

Structural Characterization of New Poly(ethylene oxide)-Based Alkaline Solid Polymer Electrolytes

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ABSTRACT: A new class of alkaline solid polymer electrolytes (SPEs) based on poly(ethylene oxide) (PEO), potassium hydroxide (KOH), and water was investigated. The structure of the SPEs was studied by differential scanning calorimetry, thermogravimetric analysis (TGA), X-ray diffraction, and optical microscopy techniques. The existence of a crystalline complex between PEO, KOH, and H₂O was evidenced for some compositions, depending on the O/K ratio. A possible structure was proposed, and a schematic phase diagram was established for this PEO–KOH–H₂O system. The first conductivity measurements also revealed the great interest of these systems, with conductivity values up to 10⁻³ S/cm. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 601–607, 1997

Key words: solid polymer electrolytes; poly(ethylene oxide); potassium hydroxide; structure; crystalline complex

INTRODUCTION

The history of solid polymer electrolytes (SPEs) is less than 20 years old. Although the complexing properties of polyethers, such as poly(ethylene oxide) (PEO), have been recognized for a long time,¹ Wright and colleagues were the first to observe and report the conducting properties of PEO complexes with sodium and potassium thiocyanates and sodium iodide.^{2,3} Almost 5 years later, Armand et al. initiated a tremendous research effort, by first considering those polymer-salt complexes as SPEs with possible applications in secondary batteries.⁴ This motivated the study of a great number of polymer-salt complexes,⁵⁻⁹ and the knowledge has now reached a level which allows the obtention of new materials with desired properties, e.g., high ionic conductivity and

amorphous structure. However, a great effort is still to be done in order to obtain real adequate polymer electrolytes, with low price, no toxicity, and good mechanical and electrochemical properties for applications in thin film batteries. A few years ago, our research team studied and patented KOH-, H₂O- and PEO-based SPEs,^{10,11} and we have been dealing with this area since that time.^{12,13} Such alkaline SPEs represent a new class of materials, because of their composition, their preparation mode, and the fact that the polymeric matrix is not modified in any way. No mention could be found in the literature of PEO/KOH mixtures meeting these requirements. Their advantages, such as an easy preparation, the low price, the abundance of their basic components, and their high ionic conductivity at room temperature, make them attractive materials for applications in batteries. However, in order to establish a correlation between the composition and the conducting behavior, it is necessary to improve

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the knowledge of their structure. We present here a thorough study of the structure of this new family of SPEs.

EXPERIMENTAL

Commercial PEO (Fluka; average molecular weight, 20,000) and potassium hydroxide (Fluka) were used as starting materials. The compositions were prepared by direct mixing of the components at approximately 90–100°C; they were then allowed to cool slowly at room temperature.

The calorimetric experiments were performed on a Perkin-Elmer DSC 2C apparatus with large-volume stainless steel capsules. The heating rate for all experiments was 10°C/min, whereas the cooling rate was varied in order to study its influence on the thermal properties of the electrolyte. The temperature range was –3–177°C for the determination of melting temperatures and –103––3°C for the study of glass transition temperatures. All samples were run at least three times over the indicated temperature range. The temperatures reported in this study are onset temperatures ($\pm 0.1^\circ\text{C}$).

TGA experiments were also carried out on a DuPont 9900 thermobalance under a dry nitrogen atmosphere, with a heating rate of 20°C/min and with platinum pans. X-ray experiments were performed on two different pieces of equipment: a Philips goniometer using the reflection technique for the experiments at room temperature, which were performed on powders, and a Synchrotron (LURE, Orsay) beam using the transmission technique for the experiments at high temperatures. The wavelength of the radiation is $\lambda = 0.154$ nm for the reflection technique and $\lambda = 0.145$ nm for the transmission technique. The X-ray spectra reported here use a θ (degrees) scale ($\pm 0.1^\circ$).

Some optical microscopy experiments under polarized light were also performed with a Leitz microscope with a heating sample holder and cross-polarizer and equipped with a camera. The samples were heated up to approximately 150°C and then allowed to cool slowly. Each time a new phase appeared, a photograph was taken and the temperature was picked up.

