Investigation of New Ion-Conducting ORMOLYTES: Structure and Properties

KARIM DAHMOUCHE, MOHAMED ATIK, NILSON C. MELLO, TITO J. BONAGAMBA,
HORACIO PANEPUCCI AND MICHEL A. AEGERTER

Instituto de Física de São Carlos, Universidade de São Paulo, Caixa Postal 369, 13560-970, São Carlos-SP, Brasil

PATRICK JUDEINSTEIN

Lab. de Chimie Structurale Organique, URA CNRS 1384, Université Paris sud 91405, Orsay, France

Abstract. Two families of hybrid organic-inorganic composites exhibiting Li^+ ionic conduction (ORMOLYTES) have been prepared by the sol-gel process. The first family, prepared from a mixture of 3-isocyanatopropyl-triethoxysilane, O,O' Bis (2-aminopropyl)-polyethyleneglycol (or O,O' Bis (2-aminopropyl)-polypropyleneglycol) and lithium salt, presents chemical bonds between the organic and the inorganic phase and an ionic conductivity σ higher than 10^{-4} S m^{-1} at room temperature. Their properties have been related to their structure using liquid state NMR measurements of ^{7}Li between $-100°$C and $+100°$C and the DMTA technique. In the second family, prepared by ultrasonic method from a mixture of tetraethoxysilane (TEOS), polyethyleneglycol (PEG) and lithium salt, the organic and inorganic phases are not chemically bonded. Ionic conductivity σ has been studied as a function of the polymer chain length and concentration. Values of σ up to 10^{-2} S m^{-1} at room temperature have been obtained (with a silica-PEG$_{300}$ system, PEG/TEOS $= 40\%$ in weight). Again, structure was investigated by liquid state ^{7}Li NMR measurements.

Keywords: hybrid materials, ORMOLYTES, ionic conductivity, nuclear magnetic resonance (NMR), polymers, SiO$_2$-PEG, SiO$_2$-PPG

1. Introduction

Many studies have been reported in the field of solid electrolytes [1] due to their potential for various applications such as batteries, energy and data storage, sensors, electrochromic and photochromic devices [2]. Systems showing conductivity induced by the addition of lithium offer the most favorable properties [3]. Recently, studies have been reported on hybrid materials obtained by reacting silicon alcoxide with polyethers [4–6] showing that poly(ethylene)oxide could act as a "solid" solvent for numerous chemical species, while the structural silica network reinforces mechanically the final material. Specific physical properties can be obtained by dissolving suitable doping agents within such networks, for example, lithium salt for ionic conductivity. The tailoring of the properties is strongly related to the connectivity of the two phases and the mobility of both the structural network and the active species.

This work reports on the preparation and structural properties of new hybrid ionic conductors SiO$_2$-PEG or SiO$_2$-PPG with and without covalent organic-inorganic chemical bonds. The mobilities of the polymer chains and Li$^+$ ions, have been determined by NMR spectroscopy and ionic conductivity measurements, respectively.

2. Experimental

All chemical reagents are commercially available (Fluka, Aldrich). For the first family (Type I) equimolar amounts of 3-isocyanatopropyltriethoxysilane and O,O' Bis (2-aminopropyl)-polyethyleneglycol (i.e., NH$_2$-PEG$_{800}$-NH$_2$) or O,O' Bis (2-aminopropyl)-

polypropyleneglycol (i.e., NH_2-PPG_{4000}-NH_2) were stirred together in tetrahydrofuran (THF) under reflux for 6 hours. THF was evaporated and pure hybrid precursors $(OEt)_3Si\_PEG_{800}\_Si(OEt)_3$ or $(OEt)_3$ $Si\_PPG_{4000}\_Si(OEt)_3$ were obtained. 0.5 g of one of these precursor was mixed with 1 ml of ethanol containing NH_4F ($NH_4F/Si = 0.005$) to which were added desired quantities of the lithium salt ($LiClO_4$). Finally 0.2 ml of water were added under stirring. A monolithic gel was obtained in 4 h. Ethanol was then slowly removed to give a piece of rubbery material. The existence of covalent chemical bonds between the silica network and the polymer chains has been reported [4].

