Polyether-based ion conductors

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

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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) ($M_w=5\cdot10^6$) from Aldrich, poly(octafluoropentoxytrifluoroetoxyphosphazene) (PPz) supplied by Firestone with the commercial name of PNF-200 and poly(epichlorhydrin) (PECH) ($M_w=7\cdot10^5$) 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 analized 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 I.- Thermal behaviour of the blends.

SAMPLE	Tc (°C)	Tm (°C)
PEO	44.1	69.7
PEO/PPz 75/25	40.2	68.6
PEO/PPz 50/50	38.3	68.0
PEO/PECH 75/25	35.9	70.6
PEO/PECH 50/50	29.5	63.5
PEO/PPz/PECH 66/17/17	41.0	67.0
PEO/PPz/PECH 50/25/25	39.9	65.7

Isothermal crystallization

The isothermal crystallization kinetics of all systems was analized applying Avrami's equation (10):

$$X_T = 1 - \exp(-Kt^n) \qquad (1)$$

where $\underline{X_T}$ is the weight fraction of the crystallizable material at time t, $\underline{K}$ stands for the rate constant and $\underline{n}$ is the Avrami exponent which depends on the type of nucleation and the growth geometry of the crystals.

The values of $\underline{K}$ and $\underline{n}$ were obtained for each crystallization temperature from the Y-intercept and the slope, respectively, of the plot of $\log(-\ln(1-X_T))$ versus log t.

Figure 1 shows, by way of example, one of these graphs as evidence that these systems comply with Avrami's equation.

The kinetic isothermal crystallization parameters are compiled in Table II. Figure 2a shows a variation of the rate constant logarithm plotted against blend composition, expressed as the percentage of crystallized polymer, at crystallization temperature of 52°C. When a polymer crystallizes in the presence of another polymer, which acts as a total or partial

Figure 1.- Avrami's plot of PEO/PPz/PECH 66/17/17 blend.

dilutant, two processes may occur, both with a direct impact on the crystallization rate. On the one hand, a nucleating effect may take place, which will increase the number of nuclei as compared to those formed in the absence of the diluting polymer at one and the same crystallization temperature. This nucleating effect translates into a higher crystallization rate. On the other hand, an inhibitor effect may be present reducing the number of nuclei, which, in turn, will slow down the crystallization rate. If the polymer crystallizes in the presence of another, with which it forms a totally incompatible blend, the crystallization rate should not be influenced by the presence of the second component. In our case and referring to the binary
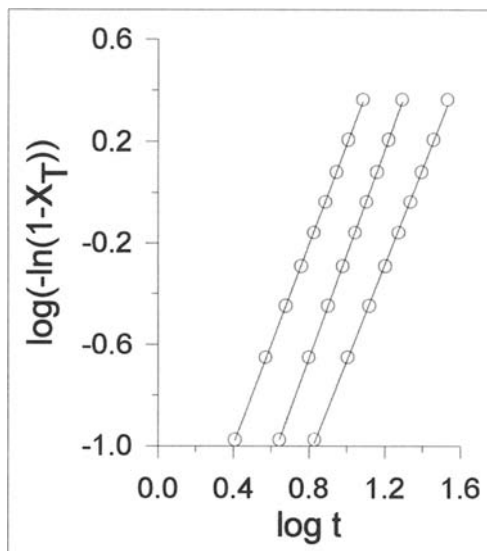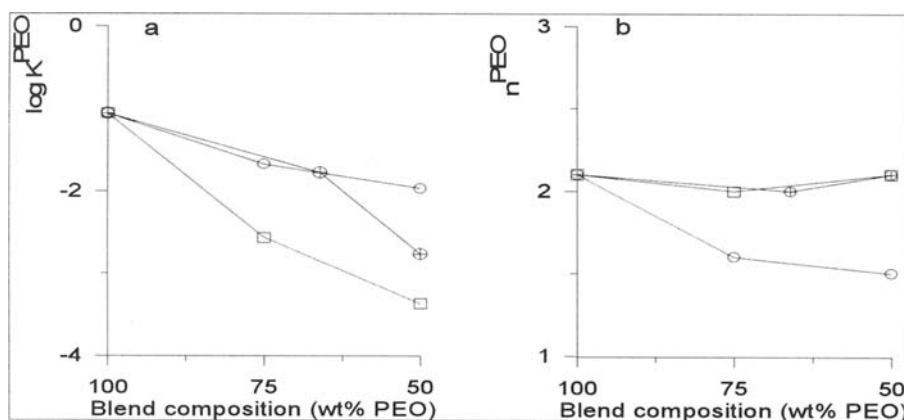

