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Effect of salt nature on structure and ionic conductivity of sodium-doped siloxane–PPO ormolytes

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Abstract

Siloxane–polyoxypropylene (PPO) hybrids obtained by the sol–gel process and containing short polymer chain have been doped with different sodium salts NaX (X = ClO_4, BF_4 or I). The effect of the counter-ion (X) on the chemical environment of the sodium ions and on the ionic conductivity of these hybrids was investigated by ^{23}Na NMR, small angle X-ray scattering (SAXS), complex impedance, Raman spectroscopy and differential scanning calorimetry (DSC). Results reveal that the different sodium salts have essentially the same effect on the nanoscopic structure of the hybrids. The formation of immobile Na^+ cations involved in NaCl-like species could be minimized by using a low amount of HCl as hydrolytic catalyst. The differences in the ionic conductivity of hybrids doped with different sodium salts were correlated with the proportion of Na ions solvated by ether-type oxygen of the polymeric chains and by the carboxyl oxygen located in the urea groups of the PPO chain extremities.

Keywords: Hybrid materials; Nanocomposites; Ionic conductivity; Sol–gel processes

1. Introduction

A novel class of solid electrolytes, called ORMOLYTES (ORganically MOdified electroLYTES) have emerged in the past years[1–3] that combine ionic conductivity and optical transparency which are desirable for the development of electrochromic devices and fuel cells. An interesting family of sol–gel-derived ormolytes are based on hybrid materials constituted of polyoxyethylene or polyoxypropylene chains grafted to siloxane nanoparticles.[4–6] Specific physical properties can be obtained by dissolving suitable doping agents within such hybrid networks, for example, alkaline salts and polymetalates which induce ionic conductivity[4,5] and photochromic properties,[6] respectively. It is well established that ionic conduction in polymer electrolytes occurs within the amorphous phase via a liquid-type migration of the doping cation assisted by segmental motions of polymeric chains. Spectroscopic studies (IR, Raman)[7,8] and molecular dynamic simulations[9] showed that cations are dissolved in the classical polyoxyethylene (PEO) polymer as “free ions” or associated with anions to form ion-pairs or even larger aggregates. The amount of these species depends on the nature of the polymer and of the counter-ion and also on the salt concentration, but it seems that “free cations” contribute to the ionic conductivity mechanism for the larger extent.[10] Lithium-doped siloxane–polyoxyethylene ormolytes were recently characterized by ^{7}Li nuclear magnetic resonance (NMR), differential scanning calorimetry (DSC) and ionic conductivity and it has been demonstrated that the cationic mobility, as in classical polymeric electrolytes, is assisted by segmental motion of the polymer.[5] The tailoring of the properties in such systems is related to the connectivity between the siloxane and the polymeric phases and to the mobility of the structural network and active ionic species. In short, in both classic organic

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polymeric ionic conductors or ormolytes, the conductivity is related to the motion of polymeric matrix and to the cation mobility, but the influence of the counter-ion on the cation environment and on ionic conduction properties is not well known. Furthermore, the acid or base catalyst used in the hydrolytic sol–gel route leads to the precipitation of alkaline halide salts that do not contribute to ionic conduction.[11]

The work reported here is mainly devoted to the correlation between ion-conduction properties and structure in siloxane–polyoxypropylene (PPO) hybrids using complementary techniques: ^{23}Na NMR, small angle X-ray scattering (SAXS), complex impedance, Raman spectroscopy and differential scanning calorimetry (DSC). These analyses have been applied for ormolytes doped with different sodium salts and aim to understand how the nature of the counter-ion should affect both the preferential environment of the sodium ions and the ionic conductivity. The hybrid material contains two types of oxygen atoms that play a role in the solvation of alkali salt. The first one is related to ether-type oxygen of the polymeric chains and the second is the carboxyl oxygen located in the urea groups of the chain extremities.

