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Polymer Blend for Electrolyte and Electrode Coatings

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Summary: The thermal and morphological properties of PEO/copolyether electrolyte and carbon black composite have been studied. A copolyether poly(propylene glycol)-*block*-poly(ethylene glycol)-*block*-poly(propylene glycol) bis(2-aminopropyl ether) was used at 20 wt.-% in relation to PEO in order the improve the carbon black dispersion through interaction with the amino end capped function. The polymer matrix presented semicrystalline structure and the addition of $LiClO_4$ and carbon black decreases significantly the crystallinity of the system. Sub-micrometric dispersion of carbon black was observed. The conductivity results as a function of temperature exhibited a typical VTF behaviour for the electrolyte. Almost constant conductivities of 2×10^{-4} $S \cdot cm^{-1}$ were observed for the composite with 5 wt.-% of carbon black, in the range of temperature between 35 and 95 °C, which indicates a significantly contribution of electronic conduction.

Keywords: AFM; coatings; composites; DSC; electrolyte; polyethers; polymeric

Introduction

Nowadays electrical equipments are requiring integrated energy storage systems which associate high energy density with short charge time and high number of charge/discharge cycles.[1–5] To answer these requirements, an electrochemical capacitor that uses accumulated charges of an electric double layer formed at the interface *high porous electrode/electrolyte*, associated with batteries, can be used.[4] The use of electrode composites produced by the dispersion of porous carbon black in a polymer electrolyte (polymer + salt) is one of the potential techniques to produce a double layer electrochemical capacitor.[3,5,6] Solid polymer electrolyte might enhance electrochemical capacitors' technology by replacing the liquid electrolyte currently in use and thereby allowing the fabrication of flexible, compact, coated solid state structures, free from leaks and available in a variety of geometries.[7]

The deposition of polymeric films for production of electric-electronic devices can be accomplished through processes such as spin coating, spray coating and inkjet printing techniques, involving both solutions or suspensions.[8,9] These processes produce films with high quality at low energy cost, allowing to choose the substrate and to control the film thickness.[8,9] In the presented work, a procedure for fluids (solutions or dispersions) preparation and deposition of reproducible polymeric layers through the spray coating technique was developed. Stages of both, polymer and salt dissolution, as well as carbon black dispersion through mixing and sonication were followed by carefully dry procedures.

A polymeric blend of high molecular weight poly(ethylene oxide) (PEO) and low molecular weight block copolyether was selected to be matrix for $LiClO_4$ dissolution and carbon black dispersion. The copolymer poly(propylene glycol)-*block*-poly(ethylene

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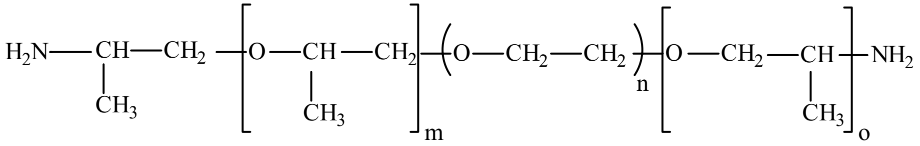

$H_2N-CH(CH_3)-CH_2-[O-CH(CH_3)-CH_2]_m-(O-CH_2-CH_2)_n-[O-CH_2-CH(CH_3)]_o-NH_2$

Scheme 1.
Interaction of the amine end chain with carbon.

glycol)-*block*-poly(propylene glycol) bis(2-aminopropyl ether) NH_2-PPG-PEG-PPG-NH_2 was mixed with PEO in order to decrease the crystallinity of the matrix and increase carbon black dispersion through interaction of the amine end chain with carbon.[10]

Our group has reported previously[3,5] the study of electrochemical capacitors using a PEO mixed with PEG 400 as plasticizer[3] or an aliphatic thermoplastic polyurethane[5] as matrix. In those works, the films were prepared by conventional casting procedure and several experimental difficulties were presented, leading to a low reproducibility of the devices. The polyurethane matrix showed the best results mainly because the electrolyte and carbon black composites presented high conductivities.[5] The adequate dispersion of carbon black, which favours electrical conductivity, is what builds up a continuous conductive network. This network was probably presents itself in our polyurethane system supported by the copolymer type structure of this material; the urethane segments may have strong interactions with carbon black.