RESULTS AND DISCUSSION

The thermal properties of a great number of compositions were investigated by use of the differen-

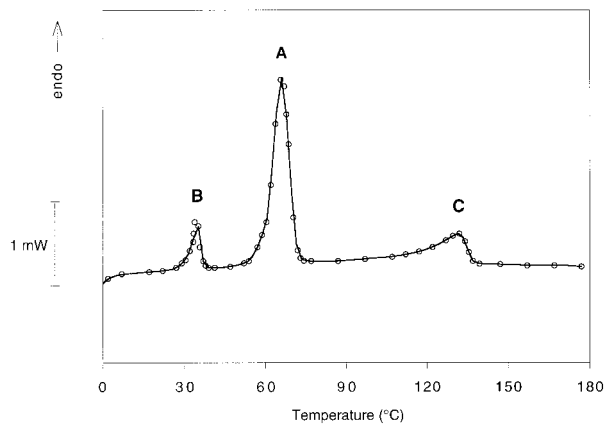


Figure 1 Typical DSC trace of a SPE containing 10 wt % water ($\text{O}/\text{K} = 2.55$).

tial scanning calorimetry (DSC) technique. The SPEs contained 10 or 20 wt % water, and the PEO/KOH weight ratio varied. In order to allow accurate comparisons of the compositions, we will further use the O/K ratio, which is the molar ratio of the heteroatoms in the polymer backbone to the potassium cations. The main results of the study are the following (for peak definition, see Fig. 1).

1. Each sample exhibited, on heating, a sharp endothermic transition (A) at a temperature of approximately 60°C, whatever the composition or the cooling rate of the sample, except for a few compositions containing a great amount of water (20 wt %) and no or few KOH (molar ratio $\text{O}/\text{K} > 9$), where the transition temperature was lower (Fig. 2). Also reported in Figure 2 is the melting temperature of pure PEO; it is identical to the transition temperature of peak A so that this endothermic transition observed in the SPEs can be attributed to the melting of a quasipure crystalline phase of PEO. This is further confirmed by the results concerning the crystallinity of this phase. The calculations using the enthalpy (peak area of endotherm A) related to the amount of PEO in the SPE allowed the determination of the crystallinity, using the theoretical value of a 100% crystalline PEO of 210 J/g.¹⁴ The results are shown in Figure 3, where the values for pure PEO and PEO/water mixtures are also indicated. A great similarity between both values is observed, which confirms

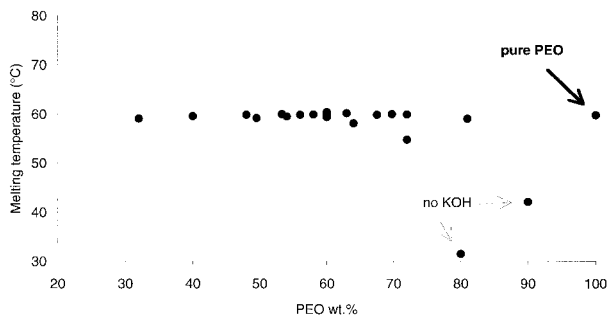


Figure 2 Melting temperature of endotherm A versus PEO wt % for different SPEs.

that a pure crystalline phase of PEO remains practically unchanged in all SPE compositions.

- In some SPEs, two other endothermic transitions were also observed—the first one (B) at approximately 27–32°C, and the second one (C) at a temperature higher than the melting of the PEO phase, typically between 82 and 147°C. The temperature of the second endotherm varied significantly with the composition, whereas the first endotherm always appeared at the same temperature (Fig. 4). The relative importance of both transitions also varied with the composition of the sample, as well as with the experimental conditions (initial temperature and cooling rate). The endotherms were indeed only observed for compositions highly concentrated in KOH, typically with $O/K < 5$ for 10 wt % water compositions and $O/K < 2$ for SPEs containing 20 wt % water. It also appeared that a low cooling rate simultaneously decreased the temperature and the enthalpy associated with endotherm C and slightly

