Polyether-based ion conductors
1. Structural and morphological characterization of precursor systems based on poly(ethylene oxide), polyphosphazene and polyepichlorhydrine

C. del Rio, J. L. Acosta
Instituto de Ciencia y Tecnologia de Polimeros (C.S.I.C.), Juan de la Cierva, 3, E-28006 Madrid, Spain

Received: 9 September 1996/Revised version: 22 October 1996/Accepted: 25 October 1996

Summary
In this work the preparation of polymer electrolyte precursor systems was carried out by means of the physical blending of poly(ethylene oxide) (PEO), a poly(fluoroalcoxi phosphazene) (PPz) and poly(epichlorhydrin) (PECH). The aim was to achieve the compatibilization of the PEO/PPz system over the third component addition. Thermal behaviour study, isothermal crystallization kinetics and spherulitic growth of these binary and ternary blends were conducted with the purpose of gaining insight into the microstructure and the morphology of these materials as a prerequisite for the polymer electrolyte development.

Introduction
In recent times a growing interest has been observed in the study of systems based on polyethers acting as polymer electrolytes in solid state batteries (1-5), taking into account that they combine the excellent properties of polymer materials (low weight, good mechanical properties, easy moulding, etc.) with the good electrical properties of liquid electrolytes. At present such batteries qualify as promising candidates for new sources of energy capable of contributing to the solution of urgent problems such as energy saving and environmental control. This is the reason why they have been included with a high priority in the major European and American research programmes (6-8).
In this work a new route for the synthesis of electrolytic polymer precursors is developed, based on previous physical compatibilization of an incompatible blend of two polymers (a polyether and a polyphosphazene) through the incorporation of a third polymeric component. This approach allows us to gain insight into the morphological and structural changes which occur in the originally incompatible blend when incorporating the third macromolecular component. The objective pursued with the synthesis of these polymer electrolyte precursor systems is to succeed in reducing or minimising the interfaces existing in incompatible blends. Interfaces, which by and large, upon salt incorporation, inhibit and constrain cation transfer and movement along the polymer chains, and hence ionic conductivity.

Experimental
The following commercial polymers were used: poly(ethylene oxide) (PEO) ($M_w=5\times10^6$) from Aldrich, poly(octafluoropentoxytrifluoroetoxyphosphazene) (PPz) supplied by Firestone with the commercial name of PNF-200 and poly(epichlorhydrin) (PECH) ($M_w=7\times10^5$) also from Aldrich.
The blends were obtained by dissolving the appropriate polymer amounts in mixtures of acetonitrile and chloroform, ensuing solvent evaporation and drying the samples under high vacuum conditions until constant weight was achieved.
Thermal behaviour was measured with a differential scanning calorimeter Mettler TA-4000. The samples were held at 100°C for 5 minutes in order to delete their thermal history and then cooled down to -100°C using a rate of 10°C/min. The melting temperature was recorded from -100°C to 100°C at a rate of 10°C/min.

Isothermal crystallization was analyzed in a Mettler differential scanning calorimeter model TA-4000. The samples were heated to 100°C where they were held for 5 minutes. Then they were rapidly cooled down (100°C/min) to their crystallization temperature. Once the samples had completely crystallized, they were brought to their melting point at a rate of 10°C/min. Spherulite growth was monitored under a Leitz Aristomet microscope coupled to a hot stage Mettler FP82HT, a Mettler FP90 central processor and a video system Hitachi KP-111. The samples were heated to 100°C for 5 minutes and then they were cooled down to the crystallization temperature where the spherulitic radii were measured as a function of time.

Results and discussion
Thermal behaviour
The study of the thermal behaviour of these polymer electrolyte precursor systems is of decisive relevance, considering that the principal factors with effects on cation mobility through the polymeric membrane are crystallinity and glass transition temperature, as ion transport is known to take place in the amorphous phase (9). If it were possible to synthesize a polymer precursor with a low Tg and very low or nil crystallinity, the final polymer electrolyte (once the salt has been incorporated) should possess higher conductivity values, as it is based on systems with a high chain flexibility in which ion transfer is favoured when the crystalline zones, which act like barriers, diminish or even disappear, so that ionic conductivity is, in fact, potentiated.

Table I compiles the crystallization and melting temperatures for the systems under study. It can be seen that both parameters diminish, for all blends, as compared to pure PEO, which is indicative of partial system compatibilization.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Tc (°C)</th>
<th>Tm (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO</td>
<td>44.1</td>
<td>69.7</td>
</tr>
<tr>
<td>PEO/PPz 75/25</td>
<td>40.2</td>
<td>68.6</td>
</tr>
<tr>
<td>PEO/PPz 50/50</td>
<td>38.3</td>
<td>68.0</td>
</tr>
<tr>
<td>PEO/PECH 75/25</td>
<td>35.9</td>
<td>70.6</td>
</tr>
<tr>
<td>PEO/PECH 50/50</td>
<td>29.5</td>
<td>63.5</td>
</tr>
<tr>
<td>PEO/PPz/PECH 66/17/17</td>
<td>41.0</td>
<td>67.0</td>
</tr>
<tr>
<td>PEO/PPz/PECH 50/25/25</td>
<td>39.9</td>
<td>65.7</td>
</tr>
</tbody>
</table>

Isothermal crystallization
The isothermal crystallization kinetics of all systems was analyzed applying Avrami’s equation (10):

\[ X_p = 1 - \exp(-Kt^n) \]  

(1)