Polymer blending is reported to be a useful tool to design electrical conductive composites by selective localization of carbon black in phases or interphases.[11] This approach regarding the formulation is the purpose in this work, as well as the goal to prepare reproducible high quality–low cost coatings by spray technique. The thermal behaviour of the polymeric constituents and coatings was evaluated by DSC. Coatings morphology and superficial composition studies were carried out by atomic force microscopic and electron microprobe respectively. The coatings conductivities were measured using impedance spectroscopy as a function of temperature.

Experimental Part

A polymeric electrolyte solution was prepared with PEO (Aldrich–$M_w = 100\,000$ g · mol^{-1}–supplier data), triblock copolymer NH_2-PPG-PEG-PPG-NH_2 (Aldrich–$M_n = 2\,000$ g · mol^{-1}–supplier data) blend in the proportion of 20 wt.-% of copolymer and $LiClO_4$ (Aldrich) in tetrahydrofuran (Synth). The electrode composite was obtained adding carbon black suspension (Black Pearls 2000–Cabot, 950 m^2 · g^{-1} –supplier data) in the electrolyte solution, at the concentration of 5 wt.-%. The salt concentration was fixed at mole ratio [O]/[Li] = 8. All reagents were used as received. After preparation, the suspensions for electrode samples were sonicated (in an ultrasonic bath) for 5 h. The solutions/suspensions were placed on substrates through spray coating technique. The solvent evaporation was carried out in a dissecator under vacuum by more than one week. Films' thicknesses were determined to be between 10 and 30 μm.

The samples' surface were analysed in an OLYMPUS BX 50 OPTIC microscope, JEOL JXA 8900RL electron microprobe (EDS = energy dispersive X-ray and WDS = wavelength dispersive spectrometer), DIGITAL INSTRUMENTS MULTI MODE WITH CONTROLLER NANOSCOPE 4 atomic force microscope. For AFM, coatings were prepared in a Si substrate. DSC was carried out with a TA INSTRUMENTS 2920 DSC, in three scanning experiments: 25–120 °C, 120 to −100 °C and −100 to 150 °C, at heating rates of 10 °C · min^{-1}, under He atmosphere.

The second DSC heat scanning was used to determine phase transitions. Coatings of electrolyte and composite were sprayed inside the DSC pans and dried for measurement. Electrical measurements were performed using an ECO CHEMIE potentiostat/impedance frequency analyzer Autolab PGSTAT 30, with a experimental cell including two stainless steel block electrodes inside a heater system to control temperature between 25 and 95 °C. The frequency range of the impedance measurements was between 1 and 5×10^5 Hz. For electrical measurements of electrolyte and composite coatings, the samples were sprayed in the stainless steel electrodes and carefully dried.

Results and Discussion

An important experimental observation in fluid preparation was the increase of solubility obtained using a polymer blend with low molecular weight amino terminated copolymer in its formulation. Previous attempts to prepare fluids with PEO (8 000 and 100 000)/$LiClO_4$ indicated lower polymer solubility and a lower homogeneity of the coatings, probably associated with the presence of lithium salt in the medium. Even in the case of the blend system the ionic force of the solution seems not to favour carbon dispersion. The goal to formulate fluids to prepare electrolyte and electrode coatings for a solid polymeric electrochemical device is a very limited situation. The presence of salt is imperative and ionic surfactant is unacceptable. The amino terminated triblock may act as a non-ionic surfactant at the same time that it can provide a special morphology, by interacting with PEO, for dispersion and organization of carbon black. Carbon black is known to present hydroxyl and carboxyl groups adsorbed onto its surface.[10] The amine can interact and react with carboxyl groups helping the hop of charge carriers between neighbours conducting agglomerates.[10] The concentration of salt was established considering the best results of conductivity for PEO based materials.[12] The concentration of triblock and PEO was tested taking under consideration that the goals was to prepare dimensional stable coatings.

It should be pointed out that the viscosity of the fluids formulation (lower than 15 cP) and degree of dispersion were specially adapted for the spray and spin coating techniques. Several tests showed that the morphological features of spin and spray coatings were similar. After the determination of the best composition and mixing procedures, the fluids prepared in this work were easily sprayed coating in aluminium, stainless steel and silicon wafers and, from the optical microscopy point of view, homogenous layers were obtained.