Figure 2.- Log K (a) and n (b) as a function of blend composition for: PEO/PECH (□), PEO/PPz (○) and PEO/PPz/PECH (⊕) at 52°C.

blends in the first place, as can be observed in figure 2a, both PPz and PECH cause the PEO crystallization rate to vary as a function of blend composition. Log K decreases inversely proportionate to the increase of the second component in the blend, a regularity which is especially prominent in the PEO/PECH systems. These findings are in good agreement with the partially compatible nature of these polymeric blends.

In the ternary systems PEO/PPz/PECH the rate constant also decreases as a function of blend composition and reaches a value intermediate between pure PEO and the binary systems, when the PEO portion in the ternary systems is 50%. These results indicate that PECH addition to the PEO/PPz system makes the PEO crystallization rate decrease, which is to be interpreted as a partial compatibilization of the system.

Figure 2b shows exponent n variation as a function of blend composition. The binary blends present distinctly different behaviours, depending on the nature of the second component. Thus, for PEO/PECH systems the values of n remain close to 2, which corresponds to a bidimensional growth pattern. Hence, PECH addition does not modify the PEO crystal growth geometry. In contrast, in the binary PEO/PPz systems exponent n drops in respect of that of

Table II.- Isothermal crystallization kinetics of the blends.

SAMPLE	Tc (°C)	Tm (°C)	n	log K
PEO	52	70.7	2.1	-1.06
	53	70.0	2.0	-1.28
	54	70.3	2.1	-1.63
PEO/PPz 75/25	52	69.2	1.6	-1.68
	53	69.6	1.7	-2.03
	54	69.7	1.7	-2.53
PEO/PPz 50/50	52	69.6	1.5	-1.97
	53	69.2	1.6	-2.24
	54	68.9	1.7	-2.82
PEO/PECH 75/25	52	72.0	2.0	-2.57
	53	72.0	2.3	-3.42
	54	72.6	2.1	-3.52
PEO/PECH 50/50	50	67.0	1.8	-2.82
	51	66.7	1.9	-3.07
	52	67.2	2.1	-3.37
PEO/PPz/PECH 66/17/17	52	68.5	2.0	-1.78
	53	69.1	2.1	-2.30
	54	69.2	1.9	-2.56
PEO/PPz/PECH 50/25/25	50	67.1	1.9	-1.64
	51	67.1	2.0	-2.14
	52	67.6	2.1	-2.77

unblended PEO, the decrease being attributable to simultaneous mono and bidimensional growth behaviours. The growth geometry of PEO in its ternary blends PEO/PPz/PECH remains unaffected, as shown in figure 2b. The n values again move around 2, which is indicative of bidimensional growth.

Spherulitic growth and nucleation factor

The experimental spherulite radius was plotted against time, calculating spherulite growth rate $G(\mu/min)$ from the slopes of the straight lines obtained for each crystallization temperature.