2. Experimental

All chemical reagents (Fluka, Aldrich) are commercially available. Equimolar amounts of 3-(isocyanatopropyl)-triethoxysilane (IsoTrEOS) and O,O'-bis(2-aminopropyl)-polyoxypropylene were stirred together in tetrahydrofuran (THF) under reflux for 15 h. THF was evaporated and the hybrid precursor $(OEt)_3Si–(PPO)–Si(OEt)_3$ with PPO molecular weight of 300 g/mol (labeled PPO300) was obtained. A 0.5 g of the precursor was mixed with 0.6 mL of ethanol containing HCl, used to catalyze the hydrolysis of the $-Si(OEt)_3$ groups, and 0.15 mL of a sodium salts NaX ($X = ClO_4$, BF_4 or I) aqueous solution ($[Si]/[H_2O] = 0.067$). The concentration of HCl catalyst was systematically varied aiming to minimize the formation of NaCl. The sodium content was defined as a function of the concentration of the ether-type oxygen of PPO chains: $[O]/[Na] = 15$. Gelation occurred in a few hours and the samples were dried under vacuum at 80 °C for 24 h. Monolithic pieces with thickness of 0.5 mm were obtained.

The glass transition temperature (T_g) was determined from DSC measurements performed on 10 mg samples with a scan rate of 10 °C/min from −60 to 250 °C using a differential scanning calorimeter TA instrument model Q100.

The ionic conductivity was determined by complex impedance spectroscopy measured at room temperature (25 °C) with a Solartron 1260 spectrometer, in the 1 Hz–10 kHz range and applied voltage amplitude of 5 mV. Coole–Coole plots (semi-circles) were computed from the raw experimental data. The intersection in the imaginary impedance at low frequency with the real impedance axis corresponds to the ionic conductance of the samples and hence the ionic conductivity can be calculated knowing the sample thickness and the area of the electrodes.

SAXS analysis was performed at room temperature using the SAS beamline of the National Synchrotron Light Laboratory (LNLS), Campinas, Brazil. This beamline is equipped with an asymmetrically cut and bent silicon (1 1 1) monochromator, which yields a monochromatic ($\lambda = 1.608$ Å) and horizontally focused beam. A vertical position-sensitive X-ray gas detector and a multichannel analyzer were used to record the SAXS intensity, $I(q)$, as a function of the modulus of the scattering vector $q = (4\pi/\lambda)\sin(\varepsilon/2)$, ε being the scattering angle.

^{23}Na ($I = 3/2$) solid-state NMR-MAS (magic angle spinning) spectra were recorded in a NMR spectrometer (Varian) operating at 300 MHz and 7.05 T. The Larmor frequency for ^{23}Na is 79.34 MHz at 7.05 T. The spectra were obtained from the Fourier transform of the free induction decays (FID) following a single $\pi/2$ excitation and a dead time repetition rate of 2 s. Proton decoupling was always used during acquisition. Chemical shifts are reported relative to a $NaCl/H_2O$ 1 M reference standard.

Raman data were recorded using the RXN1-785 Raman spectrometer from Kaiser Optical Systems Inc. (KOSI) equipped with a near IR laser diode working at 785 nm as excitation light and with a CCD detector for providing simultaneous full spectral collection of Raman data from 100 to 3450 cm^{-1}. The transmitted laser power at the sample position was about 25 mW.

3. Results

The effect of the concentration of HCl used to catalyze the hydrolysis of $Si(OEt)_3$ groups on the formation of immobile Na species in $NaClO_4$-doped samples was analyzed by ^{23}Na NMR and presented in Fig. 1. The peak around 7 ppm corresponding to NaCl-like species[11] is observed in hybrids prepared from ethanolic solution containing HCl concentration higher than 0.0001 M. Below this limit, only the broad band near to −20 ppm typical of mobile sodium is apparent.

