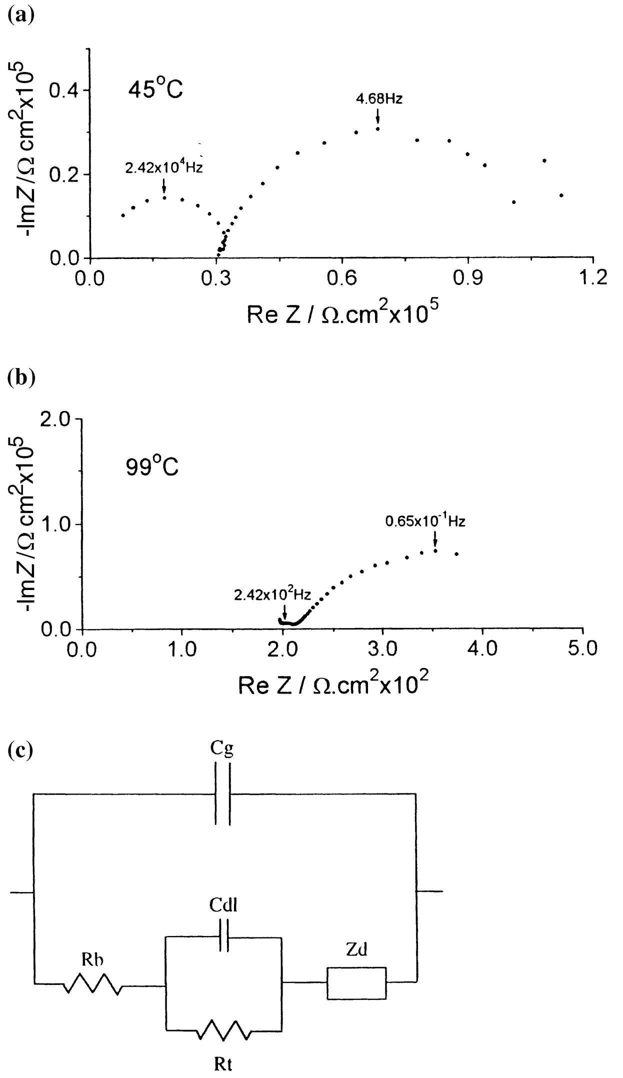

Fig. 7. Complex impedance spectra of a Zn/(PEO)$_8$ZnCl$_2$/Zn cell at 45 °C (a), 99 °C (b) and total equivalent circuit of the cell with the circuit elements: bulk resistance, R_b; geometric capacitance, C_g; charge transfer resistance, R_{ct}; double layer capacitance, C_{dl}; diffusion impedance, Zd (c).

main feature observed is the steep rise in conductivity over relatively small temperature intervals for all compositions except for the 4:1. Discontinuities on the conductivity plots correspond to those predicted by the phase diagram for the melting of the eutectic. The variation of the conductivity in this region is larger for $n = 16$ and lower for $n = 8$, because the mass fraction of the amorphous phase formed when the eutectic melts is larger for the more dilute electrolyte, and smaller for the more concentrated electrolyte. On either side of this transition the relationship exhibited is an Arrhenius type behaviour.

It is known that the state of thermodynamic equilibrium in polymer electrolytes, especially at low temperatures, is difficult to reach, because of the slow nature of the ion-transport mechanisms and crystallization kinetics [17]. Thus, in practice, in an electrolyte formed at the exact composition corresponding to an identified crystalline complex, there are always amorphous phases together with the crystalline material below the melting temperature of the complex. So, it is not surprising, that the temperature dependence of conductivity of the (PEO)$_4$ZnCl$_2$ electrolyte is better described by the VTF equation, supposing that the degree of crystallinity of the electrolyte was not sufficiently high to lead to an Arrhenius conductivity behaviour. Traces of humidity left in the material may again be responsible, in part, due to the amorphicity of the electrolyte.

