# Morphological Characterization of $\gamma$ -LiAlO<sub>2</sub>-Filled Composite Polymer Electrolytes Containing LiPF<sub>6</sub>

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**ABSTRACT:** Morphological properties of composite polymer electrolytes based on blends of polyethylene oxide (PEO) and a perfluorinated polyphosphazene (PPz) containing LiPF<sub>6</sub> as lithium salt and a finely divided ceramic filler,  $\gamma$ -LiAlO<sub>2</sub>, were studied by using polarizing optical microscopy and differential scanning calorimetry (DSC). A parallel study was performed on propylene carbonate plasticized composite polymer electrolytes. Results indicate that both the morphology and the thermal properties depend upon the composition of the polymer host, a result not observed in composite polymer electrolytes having the same polymer composition containing LiCF<sub>3</sub>SO<sub>3</sub> as lithium salt. The incorporation of the ceramic filler at the lower concentration tested (10% by wt) has practically no effect on the thermal behavior of the samples; whereas, differences were clearly distinguished at a concentration of ceramic material of 20 wt %. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1023–1030, 1999

**Key words:** polymer electrolytes; LiPF<sub>6</sub>; PEO; perfluorinated polyphosphazene; composites; morphology; thermal properties

## **INTRODUCTION**

Polymeric solid electrolytes have attracted much attention because of their application in electronic devices, especially rechargeable batteries.<sup>1,2</sup> The basic requirements for high-ionic conductivity in polymer electrolytes are, first, that the polymer host contain polar subunits, which can be complex and dissolve ions, thus providing a reasonable dielectric medium, and, second, that the polymer has a low glass transition temperature, which ensures high segmental mobility of the polymer chain, creating a fluctuating environment that promotes ion diffusion.<sup>3–7</sup> In this way, various polymer media have been tested, consisting mainly of such polyethers as poly(ethylene

Contract grant sponsor: Plan Nacional de Investigación Ciantifica y Desarrollo Tecnológico; contract grant number: Mat95 0203. oxide) (PEO),<sup>8,9</sup> poly(propylene oxide) (PPO),<sup>10,11</sup> polymers having short chain oligoethers attached to such flexible backbones as polyphosphazenes<sup>12</sup> and polysiloxanes,<sup>13,14</sup> or such noncrystalline polyethers as oximethylene-linked polyethylene oxide.<sup>15</sup>

It is known that, in the process of lithium salt dissolution in a polymer, in addition to the formation of a new phase because of the polymer-salt complex, there is a rise in the glass transition temperature, with the subsequent effect of a constrained diffusion of the lithium ions through the membrane.<sup>16,17</sup> To solve this problem, new polymer electrolytes based upon blends, copolymers, and so forth have been developed.<sup>18,19</sup> Other problems deal with poor mechanical properties and dimensional stability, and the existence of an electrochemical stability window, from which irreversible redox processes take place, enabling use of these polymer electrolytes in batteries with a broad choice of redox couples as cathode materials. One method proposed to improve mechani-

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cal properties and, at the same time, the dimensional stability of these materials, is the addition of a finely dispersed ceramic filler, which provides a rigid matrix without significantly affecting polymer conductivity, to the polymer electrolyte.<sup>20,21</sup> Scrosati et al.<sup>22</sup> demonstrate that the addition of γ-LiAlO<sub>2</sub> ceramic powder to PEO-based electrolytes provided a rigid matrix without significantly affecting polymer conductivity and, at the same time, enhanced the electrochemical properties of the material, particularly the stability of the lithium/electrolyte interface.<sup>23,24</sup> Our recent work<sup>23,24</sup> investigated the effect of blending PEO with a fluorinated polyphosphazene (PPz) together with changes produced on the morphology and the ionic conductivity of the polymer electrolyte by the incorporation of different plasticizers. In this work, we report a comparative study of the morphological properties of [PEO/PPz]<sub>8</sub>LiPF<sub>6</sub> electrolytes containing different concentrations of  $\gamma$ -LiAlO<sub>2</sub> to assay the effects produced by the ceramic powder addition on the crystalline morphology of the polymer electrolyte. In a second stage, a parallel study was made by incorporating a plasticizer (propylene carbonate) to the composite polymer electrolyte.