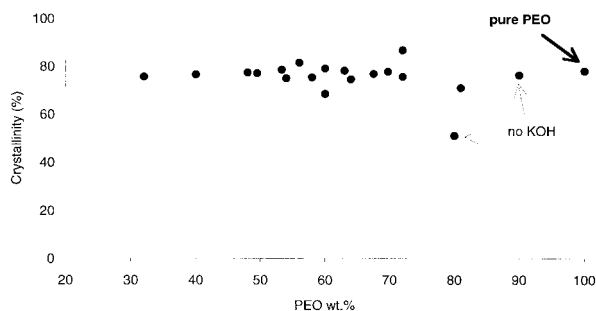


Figure 3 Crystallinity of the PEO phase versus PEO wt % for different SPEs.

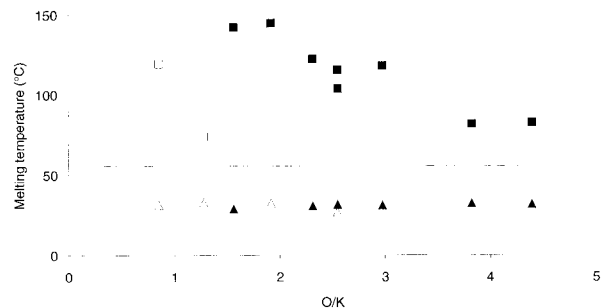


Figure 4 Melting temperature of endotherms (triangles) B and (squares) C versus molar ratio O/K . Closed symbols, 10 wt % water; open symbols, 20 wt % water. The dashed line stands for the melting temperature of pure PEO.

increased the enthalpy of endotherm B without significantly modifying its onset temperature. The experiments carried out with different initial temperatures showed that the first endotherm at about 27–32°C is only present when the initial temperature is lower than ca. 7°C. Furthermore, the necessary initial temperature to reach for the first endotherm to be present decreases as the KOH concentration increases.

These results led to the following hypothesis. The second endotherm C seems to be associated with the melting of a crystalline complex containing PEO, KOH, and possibly water. The formation of such a complex is frequently observed with PEO-based SPE containing alkaline salts.^{15–17} The melting temperature of the complex, as well as its melting enthalpy, decreases with increasing O/K ratio, tending to reach the melting temperature of the PEO phase when no KOH is present. This is the expected behavior, and it suggests that a minimum amount of KOH is necessary for the crystallization of the complex to occur. Below this minimum concentration, KOH is fully solvated by the polymeric matrix and/or the water present and no crystallization can be observed. Moreover, the observation that a pure crystalline polymeric phase A remains almost unchanged by the presence of the salt seems to suggest that the formation and crystallization of the complex surprisingly occur with the contribution of the amorphous phase of the PEO.

The fact that endotherm B always appears at the same temperature in all compositions sug-

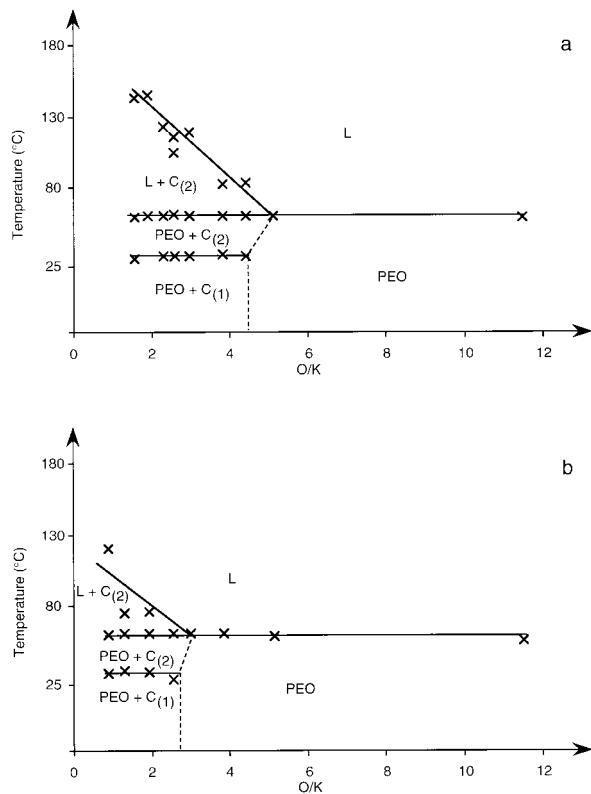


Figure 5 Suggested phase diagrams for SPEs containing (a) 10 wt % water, (b) 20 wt % water. L, liquid; $C_{(1)}$, complex (form 1); $C_{(2)}$, complex (form 2).