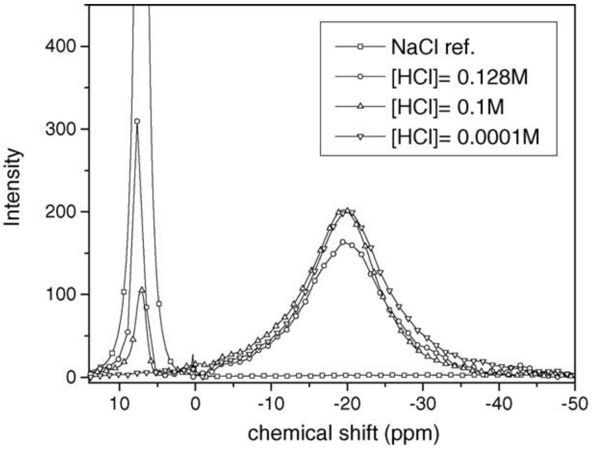

Fig. 1. Room temperature ^{23}Na solid-state NMR-MAS spectra for siloxane–PPO $NaClO_4$-doped hybrids prepared with different HCl contents.

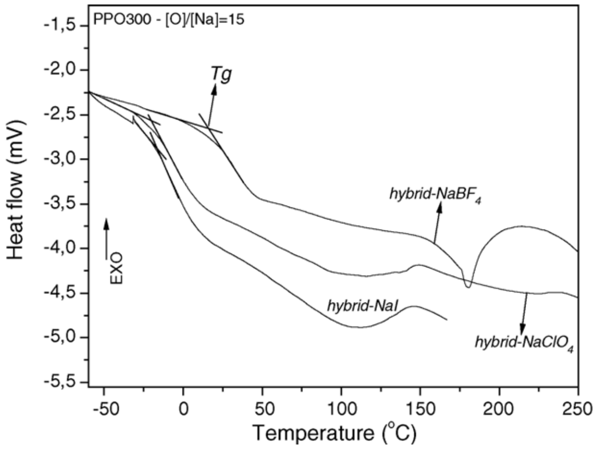

Fig. 2. DSC curves for siloxane–PPO hybrids doped with $NaClO_4$, NaI and $NaBF_4$ with [O]/[Na] = 15.

Thus, the structural and electrical characterization reported in the following corresponds to hybrids prepared with 0.0001 M of HCl catalyst.

The DSC thermograms for hybrids doped with the different sodium salts NaX ($X = ClO_4$, BF_4 and I) are shown in Fig. 2. The polymeric phase of all materials is in an amorphous state, since no melting transition is observed. However, an endothermic peak located at 180 °C appears for $NaBF_4$-doped hybrids, which is associated with PPO degradation. The observed second order transition (glass transition) occurs essentially at lowest temperature for $NaClO_4$ (−21 °C) and NaI (−14 °C) doped samples (Table 1). Otherwise, T_g increases up to 14 °C for the $NaBF_4$-doped sample (Table 1). It is important to note that the structural and the electrical properties presented in this paper were investigated at room temperature (∼25 °C), i.e. above the T_g for all samples.

Table 1 shows the ionic conductivity at room temperature (25 °C) for the studied hybrids. For all samples, low values of conductivity are observed. The $NaClO_4$-doped hybrid is the best ionic conductor, while the $NaBF_4$-doped composite exhibits the lowest conductivity value. This illustrates, as already observed in classic organic polymer electrolytes,[10] the influence of the nature of the counter-anion on the electrical properties of the Na-doped ormolytes.