# **EXPERIMENTAL**

All the preparation procedures were carried out in an argon-filled dry box with a water content < 1 ppm. PEO (Aldrich,  $M_w$  5,000,000) was dried under vacuum at 60°C during 24 h and stored inside the dry box. Poly(octofluoropentoxy-trifluoro-ethoxy phosphazene) (PPz) was supplied by Firestone under the trade name PNF200. This polymer was purified by dissolving it in acetone, precipitating in distilled water, drying under vacuum at 100°C 24 h, then storing it. Propylene carbonate, PC, was an Aldrich product and was used as received. Lithium hexafluorophosphate, LiPF<sub>6</sub> was dried under vacuum at 100°C during 24 h. The ceramic filler  $\gamma$ -LiAlO<sub>2</sub> (Aldrich) was dried under vacuum at 140°C during 24 h. Polymer electrolytes were obtained by dissolving the appropriate amounts of polymers and salt in acetonitrile (Aldrich, stored over 4 Å molecular sieve), then casting over teflon plates to eliminate the solvent, following by vacuum drying until reaching constant weight. For composite electrolyte preparation,  $\gamma$ -LiAlO<sub>2</sub> was added to this solution and was finely dispersed by an ultrasonic stirrer, then was cast over Teflon plates to elimi-

Table IDenomination and SampleComposition

	Composition							
Sample	PEO/PPz <sup>a</sup>	O : Li Molar Ratio	$\gamma$ -LiAlO <sub>2</sub> <sup>b</sup>	PC <sup>b</sup>				
PEO	100/0	0	0	0				
PEO/PPz	80/20	0	0	0				
ELE-1	100/0	8	0	0				
ELE-2	80/20	8	0	0				
ELE-3	80/20	8	0	80				
ELE-4	80/20	8	10	0				
ELE-5	80/20	8	20	0				
ELE-6	80/20	8	10	80				
ELE-7	80/20	8	20	80				

<sup>a</sup> wt %.

<sup>b</sup> wt % relating to polymer.

nate the solvent, following by vacuum drying. Optical micrographs show a uniform dispersion of the ceramic filler under these experimental conditions. The O/Li mol ratio was in all cases 8 : 1. Plasticized samples contain an 80 wt % of propylene carbonate relative to the weight of polymer. The content of ceramic filler was 0, 10 and 20 wt relative to the polymer. The denomination and composition of the different samples are compiled in Table I.

Crystalline morphology was followed through optical microscopy by using a Leica Aristomet optical polarizing microscope equipped with a Mettler FP90 hot stage. Samples were melted at 140°C for 5 min, then crystallized at 10°/min to room temperature.

Glass transition temperatures and thermograms were recorded in a Mettler TA4000 differential scanning calorimeter (DSC) operated under nitrogen. Samples were loaded in hermetically sealed aluminium pans, cooled to  $-100^{\circ}$ , then heated to 140°C at 5°C/min and held there for 5 min. Samples were then annealed to  $-100^{\circ}$ C at a cooling rate of 10°C/min. Finally, a second melting process was then recorded by heating up again to 140°C at a heating rate of 5°C/min. Glass transition temperature were measured on the inflexion point on the heat flow jump. Several samples, however, show a very small jump; a criteria was fixed then taken as  $T_g$  value that of the peak minima on the derivative curve, which mathematically should correspond to the value measured on the inflexion point. Thermograms in which two or more peaks overlapped were decon-



**Figure 1** Polarizing optical micrographs of "as cast" PEO, the PEO/PPz blend, and the polymer electrolytes ELE-1 and ELE-2 samples.

voluted using a peak analysis software package (Peakfit from Jandel Scientific) using a five parameter adjusting equation.