Figure 3 is a plot of the spherulite growth rate of PEO (G^{PEO}) against the crystallization temperature of each of the experimental samples. G^{PEO} is observed to be influenced by both, T_c and the nature and portion of

Figure 3.- G vs Tc for: PEO (+); PEO/PPz 75/25 (○) and 50/50 (●); PEO/PECH 75/25 (□); PEO/PPz/PECH 66/17/17 (∗) and 50/25/25 (■).

the second component in the blend. Thus G^{PEO} decreases in respect of pure PEO in all binary and ternary systems, with the exception of the composition PEO/PPz 75/25. In this latter case the G^{PEO} vs. T_c graph seems to overlap with the respective pure PEO graph, which suggests that in this composition spherulite growth remains unaffected by the presence of PPz.

The lowest G values correspond to the ternary blends, which can be interpreted as evidence of the compatibilizing influence exerted by PECH on the polymers in the melt. The spherulite morphology observed in these systems can be assessed in the photographs reproduced in figure 4, representing the synthesized blend types used. Only in one instance, i.e. the system PEO/PECH 50/50, the morphology changes and ceases to be spherulitic, as clearly shown in the respective photograph (Figure 4d). It is this morphological change which causes the absence of results for this sample.

The nucleation factor K_g represents the free energy necessary to form a nucleus of critical size. Its value is determined from the equation describing spherulite growth rate for crystalline polymers when containing a diluting polymer (equation 2);

$$lnG - ln\phi_2 + \frac{U^*}{R(T_c - T_\infty)} - \frac{0.2T_m ln\phi_2}{\Delta T} = \alpha = lnG_0 - \frac{K_g}{T_c(\Delta T)f} \tag{2}$$

where G_0 is the pre-exponential factor which comprises all temperature independent factors; U^* is a universal constant related to the activation energy necessary to move the chains in the melt (kcal/mol); T_∞ is the hypothetical temperature at which the molecular movements associated with the creep flow cease and it is defined as $T_\infty = T_g-C$ (K) where C is a constant
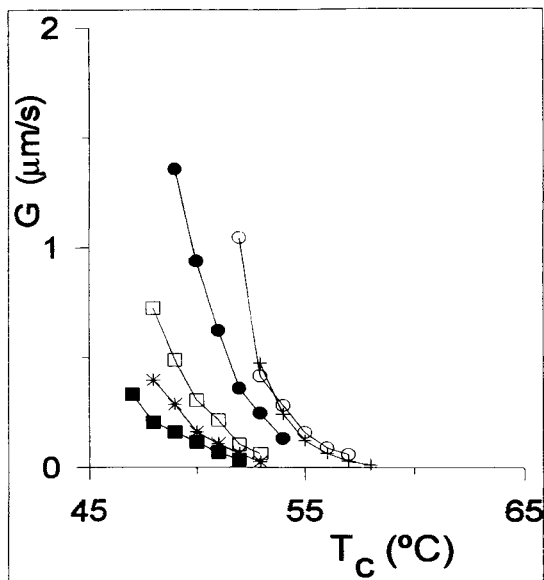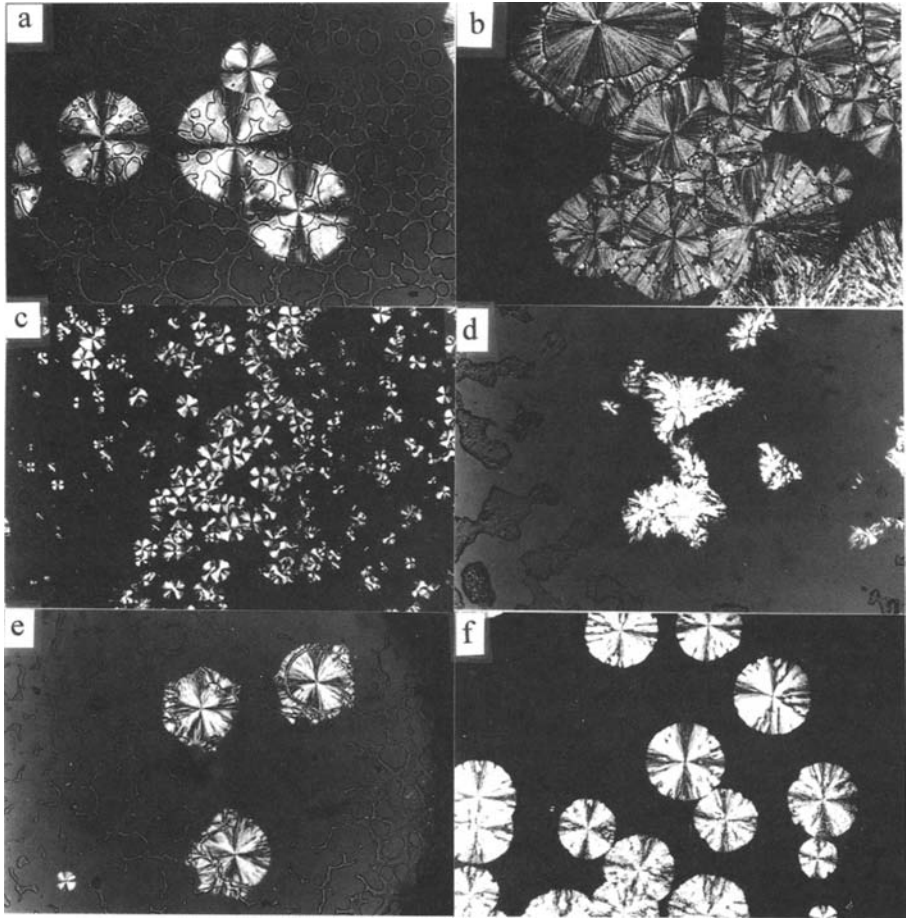
Figure 4.- TOM photographs; (a) PEO/PPz 75/25; (b) PEO/PPz 50/50; © PEO/PECH 75/25; (d) PEO/PECH 50/50; (e) PEO/PPz/PECH 66/17/17 and (f) PEO/PPz/PECH 50/25/25.

