NMR and Conductivity Studies of Ethylene Oxide−Epichloridrine Copolymer Doped with LiClO₄

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The copolymer ethylene oxide and epichloridrine doped with lithium perchlorate shows interesting properties as an ionic conducting polymer mainly because of its amorphous structure at room temperature and its low glass transition temperature ($T_g = -40$ °C). ¹³C, ⁷Li, and ¹H nuclear magnetic resonance studies were performed in order to analyze the interactions between the polymer matrix and the dopant salt with solvent molecules. These studies and conductivity measurements were used to investigate the influence of the preparation method and the properties of the solvent on the physicochemical characteristics of the polymer electrolyte. Experimental results show that solvent molecules are retained in the solid polymer electrolyte, strongly modifying its ion transport dynamic. This fact can be related to the increase in the ionic conductivity when solvent molecules rest inside the polymer matrix, producing a plasticizing effect.

Introduction

Polymeric electrolytes are composed of a polar matrix polymer and lithium salts forming a solid salt solution. These systems have a high ionic conductivity and they have received considerable attention in the past decade because of possible technological applications in advanced electronic devices (solid state lithium batteries, supercapacitors, electrochromic displays, etc.).[1,2] The family of poly(ethylene oxide) (PEO) polymers has been extensively studied because of its properties as a polar matrix material.[3] However, its high transition temperature to the amorphous phase (∼65 °C) and its high tendency to crystallize lead to low ionic conductivity and poor mechanical properties at room temperature.[4−6] To obtain better properties at room temperature, the PEO must be modified to have a larger proportion of the amorphous phase.[7] This structural modification of the PEO matrix can be obtained using substituted monomers in order to produce another polymer, a copolymer, or a terpolymer. Another method to improve the conductivity and mechanical properties of the solid electrolyte is the addition of inorganic and organic soluble additives to increase the segmental motion of the polymer matrix in order to aid the ion transport in the solid electrolyte.[8−10]

The copolymer of PEO with epichloridrine, poly(epichloridrine-*co*-ethylene oxide) (PEPI−PEO) has been proposed as a solid electrolyte because of its capacity to combine with the salt cations to form a homogeneous solid solution with good conductivity at room temperature.[11,12] The glass transition temperature of PEPI−PEO is ca. −40 °C,[13] and it is amorphous at room temperature and shows a high thermal stability in a wide temperature range. For this reason, good ionic conductivity is expected when inorganic salts are dissolved into the PEPI−PEO matrix. The elastomer PEPI−PEO shows interesting characteristics such as high elasticity at low temperatures and good resistance to solvents, and it allows for a wide range of working temperature (−40 to 150 °C).[13]

In this work, nuclear magnetic resonance (NMR) and conductivity measurements have been performed with PEPI−PEO copolymer doped with lithium perchlorate salt in different [O/Li] ratios. Tetrahydrofuran (THF) and acetone were used as solvents in the preparation process. The aim of these studies is to identify the role of the solvent and the effect of the dopant on the conductive properties of the solid electrolyte. ¹³C, ⁷Li, and ¹H NMR spectra were used, together with conductivity measurements, to characterize the chemical process involved in the formation of the solid electrolyte.

Experimental Section

PEPI−PEO copolymer (1:1) was provided by DINACO (São Paulo, Brazil) under the commercial denomination Hydrin C. The PEPI−PEO was purified by dissolution in THF (Merck) followed by coagulation in ethanol (Merck). The process was repeated three times, and the PEPI−PEO obtained was dried in vacuum. Solid solutions (purified (PEPI−PEO)−LiClO₄ (Riedel-de Haën)) were prepared from 1.0 g of PEPI−PEO + 30 mL of solvent by three different methods:

Method A. Samples were prepared by dissolution of PEPI−PEO copolymer and different quantities of LiClO₄ in THF. The drying process was carried out at room temperature under vacuum (10^{-4} Torr) for 72 h.

Method B. Samples were prepared by dissolution of PEPI−PEO copolymer and different quantities of LiClO₄ in acetone (Merck). In this case, the copolymer was not completely dissolved by the solvent, and the incorporation of LiClO₄ was produced by diffusion. The drying process was carried out at room temperature under vacuum in the same way as in method A.

Method C. Samples were prepared in the same way as method B, but in order to improve the diffusion process, the temperature was maintained at 40 °C for 72 h and the samples kept covered with acetone. Then the drying process was carried out at 55 °C for 120 h under a nitrogen stream.