## **RESULTS AND DISCUSSION**

## **Optical Microscopy**

Figure 1 shows micrographs obtained using cross polarizers of "as cast" PEO, the polymer blend under study (PEO/PPz 80/20 by weight) and the polymer electrolytes ELE-1 and ELE-2. First, it must be pointed out that all samples present a crystalline morphology, but although PEO show a great number of small size spherulites, PEO/PPz blend micrograph shows interpenetrated spherulites, with a much bigger size when compared to those obtained for the unblended PEO and a much better defined morphology, being the maltese cross structure easily discernable. Considering that previous studies demonstrate that PEO and the perfluorinated polyphosphazene we used in this study lead to a noncompatible system when blended,<sup>25</sup> this behavior can be explained in terms of a diluent effect of the PPz on the PEO crystallization process, thus leading to a decrease in the number of the number of growing crystallization nuclei and a decrease in the crystallization rate, both factors resulting in the appearance of a small number of spherulites with a welldefined crystalline morphology. The polymer electrolyte ELE-1 again shows interpenetrated spherulites, the maltese cross structure not being detected at the magnification employed, the great size of the spherulites, again, are remarkable as compared with those previously obtained for PEO under the same experimental conditions. The polymer electrolyte ELE-2 micrograph, however, shows a great number of small size crystalline structures. Looking at the results, it is clear that the morphology of the systems depends on the composition of the polymer host. However, an opposite behavior was observed when comparing the crystalline structures developed by the polymers and the polymer electrolytes. This can be explained by considering that PPz acts as a diluent on the PEO crystallization process; whereas, the solvating of the lithium salt  $LiPF_6$ by the ether oxygen of the PEO leads to the existence of a new crystalline phase, probably with a different nucleation and growing mechanism. Plasticized samples (not shown) did not show a detectable spherulite morphology under the microscope, even the samples develop a certain degree of crystallinity, as we demonstrate later in the analysis of the DSC results.



**Figure 2** Polarizing optical micrographs of PEO, ELE-1, and ELE-6 samples crystallized from the melt at 10°/min.

Relating to the melt crystallized samples, Figure 2 shows micrographs obtained for PEO, ELE-1, and ELE-6 samples crystallized from the melt at 10°/min. PEO develops a very well-defined maltese cross structure, the same situation observed for the PEO/PPz blend (not shown). The polymer electrolyte ELE-1, based on PEO as polymer host, again, shows a maltese cross structure, but crystalline perfection is lower than that developed by the pure PEO sample. The ELE-6 sample shows a different behavior, showing spherulites with a lower size and a much lower degree of perfection. It should be noted that the study was centered on the polymer electrolyte samples free of ceramic filler crystalline and those containing the lower concentration of ceramic filler, because of the difficulties of observing any kind of structure when the concentration of ceramic filler reaches a concentration of 20% by weight.

#### **Thermal Analysis**

Figure 3 shows the DSC melting thermograms of "as cast" samples heated from  $-100^{\circ}$ C to  $150^{\circ}$ C at a heating rate of  $10^{\circ}$ /min. It is clear from the plot that blending PEO with the fluorinated polyphosphazene at a 80/20 by weight relative composition did not alter the melting behavior of PEO and

only has the effect of reducing the crystallinity level (Table II). On the opposite site the incorporation of the lithium salt, the corresponding formation of the PEO-LiPF<sub>6</sub> complex leads to the appearance on the thermograms of a new melting transition, located at around 92°C, associated with the melting of the crystalline PEO-salt complex, in addition to the melting transition associated to the PEO not coordinated by the  $LiPF_6$ , which takes place at 57°C, displaced, in this case, to lower temperatures relating to the pure PEO. However it must be noted that the increase on the amorphous phase, verified by lower enthalpy values obtained as well as the much higher jump observed on the thermal flow at the glass transition temperature, also associated with the amorphous phase content. Relating to the glass transition temperatures, the polymer electrolyte, as expected, presents values displaced toward higher temperatures, because of the lower degree of chain movement as a result of oxygen coordination,<sup>26</sup> ranging from a value of -57.1°C for the pure PEO to a value of -36.4°C for the ELE-1 polymer electrolyte. The DSC thermogram corresponding to the polymer electrolyte based on the PEO/PPz blend (ELE-2) shows a different behavior, with the appearance of a single peak located