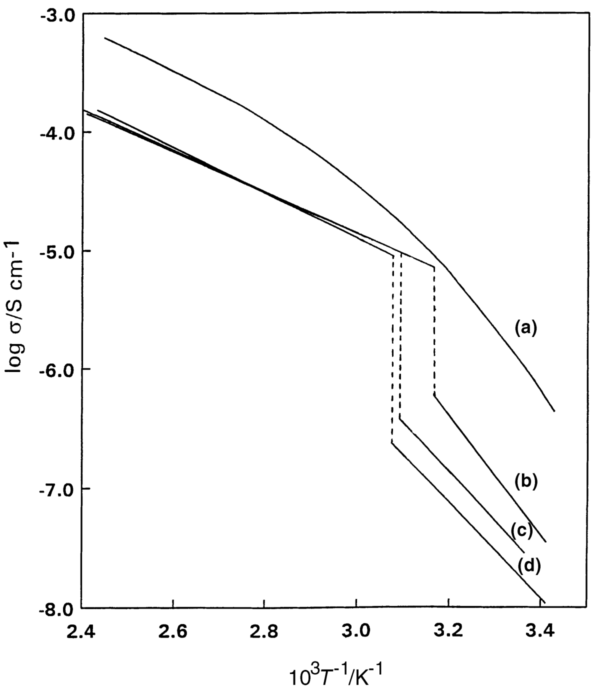

Fig. 8. Temperature dependence of the electrolyte conductivity for the (PEO)$_n$ZnCl$_2$ system. (a) $n = 4$, (b) $n = 8$, (c) $n = 12$, (d) $n = 16$.

The conductivity is maximum for the 4:1 composition electrolyte, in contrast to the conductivity results obtained by Yang *et al.* [16]. In their work, the most conductive electrolyte was (PEO)$_{24}$ZnCl$_2$. The apparent contradiction, is explained by the moisture present in our electrolyte system; this not only destroys the crystalline phase, but has a plasticization effect by increasing the mobility of the polymer chains. Besides the weakening of the interaction between the cations and the ether oxygens provoked by the possible coordination of the zinc ions by the water molecules, another mechanism for the enhancing of polymer chain mobility due to humidity, was proposed by Lauenstein *et al.*, observing the obtained NMR results in the study of the PEO-Pb(CF$_3$SO$_3$)$_2$ system [18]. In the transitions between different conformational states involved in the process of chain mobility, ether oxygen–cation bonds are broken and possibly restored again for a new chain conformation. The energy barrier for this process is lowered by the additional possible coordination sites for the cations, provided by the oxygens of the water molecules and the transitions between conformations are facilitated. This effect is also a possibility for the present polymer electrolyte system. Conductivity also aug-