The materials of the second family (Type II) were prepared by an ultrasonic method: 12.5 ml of TEOS and 4 ml of water were stirred together under ultrasound to hydrolyse the TEOS. Then the desired quantities of PEG of various molecular weights were added in neutral pH conditions. The lithium salt ($LiClO_4$) was then introduced and dissolved under ultrasound in order to obtain a transparent monophasic liquid. Gelation occurred in a few minutes and the samples were allowed to dry slowly as a monolithic piece. Studies of similar materials, prepared by the classic sol-gel method without the lithium salt, have shown that no covalent chemical bonds exist in these materials, but only weak physical bonds [5].

The electrical properties of the samples were determined by complex impedance spectroscopy between 20 and 100°C with a Solartron 1260 apparatus, in the range 1 Hz to 10 MHz, with an applied voltage amplitude of 5 mV. The samples were pieces of monolith about 0.5 mm thick, with surfaces as flat as possible. The contacts were obtained with plasticized conductive probes (Altoflex) pressed on the sample. Stable and reproductible values of the ionic conductivity σ were obtained by conditioning the dried samples under vacuum at 90°C for 24 h.

The NMR spectrum of the ^7Li, consisting only of the central transition ($-1/2 \leftrightarrow +1/2$), was studied between -100 to 90°C at 32.9855 MHz using a TEC-MAG LIBRA system and a double resonance Doty probe. The spin-lattice relaxation time T_1 was measured by inversion-recovery using proton decoupling during the Free Induction Decay (FID) acquisition to improve the signal to noise ratio and allow measurements over extended doping and temperature ranges. Linewidths were obtained using either decoupled FIDs in the inversion-recovery measurements, or without decoupling by a $\pi/2$ excitation. Full widths at half maxima (FWHM) were obtained in both cases by fitting the lineshape by Lorentzian or Gaussian functions, depending on the temperature ranges.

Differential mechanical thermal analysis (DMTA) was performed with Polymer Laboratory equipment. Measurements of the shear modulus between -100 and 100°C (with 1 Hz frequency) were carried out on circular samples of diameter 10 mm and 1 mm thick.

3. Results and Discussion

3.1. Ionic Conductivity

Type I Materials. Figure 1 presents the variation of room temperature conductivity, σ, for the chemically bonded hybrids silica-PEG_{800} and silica-PPG_{4000} as a function of the ratio [O]/[Li] (where oxygens considered are only those of the ether type). For both materials a maximum is observed for [O]/[Li] around 15, in contrast with the behavior observed in most polymeric systems in which σ_{max} occurs for [O]/[Li] = 8 [7, 8]. For pure polymers [9], the increase of conductivity with the salt concentration is attributed to long-range
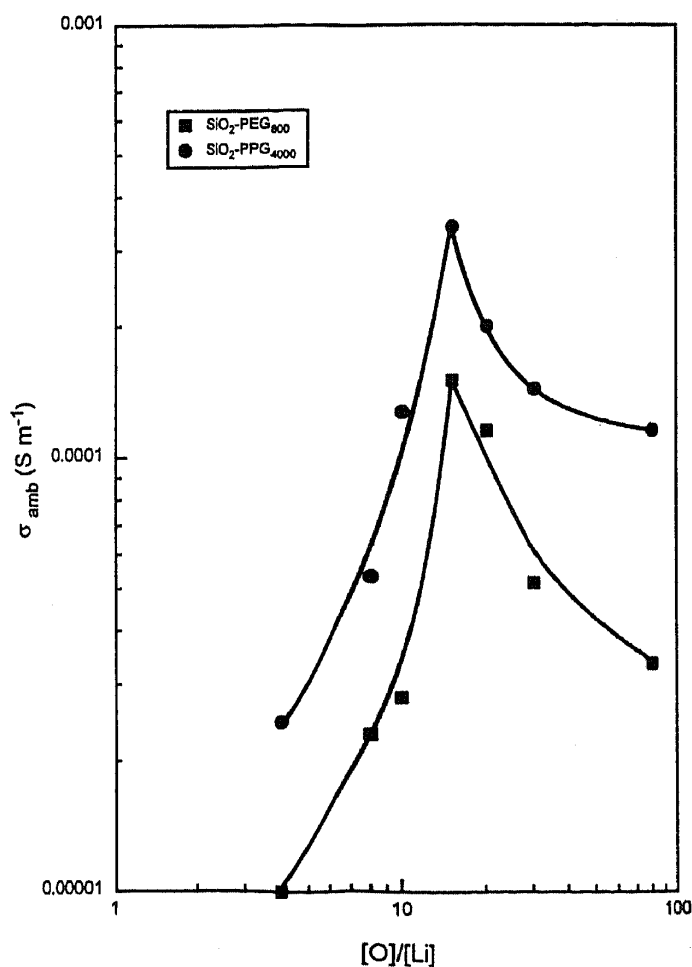