Figure 1 shows the DSC curves obtained for the polymer materials, the electrolyte system and the composite. From Table 1 it can be observed that DSC measurements for PEO and triblock copolymer show melting transitions with similar fusion heats and differences in melting temperatures. The block copolyether exhibits two separated melting peaks, the first one with a shoulder at lower temperature. A ^{13}C NMR analysis of the block copolymer indicated that the total amount of poly(proplene glycol) (PPG) does not exceed 5 wt.-% of this sample. Therefore, this is actually a poly(ethylene glycol) (PEG) oligomer terminated with a PPG-amino function and the melting features in Figure 1 can be explained as associated with the PEG block.

Figure 1 shows an insert which is a magnification of the low temperature range of the DSC curve for PEO and copolymer. Table 1 presents the values of glass transitions (T_g) for both matrix. The two copolymers glass transitions can be assigned to the PEG block ($T_g = -59\,^\circ C$) and to an arrangement produced by the PPG-amino end capped ($T_g = 1\,^\circ C$). It should be noted that the DSC analysis in Figure 1 are second heating runs and volatiles were dried before, in the first heating run.

It is known that polymer electrolytes form crystalline compounds at certain

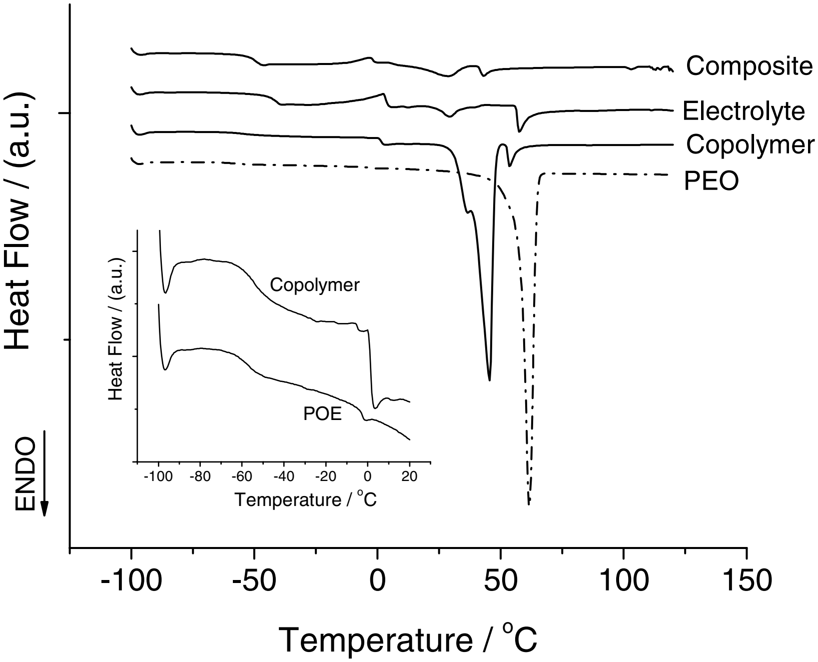

Figure 1.
DSC curves for PEO, triblock copolyether, electrolyte with $LiClO_4$ ([O]/[Li]) = 8 and composite with 5 wt.-% of carbon black.

discrete compositions of polymer and salt.[13–15] But it may also be obtained as amorphous materials along a wide range of compositions and temperatures, including ones in which the crystalline complexes can coexist.[15] In the polymer electrolyte field is frequently considered the decrease of the crystallinity as an important factor to improve conductivity. The fast ionic transport takes place in the amorphous regions of the electrolyte when it is semicrystalline.[13,14] Strategies such as the preparation of polymer blends and the addition of plasticizers and fillers can be used to reduce crystallinity of polymer electrolytes.[7,14] The presence of the amorphous carbon in the electrodes is reported to contribute in reducing the capacity of organization of the polymeric chains without reducing the mechanical properties of the system.[16]

From the DSC data (Figure 1 and Table 1), it was verified that for both—polymer electrolyte and composite electrode—there was a dramatic decrease of the crystallinity when compared to the polymeric constituent. Endothermic events can be observed for the systems with lithium salt and carbon black; however, the heats of fusion are quite smaller

Table 1.
Thermal properties (from DSC curves) of two polymer matrix, electrolyte and composite coatings.