Fig. 3 shows the SAXS patterns for siloxane–PPO hybrids doped with $NaBF_4$, NaI and $NaClO_4$. All patterns present a single peak whose position q_{max} remains essentially constant for all doping salts. The presence of such peak has already been observed for undoped and lithium-doped similar hybrids[12] and attributed to an interference effect related to the existence of spatial correlation between siloxane nanoparticles bonded at the PPO chain extremities. The average and most probable distance between siloxane clusters ($d_S = 2\pi/q_{max}$) is independent on the nature of sodium salt used as doping (24 Å). The siloxane clusters size was determined assuming spherical particles of radius R_S forming a compact arrangement using the following relation[12]:

Table 1
Glass transition temperature (T_g), ionic conductivity and correlation size L_C for siloxane–PPO hybrids doped with $NaClO_4$, NaI and $NaBF_4$ ([O]/[Na] = 15)

Doping salt	T_g (°C)	Conductivity ($\times 10^{-10}$ cm^{-1} Ω^{-1})	Correlation size L_C (Å)
$NaClO_4$	−21	18.8	66
NaI	−18	11.1	57
$NaBF_4$	14	2.2	75

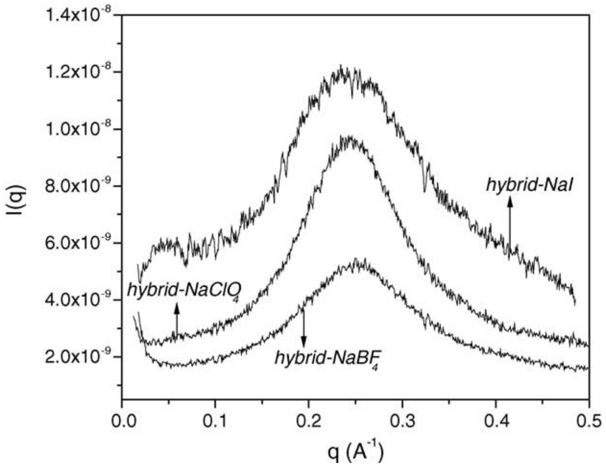

Fig. 3. SAXS intensity as a function of the scattering vector, q (Å^{-1}), for siloxane–PPO hybrids doped with $NaClO_4$, NaI and $NaBF_4$ ([O]/[Na] = 15).

$$R_S = \left(\frac{3\phi_S}{8\pi}\right)^{1/3}\left(\frac{d_S}{2}\right) \tag{1}$$

ϕ_S being the volume fraction of siloxane particles. The same value of R_S (3 Å) was found for hybrids doped with different sodium salts. Additional information about the degree of order of the siloxane clusters arrangement can be obtained from the FWHM (Δq) of the SAXS peak. An average size of the correlation volume (L_C) associated to the spatial distribution of siloxane clusters (i.e. an estimate of the size of the very disordered "supercrystal") can be obtained by applying the Scherrer equation: $L_C = 4\pi/\Delta q$. The values of L_C are shown in Table 1 for the different sodium-doped ormolytes. For all samples, the value of d_S (24 Å) and L_C are lower than observed in the undoped hybrid (26 and 140 Å, respectively).[12] Furthermore, while the interparticle distance d_S and the particle radius R_S remains essentially constant by changing the doping salt, the correlation size L_C is lower for the more conducting ormolytes (doped by NaI and $NaClO_4$).

Fig. 4 shows the ^{23}Na NMR spectra for the siloxane–PPO hybrids doped with $NaBF_4$ and $NaClO_4$ whereas the spectra of pure $NaClO_4$ and $NaBF_4$ salts are shown in the in-set. Differently from our previous results,[11] only one main peak is observed in the spectrum, whose position depends on the doping salt nature: −19.2 and −15.3 ppm for $NaClO_4$ and $NaBF_4$, respectively. However, the formation of NaCl has not been totally avoided in the $NaBF_4$-doped hybrid, as illustrated by the weak band present at 7 ppm.