All samples were stored under nitrogen atmosphere. The [O/Li] ratio range studied was 600−0.3.

The high-resolution solid-state NMR experiments were made in a 2 T home-built spectrometer using a Doty double-resonance

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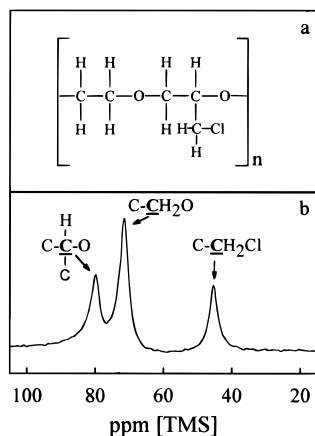**3470** *J. Phys. Chem. B, Vol. 101, No. 18, 1997*

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Figure 1. (a) Structural formula of PEPI−PEO copolymer. (b) ^{1}H-decoupled ^{13}C NMR spectrum of pure PEPI−PEO copolymer. Line assignment is inserted in the figure.
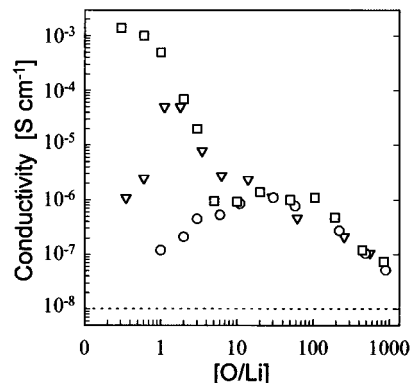

Figure 2. Conductivity values at room temperature as function of [O/Li] ratio for PEPI−PEO copolymer: (▽) samples prepared with method A; (○) samples prepared with method B; (□) samples prepared with method C. The dotted line represents the conductivity of the pure PEPI−PEO copolymer.

probe. The pulse sequences employed were programmed with a Tecmag Libra system. The NMR spectra of ^{13}C, [7]Li, and ^{1}H were obtained from the fast Fourier transform (FFT) of the digitized free induction decay (FID) after a 90° pulse excitation shorter than 10 μs. Measurements of the ^{13}C spin lattice relaxation time (T_1) were performed using the standard inversion recovery pulse sequence (180°−τ−90°) with delay times (τ) varying from 0.1 ms to ~7T_1. For each T_1 value determination, at least 18 data points were taken. For all ^{13}C measurements ^{1}H decoupling was used during the acquisition.

Conductivity measurements were carried out at 25 °C using a 1286 Solartron electrochemical interface combined with a 1250 Solartron frequency response analyzer. The conductivity values were obtained by the ac impedance technique in the frequency range 0.01−65 000 Hz. It was used with a cell of two gold electrodes of 0.2 cm[2] of geometrical area. The sample thickness was 0.5 mm.

Results and Discussion

Figure 1a shows the structural formula of PEPI−PEO copolymer and Figure 1b shows the [1]H-decoupled ^{13}C spectrum of pure PEPI−PEO prepared as described in the Experimental Section. Three lines centered at 80.3, 71.2, and 45.6 ppm [TMS] can be observed. The line at 80.3 ppm was assigned to a secondary carbon bonded to an oxygen atom. The second line at 71.2 ppm corresponds to a primary carbon bonded to an oxygen atom, and the third line, at 45.6 ppm, was assigned to a secondary carbon bonded to the chlorine atom.

Figure 2 shows the solid solution conductivity as a function of [O/Li] ratio for samples prepared with methods A−C. For [O/Li] ratios larger than 20 the conductivity increases with LiClO$_4$ concentration and does not depend on the sample preparation method. However, for [O/Li] smaller than 20 it is possible to observe, in Figure 2, an important dependence of the conductivity behavior on the sample preparation method. The conductivity of samples prepared by method A shows a sharp increase for a [O/Li] ratio between 20 and 1 with a maximum at ca. 2. For [O/Li] ratio less than 1, the conductivity values decrease notably. The conductivity of samples prepared by the method B reaches a maximum for [O/Li] ratio of ca. 20. Below that, the conductivity decreases in the same way as for the samples of method A. The conductivity of samples of method C shows a behavior similar to samples of method B up to a [O/Li] ratio of ca. 10 but beyond that, increases up to 10^{-3} S cm^{-1}. It is important to remark that at room temperature PEPI−PEO copolymers obtained with methods A and C present
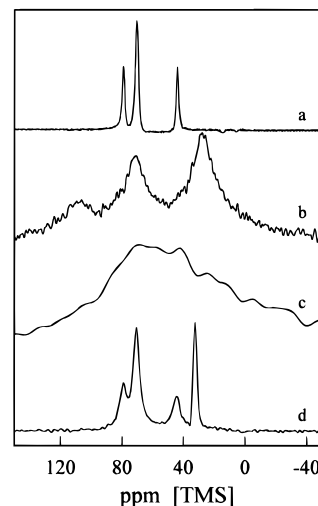
Figure 3. ^{1}H-decoupled ^{13}C NMR spectrum of (a) pure PEPI−PEO copolymer, (b) PEPI−PEO/LiClO$_4$ solid solution prepared with method A, (c) PEPI−PEO/LiClO$_4$ solid solution prepared with method B, and (d) PEPI−PEO/LiClO$_4$ solid solution prepared with method C. All solid solutions correspond to a [O/Li] ratio equal to 1.