Material	Melting points (T_m) (peak)	Heat of fusion (ΔH_m)	Glass transitions (T_g) (onset)
	°C	$J \cdot g^{-1}$	°C
Poly(ethylene oxide)	62	120	−59
Copolymer PPG-PEG-PPG-amino	45 and 54	115 and 5	−59 and 1
Polymer Electrolyte–$LiClO_4$ ([O]/[Li]) = 8	29 and 58	5 and 9	−44 and −3
Composite Electrode—5 wt.-% carbon black	29 and 43	11 and 2	−52 and −2

compared to the matrix. Two endothermic events and two glass transitions were observed for electrolyte and composite similar to what is observed for the copolymer. These results should be discussed considering that there is 20 wt.-% of copolymer in the blend matrix and that the copolymer is formed by 95 wt.-% of PEG. The addition of salt to the blend produced the decrease of the first melting transition to 29 °C, with an abrupt decrease in heat of fusion, and the increase of the first glass transition to −44 °C. This is a typical result for an electrolyte system. Lithium cations coordinate with ethylene oxide units leading to the formation of a more rigid amorphous structure and the molar ratio [O]/[Li] is a known eutectic composition for PEO:$LiClO_4$ system[12] which implies in crystallinity decrease. The second glass transition of the electrolyte at −3 °C is similar to the value of second T_g for the copolymer ($T_g = 1$ °C) and may indicate that there is no interaction between lithium cation and the end capped PPG-amino function.

For the composite an important difference in results from Table 1 is the first glass transition value that is −52 °C. This may indicate that the carbon black disturbs the interactions between salt and polymer matrix allowing an increase in chain segment flexibility. No change was observed for the second T_g, but a decrease in the second melting temperature and heat might indicate some degree of interaction between carbon black and the copolymer matrix.

The optical microscopy images (not shown) confirmed the presence of crystallization in the electrolyte. However, for a high magnificated AFM image [Figure 2(a)] in phase contrast mode it is observed a completely homogenous sample. The same chemical composition, in all electrolyte surfaces, was verified by EDS microanalysis (not shown). These results allow the conclusion that there is no phase segregated lithium salt or polymer:salt complex and that PEO/copolymer matrix are quite compatible.

In the electrode coatings, two distinct regions were verified: a smooth and a rugous one. The EDS microanalysis data shows that both regions have carbon black, polymer and salt. This can also be confirmed by WDS mapping (Figure 3) and AFM images [Figure 2(b) and (c)].

The images obtained by AFM [Figure 2(b) and (c)], show that the carbon black is dispersed in the electrolyte matrix with a tendency to form sub-micrometric agglomerates. The surface AFM images do not show information concerning the bulk dispersion in these 10–30 μm coatings. The WDS carbon mapping presented in Figure 3(b) is more informative in this sense. The depth probed by this technique is of approximately 1 μm. It should be noted that the black/white scale for the WDS mapping causes some difficulties in the analysis of this image. Similar grey colours are assigned to different concentrations of carbon. It should be considered that carbon atoms also constitute the polymer matrix. Therefore, we are proposing to observe only the distribution of white regions as an indication of carbon network formation through the sample. The black regions are probably associated with high salt concentrated phases.

Figure 4 shows conductivity results as a function of temperature for the polymer electrolyte and the composite electrode coatings. A great number of works in polymer electrolytes, involving several polymers, blends, salts, and preparation methods are reported in the literature.[5,7,12–15] Conductivity values for solid polymer electrolytes at room temperature are between 10^{-9} and 10^{-5} $S \cdot cm^{-1}$[12] depending on the degree of crystallinity, salt concentration and several other parameters. The observed conductivity for our polymer electrolyte was of 1×10^{-5} $S \cdot cm^{-1}$ at room temperature, which is coherent with the best results of several other works.[12,14] The behaviour of electrolyte conductivity as a function of temperature (Figure 4) can be fit with the VTF model[13] which is typical for ionic conductivity in amorphous solid polymer electrolyte.[12]