Figure 1. Ionic conductivity versus lithium concentration for the SiO_2-PEG_{800} and SiO_2-PPG_{4000} samples (Type I materials).
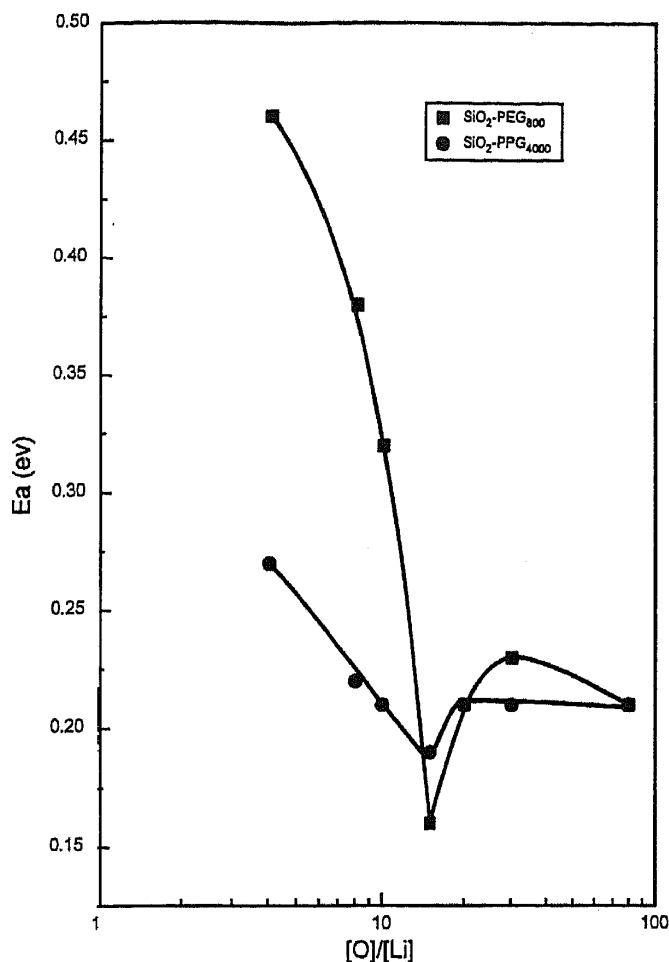
Figure 2. Activation energy versus lithium concentration for the SiO$_2$-PEG$_{800}$ and SiO$_2$-PPG$_{4000}$ samples (Type I materials).

Table 1. Effect of the polymer chain length in Type II materials.

Sample	SiO$_2$-PEG$_{300}$	SiO$_2$-PEG$_{600}$	SiO$_2$-PEG$_{1000}$
PEG/TEOS (weight %)	40	40	40
[O]/[Li]	4	4	4
σ_{amb} (S m^{-1})	$9.2 \cdot 10^{-3}$	$3.5 \cdot 10^{-4}$	$8 \cdot 10^{-5}$
E_{a1} (eV)	0.05	0.05	0.2
E_{a2} (eV)	0.19	0.23	0.45

Type II Materials. Tables 1 and 2 present the variation of the ionic conductivity for different Type II materials (not chemically bonded) as a function of the polymer chain length and concentration. The ionic conductivity σ increases when the polymer chain length decreases. It is known that the conductivity occurs via a liquid-like motion of cations through the segmental motion of the neighboring polymer chains [1]. Therefore, the PEG chain mobility decreases as the chain length increases. A similar behavior was observed with samples without lithium [4].