conductivities higher than those of other polymers doped with lithium salts[14−17] and similar to that obtained by adding other inorganic or organic soluble additives.[18−22]

To analyze the effect of the preparation method on the conductivity behavior, ^{1}H-decoupled ^{13}C NMR spectra were carried out on pure PEPI−PEO copolymer and samples prepared by methods A−C with [O/Li] ratio equal to 1 (Figure 3). For comparison, Figure 3a shows the ^{13}C spectrum of the pure polymer with the three characteristic polymer lines as already discussed. Figure 3b shows the spectrum for the sample prepared by method A, where it is possible to observe the broadening of the polymer lines and the appearance of new lines, some of them corresponding to THF. In the case of samples prepared by method B (Figure 3c) a large broadening of the polymer lines is observed. For samples prepared by method C (Figure 3d) there is only a small broadening of the polymer lines. Here, it is important to note the presence of new lines in this spectrum associated with the presence of acetone in the solid solution. From Figure 3 it is evident that the magnitude of the peak broadening is strongly dependent on the sample preparation method. This broadening is usually observed in ionic conducting polymers[23] and it is produced by the presence of Li$^+$. This fact reflects a less effective motional narrowing due to the reduction of the segmental motion of the polymer
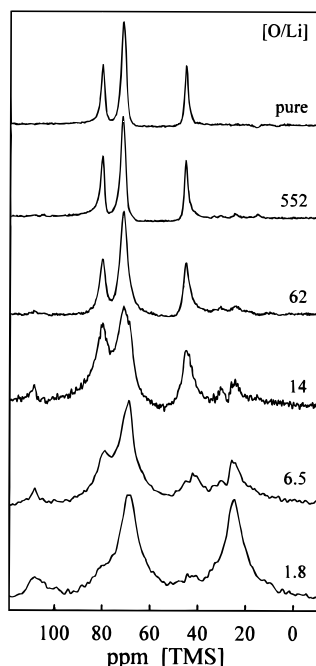
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Figure 4. ^{1}H-decoupled ^{13}C NMR spectra of PEPI−PEO/LiClO$_4$ solid solution prepared with method A for different [O/Li] ratios.

Figure 5. ^{1}H-decoupled ^{13}C NMR spectrum of (a) pure THF, where the lines at 67.9 and 25.8 ppm correspond to a carbon−oxygen bond and a carbon−carbon bond, respectively, (b) THF/LiClO$_4$ saturated solution, and (c) PEPI−PEO/LiClO$_4$ solid solution prepared with method A. The [O/Li] ratio is equal to 5. Lines marked as α correspond to the polymer carbon, β to the THF carbon lines, and γ to the new lines in the spectra.

Figure 6. ^{1}H-decoupled ^{13}C NMR spectra of PEPI−PEO/LiClO$_4$ solid solution prepared with method C for different [O/Li] ratios.

matrix. It is caused by the electrostatic interaction between the ionic salt and the polar sites in the polymer chain, which has the effect of increasing the chain rigidity. Therefore, in Figure 3, the ^{13}C line width illustrates the differences in the chain mobility among the samples prepared by methods A−C. All samples have the same [O/Li] ratio, so differences in the conductivity must be due to different chain mobility and it is accompanied by the diminution of the ^{13}C line width. The different mobilities can be related to the presence of solvent, which behaves as a plasticizer, in the polymer matrix. Here, it must be pointed out that these two contributions to the conductivity, ionic carriers and solvent platicizer effect, had opposite effects on ^{13}C line widths: while conductivity increases for lower [O/Li] ratio, the ^{13}C line width broadens; however, NMR line widths diminish because of the effect of solvent.