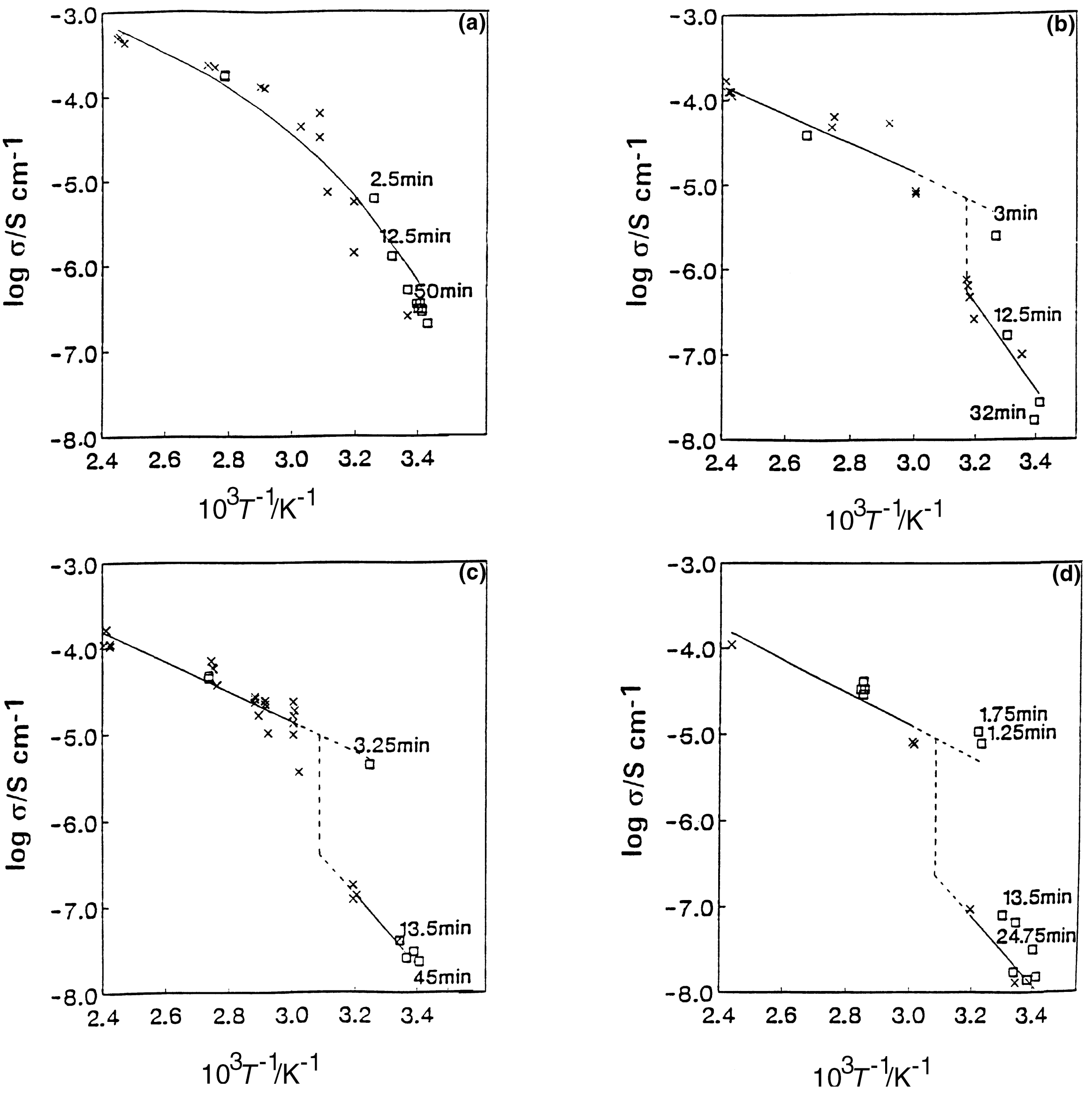

Fig. 9. Electrolyte conductivity of $(PEO)_nZnCl_2$ during heating (×) and cooling (□). Values of the cooling times are indicated. (a) $n = 4$, (b) $n = 8$, (c) $n = 12$, (d) $n = 16$.

ments with hydration through the dissociation of ion pairs, triplets and higher ion aggregates, possibly formed in the polymer electrolytes, less mobile than 'free ions'. This is provoked [19] by the high dielectric constant of the water ($\varepsilon^{20\,°C} = 80.20$). The role of the present moisture in increasing the conductivity, is more determinant for the more concentrated electrolyte, as observed for the PEO–Pb, Zn $(CF_3SO_3)_2$ systems [18]. While dried $(PEO)_4ZnCl_2$ electrolyte [16] shows conductivity values of about 1.5 to 2.5 orders of magnitude smaller than our hydrated electrolyte on going from the higher to the lower temperatures, the conductivity of the dried 8:1 composition electrolyte is about 1 to 1.5 orders of magnitude smaller than our sample, in the same temperature range [16]. For the $(PEO)_{16}ZnCl_2$ electrolyte there is little difference in the conductivity values between the present and Yang *et al.* samples. The conductivity value of dried $(PEO)_9ZnCl_2$ electrolyte obtained by Baril *et al.*, at 80 °C [20], is very similar to the value presented by our hydrated $(PEO)_8ZnCl_2$ electrolyte at the same temperature.

Since recrystallization of the PEO phase melted at the eutectic temperature is not immediate, it was possible to measure the conductivity on that amorphous phase, at temperatures below the transition temperature (T_t), by rapid cooling after heating to a temperature higher than T_t. Data are presented in Fig. 9. As expected, no variation in the conductivity behaviour of $(PEO)_4ZnCl_2$ electrolyte was observed, by taking the measurements after heating the sample to 86 °C, because there was no crystalline to amorphous transition.

In contrast to these results there was an enhancement in the conductivity values taken immediately after cooling from 102 °C ($n = 8$), 93 °C ($n = 12$) and 79 °C ($n = 16$), because the eutectic melted. These values declined in the same fashion as the others at high temperatures (above T_t). After extended cooling times the conductivity of all samples reverted to values near those taken without preheating, which means that the eutectic recrystallized.

This study was extended to another family of PEO based electrolytes with transition metal salts.

4. Conclusions

X-ray powder diffraction and TGA/DTA analyses allowed the construction of a pseudo-equilibrium phase diagram for the $(PEO)_nZnCl_2$ system. The existence of an intermediate compound $[(PEO)_4ZnCl_2]$, was suggested. The retention of the amorphous structure was possible for some time when a specific thermal cycling programme was performed.

The $(PEO)_nZnCl_2$ system exhibits conductivities of 10^{-4} Ω^{-1} cm^{-1} at 90 °C. For the concentrated electrolyte, $(PEO)_4ZnCl_2$, the conductivity was fitted to a VTF equation. For more dilute electrolytes the Arrhenius law seemed more appropriate.

Acknowledgement

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