The variation of the conductivity with temperature shows discrepancies with a pure Arrhenius model. Two slopes are observed, with an intercept around 50°C for all systems with activation energies 0.05 eV < E_{a1} < 0.2 eV for $T > 50$°C and 0.2 eV < E_{a2} < 0.5 eV for $T < 50$°C. Such behavior has also been observed in some polymers [10] and composite electrolytes [11] and interpreted as due to a partial crystallization and phase separation below a critical temperature. The chemical stability of Type II materials is therefore lower than that of Type I.

The ionic conductivity at room temperature increases with the polymer concentration as observed with samples without lithium [4]. In samples with high PEG concentration the influence of the silica network, which will be Van der Waals or hydrogen interactions, is negligible for the "liquid-like" polymeric

coulomb interactions. The decrease after the maximum is a consequence of the immobilization of the polymer chains by interactions with the Li$^+$ ions. In our materials, the saturation occurs at a lower concentration, showing that the PEG or PPG chain mobility is smaller when both networks are chemically bonded. The temperature variation of the conductivity follows strictly an Arrhenius law $\sigma T = \sigma_0 \exp(-E_a/RT)$. The variation of E_a with lithium concentration shows a minimum also for [O]/[Li] around 15 (Fig. 2).

Table 2. Effect of the polymer concentration in Type II materials.

Sample	SiO$_2$-PEG$_{1000}$	SiO$_2$-PEG$_{1000}$	SiO$_2$-PEG$_{1000}$	SiO$_2$-PEG$_{1000}$
PEG/TEOS (weight %)	20	40	80	100
[O]/[Li]	4	4	4	4
σ_{amb} (S m^{-1})	$4 \cdot 10^{-5}$	$8 \cdot 10^{-5}$	$1.7 \cdot 10^{-4}$	$3.3 \cdot 10^{-4}$
E_{a1} (eV)	0.2	0.2	0.14	0.14
E_{a2} (eV)	0.45	0.45	0.36	0.36
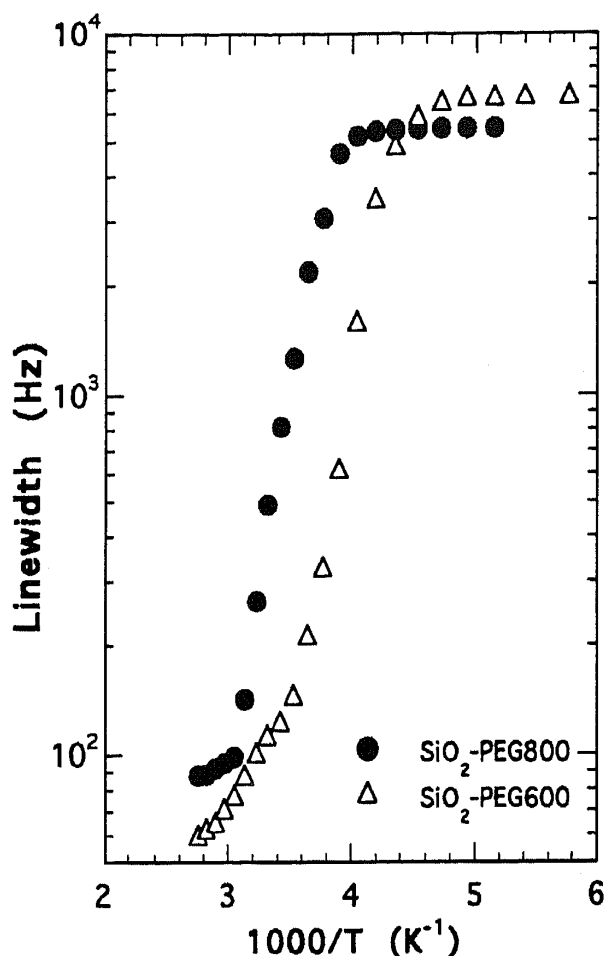
Figure 3. Temperature dependence of the ^7Li central transition linewidth in SiO_2-PEG$_{600}$ (Type II, [O]/[Li] = 4) ($\triangle$) and SiO_2-PEG$_{800}$ (Type I, [O]/[Li] = 4) ($\bullet$).

phase. When the volume of the PEG phase decreases, the influence of the interface between organic and inorganic domains becomes predominant. This effect also occurs with the lithium doped samples and influences the conductivity values.