Figure 4 shows the [1]H-decoupled ^{13}C spectra of the PEPI−PEO solid solution, prepared using THF as solvent (method A), as a function of the [O/Li] ratio. It is possible to observe a dependence of the broadening of the PEPI−PEO lines, together with the increase of intensity of THF related lines, on the amount of lithium salt. It is evident the ^{13}C polymer lines broaden with the diminution of the [O/Li] ratio. This fact indicates a decrease of chain mobility and it explains the no proportionality between conductivity and Li$^+$ concentration, showing the contribution of the chain dynamics to the conductivity mechanism. The THF-related lines are only observed in samples containing Li$^+$ ions, indicating that the lithium cation plays a role in trapping THF molecules in the polymer complex. However, the solvation of the lithium cation is not strong enough to explain the presence of solvent in the polymeric matrix, due to the small polarity of the THF ($\epsilon_{THF} = 7.6$ [24]). The no shift of the pure THF lines (Figure 5a) in the THF/LiClO$_4$ saturated solution (Figure 5b) illustrates that the interaction between the lithium salt and the solvent could be weak. On the other hand, the ^{13}C spectrum of the PEPI−PEO/THF/LiClO$_4$ solid solution shows the existence of new lines, marked as γ in Figure 5c, in addition to the PEPI−PEO and THF lines. This new lines could be explained assuming a strong interaction between the solvent molecules and the polymer structure modified by the presence of Li$^+$.
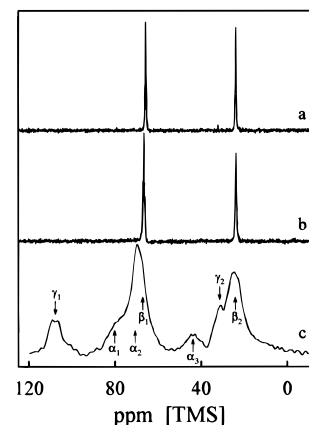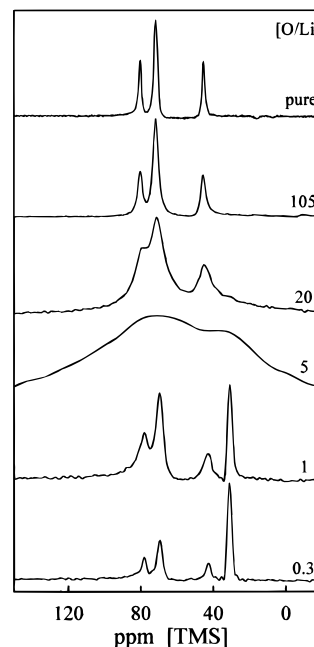
Different results are obtained with samples prepared by method C. Figure 6 shows the ^{1}H-decoupled ^{13}C NMR spectra of the PEPI−PEO solid solution as a function of the [O/Li] ratio. In this figure, it is possible to observe three ranges of Li$^+$ concentration with different behavior. For [O/Li] > 20 spectra show the broadening of the PEPI−PEO lines with the increment of the lithium concentration. For [O/Li] ratios between 5 and 20, it is possible to observe the existence of new lines in the spectra that are related to the presence of acetone in the solid solution. The acetone-related lines are broadened with lithium concentration in the same way as the PEPI−PEO lines, indicating that the acetone molecules are in a structure with low mobility. For [O/Li] < 5, there is a notorious narrowing of the PEPI−PEO and acetone lines. This fact illustrates an increase in the mobility of the polymer matrix, which is related to the abrupt conductivity increase observed for these samples (Figure 2). It can be explained assuming that the large amount of acetone present in the solid solution has an effective plasticizer effect reducing the interchain interaction
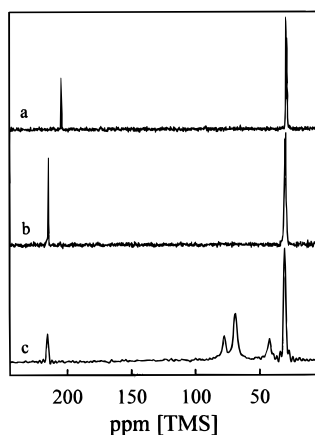
Figure 7. ¹H-decoupled ¹³C NMR spectrum of (a) pure acetone, where the lines at 205.4 and 30.5 ppm correspond to the carbon−oxygen bond and the carbon−carbon bond, respectively, (b) acetone/LiClO₄ saturated solution, and (c) PEPI−PEO/LiClO₄ solid solution prepared with method C. The [O/Li] ratio is equal to 1.