**Figure 3** Normalized DSC thermograms of "as cast" PEO, PEO/PPz samples, and the polymer electrolytes ELE-1 and ELE-2.

at 62.9°C, whose forms and temperature suggest that correspond to "free," not coordinated, PEO. This can be explained in two ways: by a restriction effect of PPz to the formation of the crystalline PEO-salt complex, or by the fact that this melting transition takes place at temperatures above 150°C. (Experimental tests at temperatures above 150°C cannot be performed because of LiPF<sub>6</sub> degradation.) Ionic conduction tests performed on these samples using complex impedance spectroscopy<sup>27</sup> show that the conductivity values obtained for ELE-2 sample are lower than



**Figure 4** Normalized DSC thermograms of "as cast" ELE-2, ELE-4, and ELE-5 polymer electrolytes.

those obtained for the ELE-1 polymer electrolyte, the value measured confirm the existence of a coordination between the ether oxygen of the PEO and the lithium salt (previous studies on PEO/ PPz polymer electrolytes containing LiCF<sub>3</sub>SO<sub>3</sub> as lithium salt demonstrate that there exists no coordination between the lithium and the PPz chains<sup>17</sup>). The glass transition in this case appears at a temperature slightly higher when compared with that of the polymer electrolyte based on PEO. This is also observed when comparing the values obtained for PEO and the PEO/PPz polymer blend.

Table IIGlass Transition and Melting Parameters Obtained for the Samples Under Studyin the First and Second Melting Scans

	T	T		T	ΔIJ	T	ΔIJ	T	ΔIJ	T	ΔIJ
Sample	(°C)	$(^{\circ}C)$	(J/g)	$(^{\circ}C)^{I_{m_{12}}}$	(J/g)	$^{I}_{m_{13}}$ (°C)	(J/g)	$(^{\circ}C)^{I_{m_{21}}}$	(J/g)	$(^{\circ}C)^{I_{m_{22}}}$	(J/g)
PEO	-57.1			69.8	175			68.4	132.0		
PEO/PPz	-52.6			69.1	90.0			66.2	67.3		
ELE-1	-36.4			57.0	29.4	92.2	33.6	48.8	20.8	92.2	2.9
ELE-2	-32.7			62.9	52.5			45.2	28.6		
ELE-3	-67.3			65.0	5.3	93.7	5.5	55.3	2.1		
ELE-4	-32.4			61.6	63.4			47.4	34.8		
ELE-5	-33.9			49.0	13.2	104.6	32.6			93.3	10.8
ELE-6	-66.6	30.9	5.4	55.5	21.4			47.3	24.1		
ELE-7	-74.3	33.0	8.2	45.3	5.7			37.5	14.4	57.8	1.7



**Figure 5** Normalized DSC thermograms of "as cast" plasticized ELE-3, ELE-6, and ELE-7 polymer electrolytes.

Figures 4 and 5 show, respectively, the effect of the incorporation of the ceramic filler  $\gamma$ -LiAlO<sub>2</sub> on the DSC melting thermograms of "as cast" nonplasticized and propylene carbonate plasticized polymer electrolytes. In the case of the unplasticized polymer electrolytes, it can be stated that the incorporation of  $\gamma$ -LiAlO<sub>2</sub> has practically no effect on the glass transition temperature of the complex, because the values obtained are of the same order of that of the polymer electrolytes not containing the ceramic filler. In the opposite case, when comparing melting data, it was observed that at the lower  $\gamma$ -LiAlO<sub>2</sub> concentration tested, the melting temperature is practically identical to that of the polymer electrolyte not containing the ceramic filler; whereas, the thermogram corresponding to the polymer electrolyte containing the higher  $\gamma$ -LiAlO<sub>2</sub> concentration shows a different profile, with the appearance of two melting peaks, one associated with the noncoordinated PEO peak that appears displaced to lower temperatures relating to the pristine PEO, plus a second peak that appears at higher temperatures, which should be associated with the melting of the coordinated PEO-lithium salt crystalline phase.