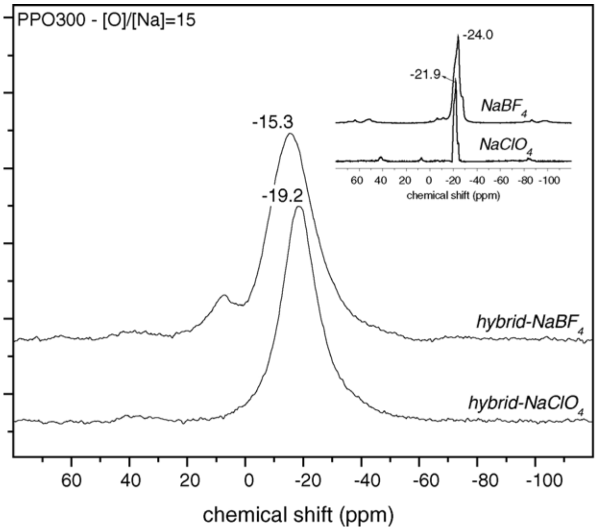

Fig. 4. Room temperature ^{23}Na solid-state NMR-MAS spectra for siloxane–PPO hybrids doped with $NaClO_4$ and $NaBF_4$ ([O]/[Na] = 15). The inset shows the ^{23}Na NMR-MAS spectra, measured in the same conditions, for $NaBF_4$ and $NaClO_4$ solid references.

Fig. 5 shows the Raman spectra of the studied hybrids between 500 and 1780 cm^{-1}. The spectra of the undoped siloxane–PPO composite and pure PPO are also presented. Several observed bands in the spectrum of the undoped hybrid are affected by the presence of the doping sodium salts and these changes depend on their nature. The first point concerns the bands related to ether-type oxygens and carbons of the polymer segments: the band located around 870 cm^{-1} in the spectrum of the undoped hybrid and attributed to the polymer–cation breathing mode[13] shifts toward 865 cm^{-1} for all the doped samples. Furthermore, the width and the shape of the band located around 935 cm^{-1} due to a mixture of CH_2 bending and C–O–C rocking[13] is affected by NaI doping, while it remains unchanged by doping with $NaBF_4$. An increase of the intensity of the band located at 1295 cm^{-1} (due to CH_2 twisting) is also observed in the spectra of the more conducting ormolytes (doped by $NaClO_4$ and NaI), which does not occur in the less conducting one (doped by $NaBF_4$). The urea groups of the PPO chain extremities are also affected by dissolving sodium salts in the hybrid matrix, as illustrated by the pronounced increase of the intensity of the band located at 1137 cm^{-1} in the spectra of the $NaBF_4$-doped sample compared to the undoped hybrid. The increase of the intensity of this band (also present in the spectrum of an undoped urea reference sample (inset in Fig. 5)) is much lower in the other doped ormolytes. Raman spectroscopy also provides information about ionic association of doping species. In the case of the $NaBF_4$-doped composite, the presence of free BF_4^- ions is attested by the band located around 765 cm^{-1}.[14]

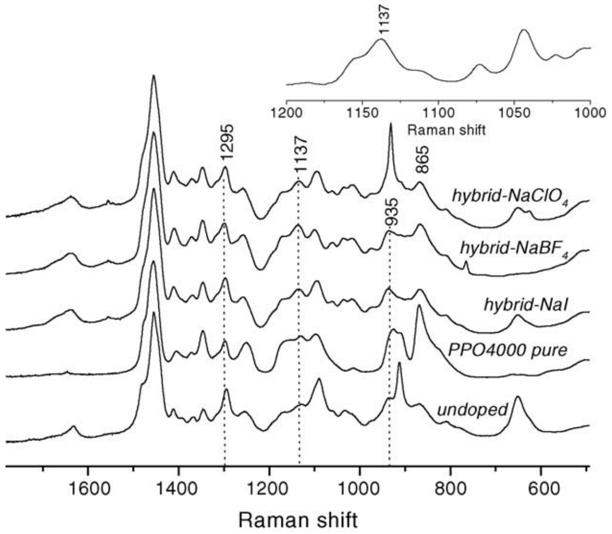

Fig. 5. Raman spectra for siloxane–PPO hybrids doped with $NaClO_4$, NaI and $NaBF_4$ ([O]/[Na] = 15). The spectra of the undoped siloxane–PPO sample and of the PPO (M_w = 4000 g/mol) are also presented. The inset shows the spectrum, measured in the same conditions, of an undoped urea solid reference.