gested a solid–solid transition. This could be a reorganization of the complex or the transition between two complexes of different well-defined stoichiometries, possibly involving water. The first form of the complex, which only appears at sufficiently low temperature, seems to be favored by slow cooling of the sample. The transition temperature is very close to room temperature, so that this form of the complex is stable only at low temperatures. This is confirmed by the first-heating DSC traces, which usually show no endotherm at 27–32°C. These DSC results allowed us to suggest a phase diagram for the PEO–KOH–H₂O compositions (see Fig. 5).

The experiments carried out at very low temperature in order to determine the glass transition temperature T_g of the SPEs also indicate the same trend. All values determined turned out to be smaller than the T_g of pure PEO. In order to allow accurate comparisons, T_g was also measured for PEO–water compositions, without KOH. The results indicate that, in the SPEs without crystalline complex phase (e.g., O/K = 5.1),

T_g is lower than that of pure PEO containing the same amount of water (Fig. 6); it seems that there is a combined plasticizing effect of KOH and water. On the other hand, for the compositions with a certain amount of crystalline complex (e.g., O/K = 1.55), the melting temperature of which is higher than that of pure PEO, T_g is found to be greater than expected (Fig. 6). The crystallization of the complex, which we showed occurs in the amorphous phase of the SPE, seems to hinder chain flexibility, thus increasing the glass transition temperature; the related transition is then strongly diminished. One of the studied compositions showing high complex content (with a high melting temperature) even exhibits a second T_g at a temperature significantly higher, suggesting that a multiphase material is obtained. Generally, most values of T_g range from approximately –83 to –68°C, whereas T_g of pure PEO is measured at about –53°C.

This behavior is significantly different from the reports in the literature, which usually describe an increase of the glass transition temperature of the polymeric matrix when an alkaline salt is added. It seems that the main point in our systems is the presence of water, although its precise role has not been fully described. However, the experiments carried out on the PEO–water compositions allowed us to reach some important conclusions: in the 10 wt % system (see Fig. 6), no crystallization (or fusion) of the water is observed on heating, which means that the water is certainly bound, because of its dual role as a solvent of both

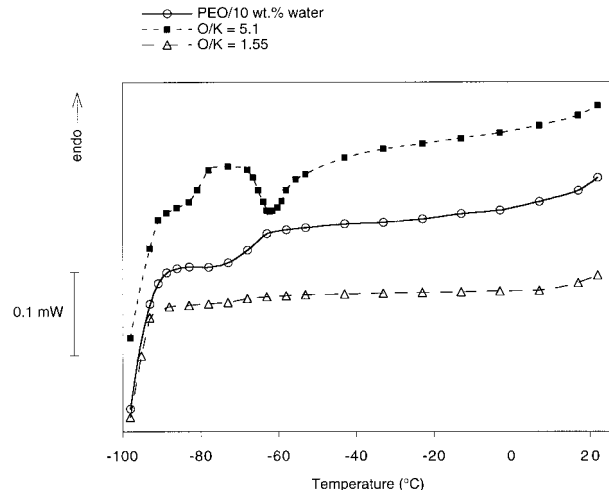


Figure 6 DSC traces showing glass transitions for different systems.