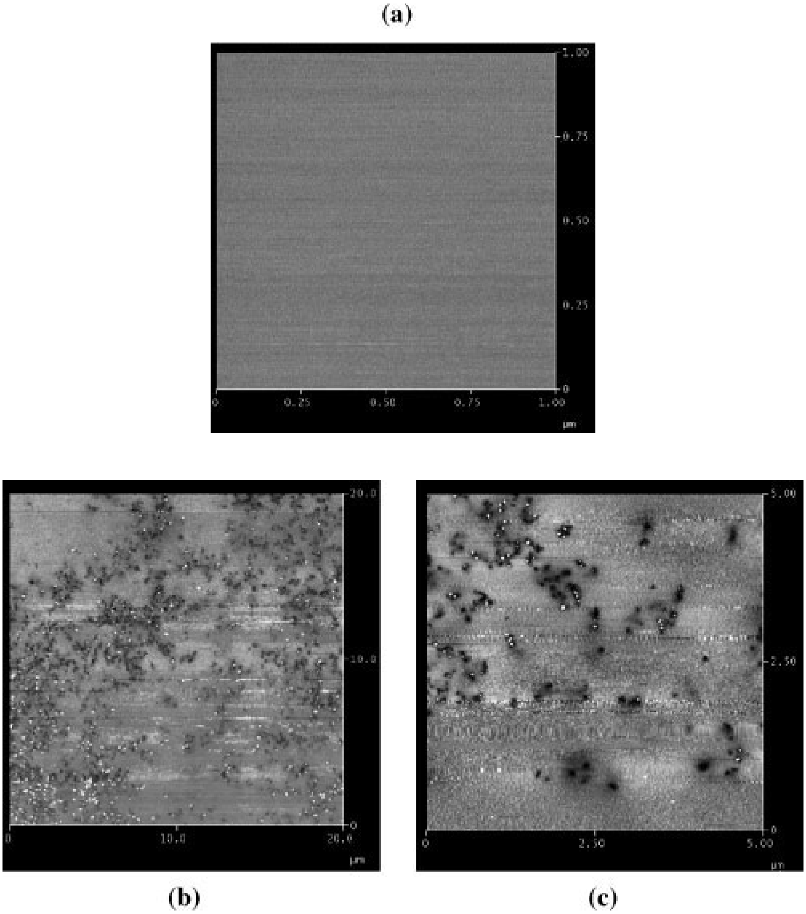

Figure 2.
Phase contrast AFM images for: (a) polymer electrolyte, (b) and (c) composite electrode. Magnifications: total length of image: (a) 1 μm, (b) 20 μm and (c) 5 μm.

For solid polymer electrode composites with carbon black at 5 wt.-% we reported previously conductivity values of 2×10^{-6} and 4×10^{-5} $S \cdot cm^{-1}$.[3,5] The best result was obtained with the polyurethane matrix, which exhibited constant conductivity as a function of temperature at concentrations higher than 15 wt.-% of black. The stability of conductivity values in the temperature range studied indicates an electronic hopping mechanism. In the present work the composite PEO/copolymer with 5 wt.-% of carbon demonstrated an improvement in the conductivity arriving to 6×10^{-5} $S \cdot cm^{-1}$ at room temperature (see Figure 4). More interesting is to observe that at 35 °C the conductivity increases abruptly to 2×10^{-4} $S \cdot cm^{-1}$ and remains approximately constant up to 95 °C. This increase after the first melting temperature may indicate the formation of a privileged network of eletronic conduction after the melting of a small amount of copolymer—see Figure 1, Table 1 and DSC discussion. Therefore, it can be proposed that the copolymer amino end capped helped to establish a continuous network for electronic migration, which is contributing to the observed conductivity.

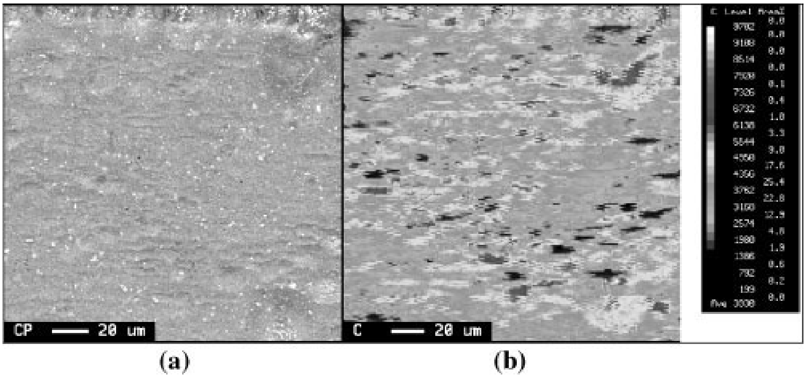

Figure 3.
(a) SEM image (backscattered electrons) and (b) WDS carbon mapping of composite electrode with 5 wt.-% of carbon black.

The ionic and electronic conductivities obtained indicated that the relatively simple procedure for the fluid preparation and coating deposition, employee in this work, made possible the creation of materials with electrical qualities, which allow their use for the construction of electrochemical capacitors.