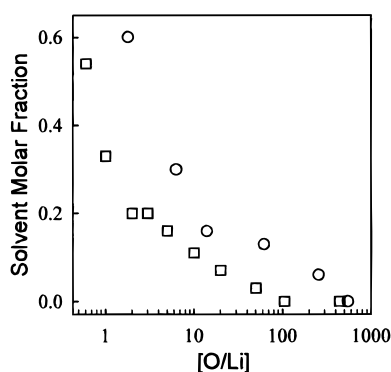**Figure 8.** Molar fraction of solvent in the solid solution as a function of [O/Li] ratio for samples prepared with methods A (○) and C (□).

and allowing a higher intrachain mobility. By comparing parts a−c of Figure 7, it is possible to conclude that acetone interactions with Li⁺ in the solid solution are strong and that they are weak with the polymer matrix. The shifting observed, in the acetone lines, is related to the strong solvation of Li⁺ ($\epsilon_{acetone} = 20.7$ [24]).

Figure 8 shows the molar fraction of solvent as function of [O/Li] ratio. The molar fraction of solvent in the solid solution was determined from the NMR spectra by calculating the ratio of the area of ¹³C solvent lines with the area of ¹³C lines of solvent and PEPI−PEO. For [O/Li] ratio > 5 the amount of THF is greater than the amount of acetone. This fact corroborates that the amount of acetone molecules depends on the solvation process of the lithium cation to be incorporated into the solid solution. At higher Li⁺ concentrations the amount of acetone has increased in proportion to THF. However, the interaction of THF with the polymer chain diminishes its plasticizer effect, this fact being evident by the presence of new NMR lines (Figure 5c).

The increase of polymer chain mobility in the samples prepared by method C for [O/Li] ratios less than 5 is shown by other NMR parameters. (a) Figure 9 shows the full widths at half-maximum (fwhm) of ⁷Li and ¹H NMR lines as a function of the [O/Li] ratio. The fwhm at [O/Li] ratio of approximately 5 indicates an abrupt transition between two polymer structures with different chain mobilities. (b) Figure 10 shows the T_1 values of ¹³C nuclei corresponding to the PEPI−PEO lines as a function of the [O/Li] ratio. These curves show an abrupt change when the polymer dynamics is modified by the presence of the plasticizer.

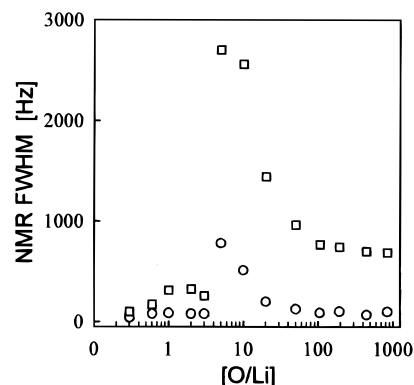**Figure 9.** (○) ⁷Li and (□) ¹H NMR full widths at half-maximum of PEPI−PEO/LiClO₄ solid solution prepared with method C as a function of [O/Li] ratio.

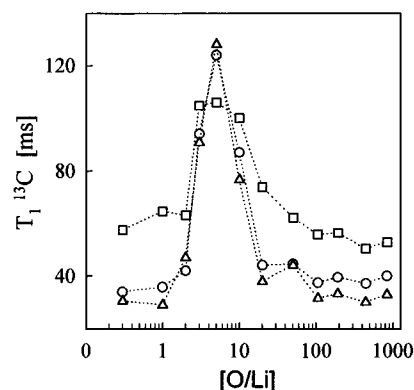**Figure 10.** T_1 of the three lines of the ¹³C spectrum of PEPI−PEO/LiClO₄ solid solution prepared with method C as a function of [O/Li] ratio: (△) 45.6 ppm (secondary carbon bonded to chlorine atom); (○) 71.2 ppm (primary carbon bonded to an oxygen atom); (□) 80.3 ppm (secondary carbon bonded to an oxygen atom).
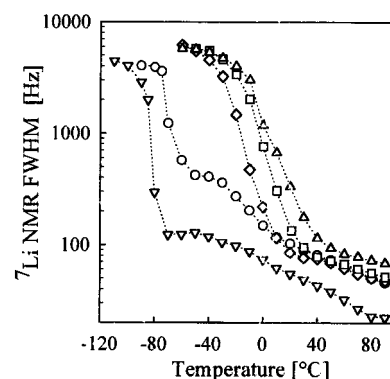

Figure 11. ⁷Li NMR full widths at half-maximum of PEPI−PEO/LiClO₄ solid solution prepared with method C as a function of temperature for different [O/Li] ratios: (▽) 0.3; (○) 0.6; (△) 5; (□) 20; (◇) 105.