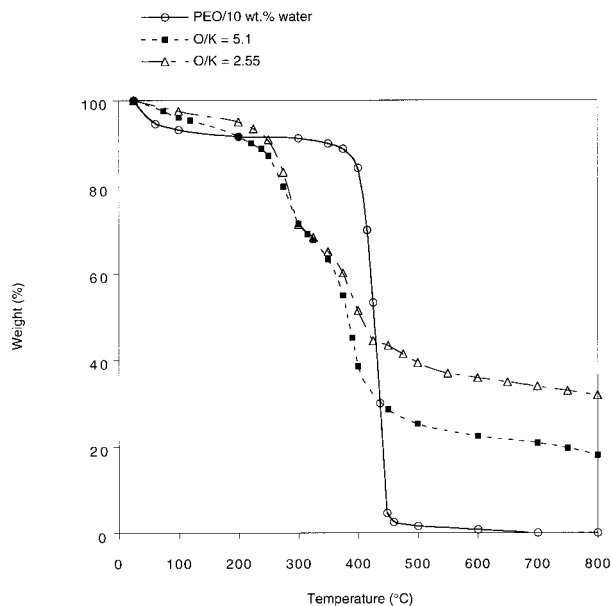


Figure 7 TGA curves of different systems.

the polymer and the salt. In the 20 wt % system, a crystallization, immediately followed by a fusion, is observed on heating, but the melting temperature of the water is as low as -15°C , much lower than the fusion of free water. The compositions containing KOH sometimes exhibit a crystallization immediately after the glass transition (probably a reorganization phenomenon), but no fusion of any kind is observed, even in the 20 wt % compositions. This confirms that the water is mostly bound and is significantly involved in solvating phenomena. This study is still under progress, and we are investigating anhydrous compositions prepared using the dissolution-evaporation technique.

The TGA experiments also reveal differences between the compositions which contain a crystalline polymer-salt complex phase and those which do not (Fig. 7). When no crystalline complex is present (e.g., $\text{O}/\text{K} = 5.1$, no endotherm C in the DSC experiments), the weight of the sample slowly decreases by an amount corresponding to the water content of the sample. Two steps are then observed in the TGA curves, one with a maximum degradation rate at approximately 280°C and the other one between 380 and 400°C . The comparison with the behavior of pure PEO indicates that these degradation temperatures are significantly lower than the only temperature observed in the one-step degradation process for the pure matrix (435°C). The same experiments car-

ried out with the related PEO-water compositions also exhibit a one-step process at temperatures between approximately 425 and 431°C . These results are in agreement with other SPE systems where the presence of an inorganic salt usually decreases the degradation temperature of the matrix, as a result of interactions between the polymer backbone and the solvated ions.¹⁸

On the other hand, when compositions that contain crystalline complex are studied (e.g., $\text{O}/\text{K} = 2.55$), a third step in the degradation mechanism is observed with a maximum rate at about 500°C . No firm explanation has been given to this phenomenon, which is still under investigation. It is likely that, in both cases, the first degradation step corresponds to the decomposition of the PEO phase, while the other steps result from further degradation of the decomposition products. However, it is important to notice that a significant difference can be observed in the degradation behavior of the two classes of SPEs, with or without crystalline complex.

X-ray experiments were also carried out on the compositions in order to further confirm the proposed hypothesis for the structure of the SPEs. Mainly, two results were obtained (Fig. 8)

1. The two major peaks observed in the X-ray pattern of pure PEO at 9.5 and 11.5° are present and of significant importance in all compositions. On the contrary, none of the major peaks from the X-ray pattern of KOH is observed as a major peak. Some peaks originating in the pure KOH pattern can, however, be observed as very small peaks in some compositions. Moreover, several peaks with important intensity can be found on the spectra of some compositions which do not originate in the PEO or in the KOH. These peaks are approximately at 17.1 , 17.6 , and 18.2° (bold lines on Fig. 8). The intensities of these peaks decrease with increasing O/K ratio. This behavior can be directly related to the observations made in the DSC experiments, and we can assume from the X-ray data that the peaks observed near 17 – 18° probably correspond to the presence of the complex form previously mentioned. This attribution is confirmed by the comparison with experimental spectra of crystalline complexes $\text{KOH}\cdot x\text{H}_2\text{O}$, which exhibit peak val-