4. Discussion

The main information given by Raman spectroscopy is the difference in nature of the coordination sites for sodium cations between the more conducting samples (doped by NaI and $NaClO_4$) and the less conducting one (doped by $NaBF_4$). Whereas in the former most of the sodium ions are coordinated by ether-type oxygens of the PPO chains (suggested by the fact that several Raman bands related to polymer segments are affected by doping), in the latter the main coordination sites for sodium seems to be the urea groups located at the PPO chain extremities. However, sodium ions interacting with ether-type oxygens also exist in the less conducting nanocomposites, since the breathing mode band is also affected by doping. This feature suggests that the coordination of sodium species by the carbonyl oxygens of urea groups hinders the ionic conductivity of siloxane–PPO hybrids.

The modifications of the coordination sites for sodium species by changing the doping salt and their correlation with ionic conductivity are confirmed by NMR spectroscopy (Fig. 4). The Na^+ resonance around −19 ppm for the $NaClO_4$-doped sample has already been reported in PPO and siloxane-based polymer electrolytes[11] doped with different sodium salts and attributed to “mobile” sodium. This confirms that in this more conducting sample most of the cations are coordinated by ether-type oxygen of the polymer chains. The less negative chemical shifts (Fig. 4) for the less conducting hybrid (doped by $NaBF_4$) is another indication of the existence of sodium ions interacting with both ether-type oxygen of PPO and carbonyl oxygen located in the urea groups of chain ends in these composites. As a matter of fact, the typical chemical shift for sodium ions exclusively correlated by urea groups is around −6 ppm, as observed in the NMR spectra of urea-based references samples (not shown).

The study of the nanoscopic structure of the ormolytes by SAXS corroborates the previous interpretations. The diminution of the siloxane interparticle distance (d_S) from 26 Å in the undoped hybrid to around 24 Å for all the doped samples is consistent with the coordination of sodium ions by ether-type oxygens of PPO chains. Such behavior has already been observed in similar hybrids doped by lithium salts and attributed to the shrinkage of the polymer phase due to the formation of crosslinks between the doping ions and ether-type oxygens of different chains.[12] The decrease of correlation volume size L_C with doping (from 140 Å for the undoped composite to less than 80 Å for all the ormolytes) indicates that the dispersion of sodium atoms in the PPO phase decreases the spatial correlation between siloxane nanoparticles. This interpretation is consistent with the fact that the decrease of the correlation size is more pronounced for the more conducting hybrids (Table 1) in which the fraction of sodium ions coordinated by the polymer phase is larger.

The necessity to have a large fraction of sodium ions coordinated by ether-type oxygens of PPO chains to improve the ionic conductivities in siloxane–PPO ormolytes is also illustrated by DSC measurements (Fig. 1 and Table 1). As already reported in polymer electrolytes,[10] larger ionic conductivities of the studied samples are obtained for lower values of glass transition temperature. In fact, the larger T_g values for the less conducting hybrid ($NaBF_4$-doped one) should also be related to the presence of NaCl aggregates attested by NMR spectroscopy. As a matter of fact, the formation of NaCl-like structures should diminish the conductivity of the electrolytes by decreasing the number of sodium charge carriers.

5. Conclusion

The ionic conductivity of sodium-doped siloxane–PPO ormolytes depends on the nature of the doping salt. The increase of the fraction of sodium atoms coordinated by the ether-type oxygens of the polymer is determinant to improve the ionic conductivity of such systems. This should be reached by avoiding the use of HCl as catalyst in the synthesis procedure, by the choice of a sodium salt presenting a high solubility in PPO in order to avoid the formation of salt aggregates, ion-pairs or triplets and by the use of hybrids containing long PPO chains in order to decrease the probability of coordination of sodium ions to urea groups.

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