The plasticizer effect of the solvent in the solid solution prepared by method C, for high amounts of lithium salt, can be clearly observed through the variation of the glass transition temperature (T_g). Figure 11 shows the variation of the fwhm of the ⁷Li NMR line as a function of temperature. It is clearly defined as the transition between the high-temperature amorphous structure, characterized by a narrow line, and a low-temperature crystalline structure with a broad line. For [O/Li] ratio > 5, the transition temperature between the amorphous phase and the more crystalline phase, T_g, increases with lithium salt concentration, but when the [O/Li] ratio is lower than 5, T_g shifts to lower temperatures. This phenomenon illustrates the

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plasticizer effect of the solvent in the polymeric matrix and its influence in the increase in the solid solution conductivity.

In summary, these experiments show a great difference between the behavior of THF and acetone inside the polymeric chain. In the case of THF, there is no evidence of an interaction between THF and Li$^+$; otherwise, solvent interactions are mainly oriented to the polymeric chain, explaining the new lines appearing in the ^{13}C spectrum. In the case of acetone, the interactions occur mainly with the ionic salt. The different behavior of both solvents is probably due to the different polar nature of the solvents ($\epsilon_{THF} = 7.6$ and $\epsilon_{acetone} = 20.7$). The THF does not show a direct interaction with the Li$^+$ ions, which results in no competition with the polymer in the solvation of the lithium cations. In the case of acetone, at low Li$^+$ concentration, the polymer is more effective in solvating the lithium cation and there are no significant amounts of solvent in the polymer matrix. When the polymer chain is saturated with Li$^+$ the incorporation of acetone in the polymeric matrix begins to be important and the plasticizer effect is evident.

The presence of the ionic salt and the solvent in the polymeric matrix could produce four different effects that can affect the conductivity: (a) the increase of the conductivity with the increase of the amount of the ionic salt; (b) the decrease of the conductivity with the decrease of the polymer chain mobility produced by electrostatic interaction between the polymeric matrix with the lithium salt; (c) the decrease of the conductivity by an increase of the ionic radii of the lithium cation (solvation layer); (d) the increase of the conductivity by the plasticizer effect produced by the solvent. For $10 < [O/Li] < 1000$, the conductivity values of all samples increase slowly because of the increase of the amount of Li$^+$. In the case of the samples prepared with THF for $1 < [O/Li] < 10$, the conductivity sharply increases, illustrating the plasticizer effect of the solvent. For $[O/Li] < 1$, the interaction of the ionic salt with the polymeric chain is predominant, leading to a decrease of the segmental motion of the polymer. In the case of samples prepared by method C, the incorporation of acetone is evidenced in two different ways: for $[O/Li]$ ratio > 5, acetone is present, solvating the cation; for $[O/Li] < 5$, the effect of the solvent as plasticizer is predominant among all the possibilities. For the samples prepared by method B, the acetone is not incorporated in the polymer because at room temperature the diffusion process is not effective. In this case the system presents a typical behavior corresponding to an increase of conductivity with the $[O/Li]$ ratio, passing through a maximum and then decreasing, in a sequence reflecting only the influence of the ionic salt concentration on the mobility of the polymeric chain.

Conclusions

The ^{13}C NMR spectra show that it is important to take into account the physicochemical properties of the solvent because the solvent remains in the solid electrolyte even after a careful drying process. The analysis of those spectra combined with conductivity measurements shows that the solvent in the solid electrolyte strongly modifies the charge transport process. This phenomenon can be mainly associated with the plasticizer effect

in the case of samples prepared with acetone at 40 °C. For samples prepared with THF and large amounts of lithium salt, the polymer interaction with the salt and THF leads to an increase of the polymeric chain rigidity.

The PEPI−PEO copolymer is shown to be a very favored solvating medium. It is able to combine effectively with the salt cations to form a homogeneous solution. Conductivity measurements show that PEPI−PEO copolymer doped with LiClO$_4$ is a good ionic conductor at room temperature, mainly, if it is prepared with THF or acetone at 40 °C. With a high Li$^+$ concentration, it can be considered a superionic conductor.[27] These characteristics illustrate that PEPI−PEO is an excellent system for studying the conductivity in solid polymer electrolytes.

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