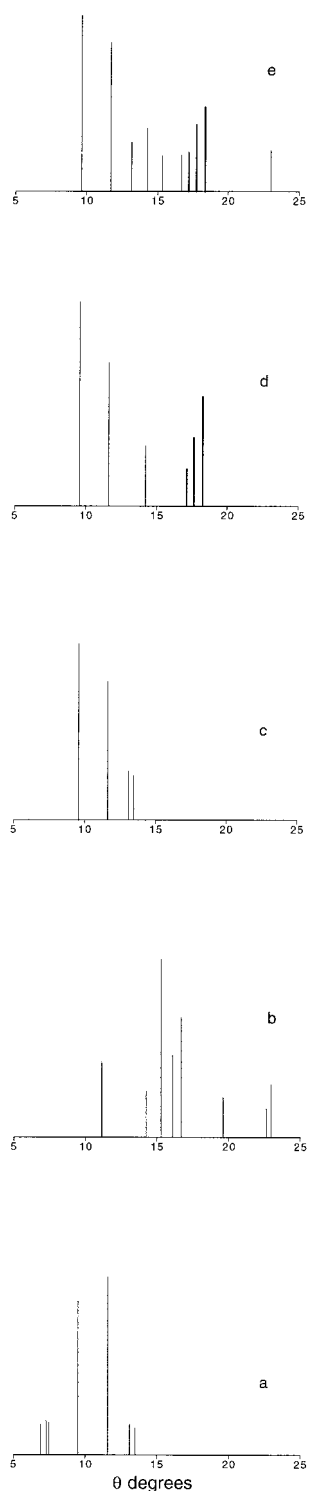


Figure 8 Schematic X-ray spectra of (a) PEO; (b) KOH; SPEs containing 10 wt % water: (c) O/K = 5.1, (d) O/K = 3.83, (e) O/K = 2.55.

ues different from the ones observed in our case.

2. The experiments carried out at higher temperatures also support this hypothesis. Indeed, it was observed that the spectrum of a typical O/K = 2.55 and 10 wt % water composition at approximately 80°C, i.e., after the melting temperature of the PEO phase, still exhibits several peaks, showing that a partial crystallinity remains which cannot be due to the PEO. This crystalline part can be attributed to the complex, which the DSC experiments indicate melts at higher temperature. As expected, the X-ray experiments performed at 150°C show no residual crystallinity.

The photographs taken during optical microscopy experiments also exhibit sharp differences between the compositions. In some SPEs, namely those which only show one endotherm (A) in DSC experiments, only one crystalline phase appears at approximately 60°C and it is very similar to the crystalline phase of PEO, i.e., it exhibits a spherulitic-type crystallization (typical Maltese cross). In the case of the SPEs where an endotherm corresponding to the polymer-salt complex is present (C), two different phases can be observed on cooling. The phase which crystallizes at higher temperature ($T \approx 110^\circ\text{C}$) is quite different from the spherulitic type. Indeed, the photographs show a phase without radial orientation (no Maltese cross). The second phase crystallizes at a lower temperature ($T \approx 60^\circ\text{C}$) and is similar to the spherulitic type of PEO. Such morphology containing two crystalline phases was already observed in the case of PEO-Li salt compositions.¹⁹

CONCLUSION

The investigation of this new family of PEO-based alkaline electrolytes containing potassium hydroxide and water is only at its beginning, but the first conductivity measurements (which will be reported elsewhere) revealed the great interest of these materials for applications to secondary batteries. Indeed, the conductivity at room temperature can reach 10^{-3} S/cm for some compositions. The study of the structure of these SPEs was performed in order to establish the relationship between structure and conducting properties. We showed that there are mainly two types

of electrolytes, those which contain a crystalline complex and those which do not, depending on the amount of water and the O/K molar ratio. They exhibit an uncommon behavior in comparison to conventional PEO-based SPEs, regarding their structure as well as their electrochemical properties. In particular, the formation of the crystalline complex seems to occur in the amorphous phase of the PEO without modifying its crystalline phase. More investigations are under progress concerning the following aspects: the quantification of the relative solvating properties of PEO and water toward potassium hydroxide, the accurate characterization of the complex in its two forms (e.g., the determination of the lattice parameters) using X-ray, and scanning electron microscopy techniques, and the influence of the SPE composition on its conducting properties.

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