3.2. NMR Spectroscopy

Motional narrowing of the ^7Li linewidth occurs around $-25°C$ for a Type II hybrid (PEG$_{600}$, [O]/[Li] = 4)) and $10°C$ for a Type I sample (PEG$_{800}$, [O]/[Li] = 4), (Fig. 3). These temperatures are higher than the PEG glass transition temperature ($T_g \approx -50°C$). The effect of the silica structure in raising the glass transition temperature is more pronounced for the ormolyte prepared with PEG$_{800}$ ([O]/[Li] = 4), which has bonding groups attached at the chain ends. DMTA data (Fig. 4) show for the same sample that T_g is higher than that given by NMR, reflecting the softening of the bulk composite material which is more strongly affected by the inorganic silica component. These results show
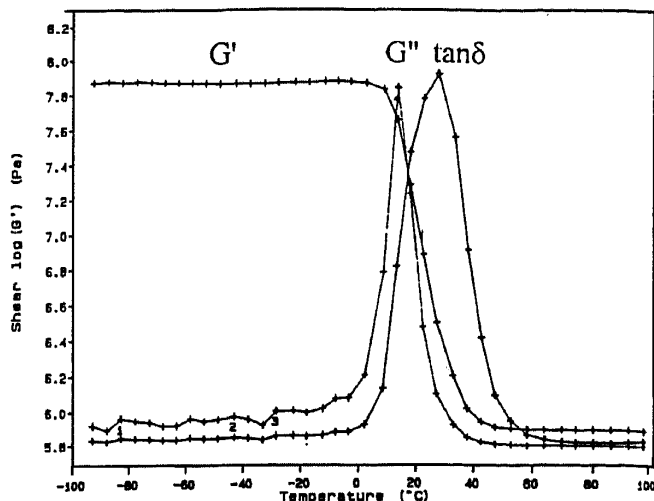

Figure 4. Shear storage modulus G', Shear loss modulus G'' and tanδ versus temperature for SiO_2-PEG$_{800}$ (Type I, [O]/[Li] = 4).

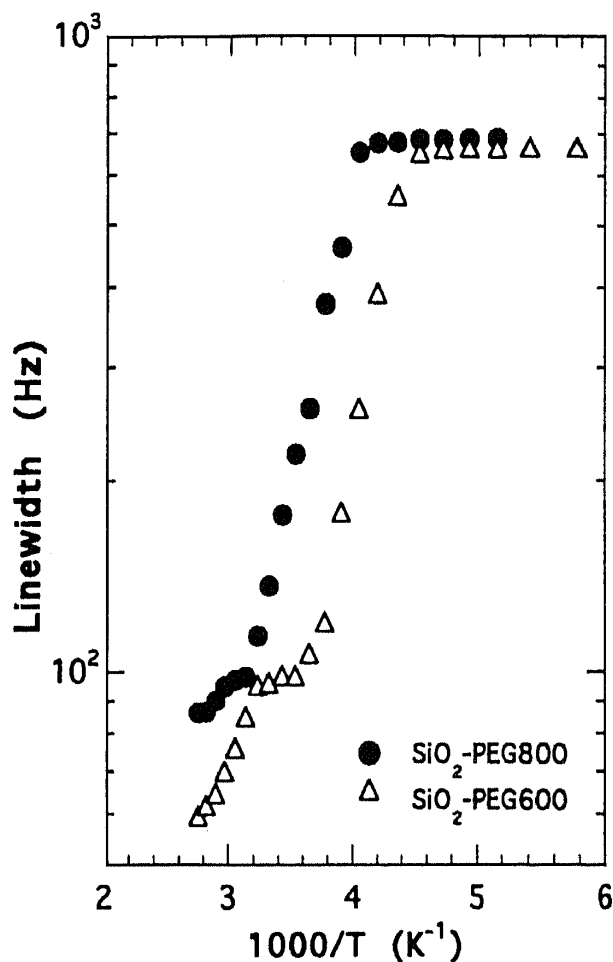*Figure 5.* Temperature dependence of the proton decoupled ^7Li central transition linewidth in SiO_2-PEG$_{600}$ (Type II, [O]/[Li] = 4) ($\triangle$) and SiO_2-PEG$_{800}$ (Type I, [O]/[Li] = 4) ($\bullet$).