Conclusion

A reproducible, low cost, methodology for preparation of fluids and polymeric coatings was established. A good dispersion of carbon black in polymeric electrode, for conductivity purposes, was obtained by spray coating technique. Thermal data showed interesting features associated with the decrease of polymer crystallinity through salt addition and the influence of carbon black addition on reducing amorphous phase rigidity. The conductivity data indicated an improvement in the ionic conductivity of the electrolyte in relation to typical solid polyether systems. The composite electrode coating with 5 wt.-% of carbon black showed conductivity values

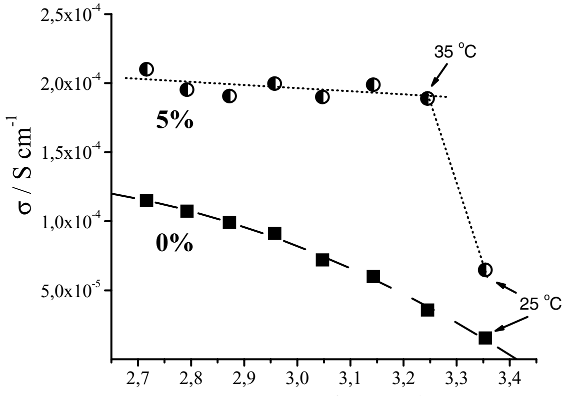

Figure 4.
Arrhenius plot (conductivity vs. 1/temperature) for polymer electrolyte (0 wt.-% of carbon black) and composite electrode (5 wt.-% of carbon black).

of approximately 2×10^{-4} S · cm^{-1}, between 35 and 95 °C, which are probably associated with ionic and electronic contributions.

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[1] Ch. Emmenegger, Ph. Mauron, P. Sudan, P. Wenger, V. Hermann, R. Gallay, A. Züttel, *J. Power Sources.* **2003**, *124*, 321.
[2] M. Frank Rose, C. Johnson, T. Owens, B. Stephens, *J. Power Sources* **1994**, *47*, 303.
[3] J. M. Pernaut, G. Goulart, *J. Power Sources* **1995**, *55*, 93.
[4] B. E. Conway, "*Electrochemical Supercapacitors: Scientific, Fundamentals and Technological Applications*", Kluwer Academic/Plenum Publishers, New York 1999, p. 698.
[5] C. A. Furtado, P. P. de Souza, G. Goulart Silva, T. Matencio, J. M. Pernaut, *Electrochim. Acta* **2001**, *46*, 1629.
[6] A. Lewandowski, M. Krzyzanowski, *Electrochim. Acta* **2003**, *48*, 1325.
[7] F. Groce, G. B. Appetecchi, L. Persi, B. Scrosati, *Nature* **1998**, *394*, 456.
[8] M. C. Blanco-Lópes, S. Gutiérrez-Fernandes, M. J. Lobo-Castañón, A. J. Miranda-Ordieres, P. Tuñón-Blanco, *Anal. Bioanal. Chem.* **2004**, *378*, 1922.
[9] G. Perçin, T. S. Lundgren, B. T. Khuri-Yakub, *Appl. Phys. Lett.* **1998**, *73*, 2375.
[10] H. G. Yoon, K. W. Kwon, K. Nagata, K. Takahashi, *Carbon* **2004**, *42*, 1877.
[11] F. Gubbels, R. Jérôme, Ph. Teyssié, E. Vanlathem, R. Deltour, A. Calderone, V. Parenté, J. L. Brédas, *Macromolecules* **1994**, *27*, 1972.
[12] F. M. Gray, "Polymer Electrolytes", in: "*RSC Materials Monographs*", 1st edition, J. A. Connor, Ed., The Royal Society of Chemistry, Cambridge **1997**, p. 175.
[13] C. Berthier, W. Gorecki, M. Miner, M. B. Armand, J. M. Chabagno, P. Rigaud, *Solid State Ionics* **1983**, *11*, 91.
[14] E. Quartarone, P. Mustarelli, A. Magistris, *Solid State Ionics* **1998**, *110*, 1.
[15] Z. Gadjourova, Y. G. Andreev, D. P. Tunstall, P. G. Bruce, *Nature* **2001**, *412*, 520.
[16] R. W. A. Franco, J. P. Donoso, C. J. Magnon, J. M. Pernaut, P. P. de Souza, *Solid State Ionics* **2000**, *136–137*, 1181.