and T_g the glass transition temperature of the blend; R is the gas constant (kcal/Kmol); ΔT is the undercooling defined as ($\Delta T=Tm^0-Tc$); ϕ_2 is the volume fraction of the crystalline polymer and f refers to a correction factor which takes into account the dependence of thermodynamic melting heat (ΔH^0) on the crystallization temperature and it is expressed as $f=2Tc/(Tm^0+Tc)$ where Tm^0 is the equilibrium melting temperature.

The nucleation factor is determined from the slope of the straight line obtained when plotting α against $1/Tc(\Delta T)f$ (taking $U^*=6997$ cal/mol and C=30 K) (12). The K_g values are reproduced in Table III. In the PEO/PPz systems the nucleation factor decreases vis-à-vis that of unblended PEO, inversely proportionate to PPz concentration. As regards the PEO/PECH blend, K_g increases drastically over the value for unblended PEO. In the ternary systems the nucleation energy is again observed to diminish with increasing presence of amorphous components. The value of K_g is above that of pure PEO while the amorphous polymer concentration remains low; whereas K_g falls below that of PEO as of a crystalline/amorphous

polymer ratio of 50%.

Table III.- Nucleation and preexponential factors.

SAMPLE	K_g (K^2)	Ln G_0
PEO	150930	48.97
PEO/PPz 75/25	51299	40.30
PEO/PPz 50/50	27020	38.08
PEO/PECH 75/25	248024	60.48
PEO/PECH 50/50	---	---
PEO/PPz/PECH 66/17/17	182734	55.21
PEO/PPz/PECH 50/25/25	119931	52.52

These results indicate that PPz reduces the energy necessary for critical size nucleus formation in PEO, this effect becoming stronger with increasing PPz portion in the blend. In contrast, PECH increases this energetic level.

The effect, however, exerted by increasing concentrations of this polymer remains unknown, because its spherulite growth kinetics could not be determined, as was stated above.

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