the superiority of the NMR technique over the DMTA measurements to assess the behavior of the polymeric component and show correlation between Li$^+$ ionic mobility and the segmental motion of the polymer chain [12].
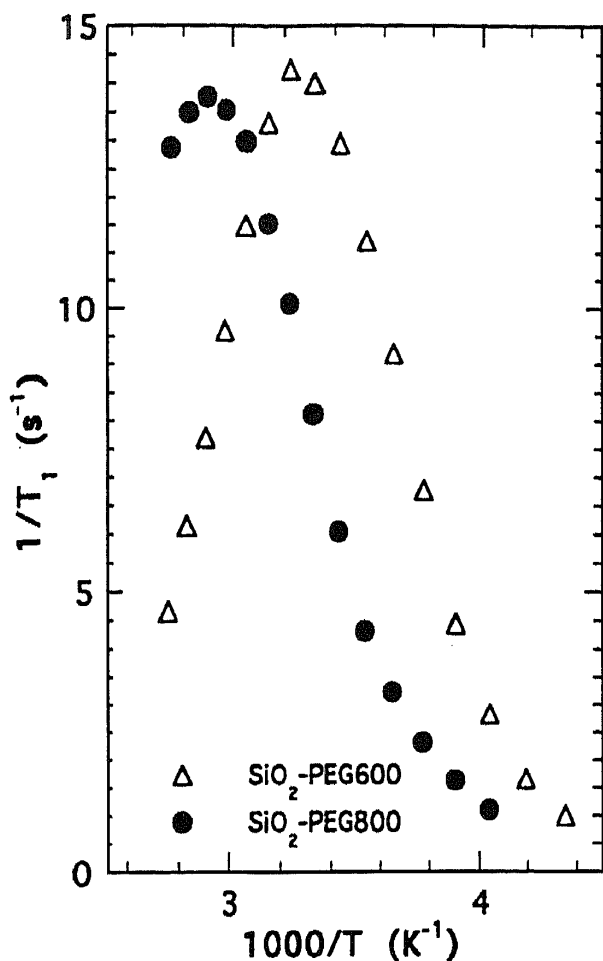
between the organic inlet and inorganic network has been studied by impedance spectroscopy, NMR and DMTA techniques.

In materials with covalent chemical bonds between the silica and the organic network, the ionic conductivity presents a maximum for $[O]/[Li] = 15$, in contrast with pure polymer electrolytes ($[O]/[Li] = 8$), indicating a smaller polymer chain mobility in these new hybrid materials.

In materials with no covalent bonds between the organic and inorganic phase, the ionic conductivity decreases with the polymer chain length but increases with the polymer concentration.

For quite similar chain length and similar lithium concentration the conductivity and the mobility of the chains are lower in covalent bonded ormolytes, as measured by complex impedance and ^7Li NMR spectroscopies.

Figure 6. Temperature dependence of the ^7Li spin-lattice relaxation rate T_1^{-1} in SiO_2-PEG_{600} (Type II, $[O]/[Li] = 4$) ($\triangle$) and SiO_2-PEG_{800} (Type I, $[O]/[Li] = 4$) ($\bullet$).

Non bonded PEG_{600} ($[O]/[Li] = 4$) chains show a second reduction in the ^7Li linewidth at about 50°C, when the proton contribution is eliminated by decoupling (Fig. 5). This extra narrowing could be due to the onset of the unbonded motion of Li^+ ions through a diffusion process [13]. This assumption is further supported by the behavior of the conductivity versus temperature (Table 1) which shows a reduction of the activation energy at the same temperature. The effect of polymer chains-inorganic silica network bonds, in the case of the PEG_{800} ($[O]/[Li] = 4$), is also clearly apparent from the T_1 data (Fig. 6), which show a shift of the $1/T_1$ maxima towards higher temperatures in comparison to the PEG_{600} ($[O]/[Li] = 4$) ormolyte.

4. Conclusion

New hybrid ionic conductors SiO_2-PEG and SiO_2-PPG doped with lithium salt have been prepared by the sol-gel process and the effect of chemical bonding

Acknowledgment

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