The glass transition temperature of plasticized samples (Table II) presents, for all samples, tem-

peratures displaced toward lower values, even lower than the value obtained for the pristine PEO. As for melting behavior, the three samples show more than one peak on the thermogram, but while the polymer electrolyte free of ceramic filler can be assigned easily to the coordinated and noncoordinated PEO, this assignment is not so easy for the plasticized samples containing  $\gamma$ -LiAlO<sub>2</sub>. The thermograms show that the zone located around 90°C appears free of any transition; whereas, that at  $\sim 60^{\circ}$ C, where the pure PEO melts, shows two peaks. However, if we analyze the effect of the plasticizer on samples with the same ceramic filler concentration, we can see that; for example, between ELE-5 and ELE-7, the electrolytes with the higher  $\gamma$ -LiAlO<sub>2</sub> concentration, the profile of ELE-7 thermogram could be explained as the result of a plasticizing effect on the crystalline phase associated with the polymer-salt complex; whereas, PEO is affected by plasticizing to a minor extent.

Previous studies on polymer electrolytes containing LiCF<sub>3</sub>SO<sub>3</sub> as lithium salt show that when melting and crystallizing the sample successively, the melting thermograms of the region associated with the polymer-salt complex show differences, this has been explained in terms of an evolution of a different nonestequiometric polymer-salt system to a more thermodynamically stable composition.<sup>28</sup> Figure 6 shows the melting and cooling thermograms obtained for PEO and the polymer electrolyte ELE-1. It is clear that, although for the pure PEO, there is practically no difference between the melting behavior before and after crystallization at 20°/min, for the case of the polymer electrolyte ELE-1, there is only one peak on the crystallization thermogram; whereas, on the second melting scan, a crystallization peak appears at higher temperatures than that of the first scan, together with a drastic decrease of the value of the enthalpy of the peal associated with the complex melting, and displacement of the PEO melting temperature to lower values. When comparing the melting thermograms obtained for the PEO/PPz blend and the polymer electrolyte ELE-2 (see Table II for data), results indicate that there is a displacement to lower values of both the enthalpy and the melting temperature for the case of the blend; whereas, for the ELE-2 complex, this displacement is much more intense.

When  $\gamma$ -LiAlO<sub>2</sub> is added, different behavior is observed, depending upon the ceramic filler concentration. The ELE-4 complex shows a behavior similar to that of the complex free of ceramic



Figure 6 Effect of thermal treatment on DSC thermograms of PEO and ELE-1 samples.

filler; that is, a decrease in the enthalpy and the displacement of the melting temperature toward lower values; however, when  $\gamma$ -LiAlO<sub>2</sub> increases, there is a decrease in the enthalpy and temperature of the peak associated with the complex; whereas, that corresponding to the PEO disappears. Plasticized samples, again, show differences, depending upon the  $\gamma$ -LiAlO<sub>2</sub> content, where a decrease on the melting temperature for the complex with the lower concentration is observed. The sample with higher  $\gamma$ -LiAlO<sub>2</sub> concentration shows one peak on the first scan; whereas, two melting transitions occur on the second melting thermogram.

# CONCLUSIONS

We examined the morphology and thermal properties of composite polymer electrolytes based on blends of PEO and a fluorinated polyphosphazene containing finly dispersed  $\gamma$ -LiAlO<sub>2</sub> ceramic powder by using DSC and optical microscopy techniques. Results indicate that both the morphology and thermal properties of the composites depend upon the composition of the polymer host. The incorporation of the ceramic filler at the lower concentration has practically no effect on the thermal behavior of the samples; whereas, differences were clearly distinguished at a concentration of ceramic of 20 wt %. Differences were observed in the melting behavior after a second melting cycle, probably because of the degradation processes of the  $LiPF_6$  salt.

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