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Physical properties of solid polymer electrolyte PEO(LiTFSI) complexes

W Gorecki†, M Jeannin†, E Belorizky†, C Roux‡ and M Armand‡

† Laboratoire de Spectrométrie Physique (CNRS UA 08), Université J Fourier, BP 87, 38402 Saint Martin d'Hères Cédex, France

‡ Laboratoire d'Ionique et d'Electrochimie des Solides (CNRS UA 1213), Institut National Polytechnique de Grenoble, BP 75, 38402 Saint Martin d'Hères Cédex, France

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Abstract. The physical properties of the ionic conductor, obtained by dissolution of lithium trifluoromethanesulphonylimide in polyethylene oxide, $(\text{PEO})_n\text{Li}^+[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$ have been investigated for several values of n . The phase diagram has been established from both DSC and NMR techniques. The diffusion coefficients of ^7Li and ^{19}F containing species, determined by the pulsed magnetic field gradient (PMFG) technique, are interpreted as the measures of the cationic and anionic transport numbers, which are concentration dependent, and t_+ reaches a value close to 0.3. This study is complemented by a systematic analysis of the behaviour of the ^7Li relaxation time T_1 versus temperature and concentration which is correlated to the glass temperature T_g .

1. Introduction

Polymer electrolytes, i.e. the ionic conductors resulting from the complexation of low-lattice-energy salts with solvating polymers, have generated over the past decade a widespread and sustained interest within the scientific community [1–3]. Such materials are at the R&D stage for applications in electrochemical devices, especially high-specific-energy batteries and electrochromic devices. Aside from such economically important states, e.g. electric vehicles, portable communication systems and smart windows, these materials feature intriguing properties in terms of basic science which motivates ongoing research.

The most studied substrate is still polyethylene oxide, PEO, which has extremely strong solvating properties for a wide variety of salts through interaction of the ether oxygens with cations. Maximum obtainable concentrations ($\geq 2 \text{ mol dm}^{-3}$) often exceed those found in liquids and some cases of complete intersolubility between the salt and PEO have now been reported [4]. PEO with the regular repeat structure $-\text{CH}_2\text{CH}_2\text{O}-$ is crystalline ($T_f \approx 339 \text{ K}$), and so are the stoichiometric complexes with salts. These complexes are well defined materials that do not participate in the ionic conductivity, which, as shown by their recently determined structure, are quite satisfactorily explained by the total occupancy of the solvation sites [5, 6].

NMR gave the first indication that the amorphous phase is responsible for ion motion [7], and since then phase diagrams have been the object of several studies to determine the domain of existence as a function of salt type, composition and temperature [4, 8–15]. In this respect polymer electrolytes materialize the new concept of the 'immobile solvent', as conductivity is controlled by the T_g -dependent chain dynamics. There is, however, no

net displacement of the centre of mass of the solvating polymer on the time scale of ion motion beyond the entanglement point [16, 17], and of course in crosslinked systems. In a simplified scheme, cations roll along the chains by (-O-) ligand exchange; the fraction of cations bound to more than one chain at a given time (transient crosslinks) is not yet known, and is the subject of controversy and possible reassessment [6]. For conductivity, the useful domain has been found to lie between pure polymer and the first (leanest) stoichiometric complex (either O/Li = 6 or 3) as determined by DSC, with which it forms an eutectic.

As for any ionic solution, a fundamental question in polymer electrolytes is the extent of dissociation and the relative mobilities of the species i.e. the fraction of the current carried by positively or negatively charged species. Both points remain controversial. Considering the low dielectric constant of the starting polymer host, ionic dissociation should be very small or favour entities such as triplets [18]. However, at higher concentrations, the effective ϵ of the medium is greatly augmented due to the polarity of the salt itself, thus inducing redissociation. The pulsed magnetic field gradient is one of the techniques that has been used to determine the diffusivity of NMR-sensitive nuclei, from which the transport numbers of the ionic species can be derived if one assumes the Nernst-Einstein law. While ^7Li diffusion in $(\text{PEO})_n\text{LiClO}_4$ could be interpreted in terms of simple cationic transport number $t_+ \approx 0.3$ [19], corroborated by other techniques, neither LiCF_3SO_3 and its homologues [20] nor LiPF_6 [21] behaved in such a clear fashion.

The trifluoromethanesulphonylimide anion was chosen as a highly delocalized anion leading to low-lattice-energy salts, favourable to the formation of easily dissociated salts in polyether-based electrolytes [15]. This salt gives the best performance, in terms of phase diagram and conductivity [4, 14, 15]. There are now indications that this family of derivatives may indeed be extensively dissociated into ions in a variety of liquid or polymeric solvents of moderate polarity [22-24].

In this paper, we report and discuss the results from a study by NMR, complemented by DSC, for the $(\text{PEO})_n\text{Li}^+\{(\text{CF}_3\text{SO}_2)_2\text{N}\}^-$ system. In the course of this work a complete phase diagram of this system became available [4, 14], in which, however, the host was PEO of medium \overline{M}_w . In the following, a high- \overline{M}_w substrate was used.

2. Experimental details

2.1. Preparation of the polymer complexes

PEO (Aldrich, molecular weight $\overline{M}_w \approx 900\,000$, $I = \overline{M}_p/\overline{M}_n \approx 2.2$ as determined by GPC) and lithium trifluoromethanesulphonylimide (LiTFSI) supplied by Hydro-Québec was stored and handled in a dry glove box under argon (< 1 ppm H_2O , O_2). Different compositions of PEO complexes were obtained at the desired n ratio by dissolution under stirring of preweighed amounts of salt and polymer in acetonitrile. The clear viscous solutions were cast in PTFE-lined moulds protected from dust, and the solvent was evaporated at 40°C . Further drying of the electrolyte was continued for a week under vacuum.

Samples from the same batches were used for DSC analysis, ionic conductivities and NMR. For the latter, 4 mm diameter NMR tubes were carefully filled with polymer fragments, then sealed under argon without exposure to the atmosphere. As a rule, all materials were protected from degradation by air or light by storage under argon and in the dark.

2.2. NMR

Three kinds of experiment were performed with NMR techniques using a home-made spectrometer working at 95 MHz for the ^7Li nucleus and at 80 MHz for the ^1H and ^{19}F nuclei.

(i) When the polymer sample $(\text{PEO})_n(\text{LiTFSI})$ has a semicrystalline character, which means that both purely crystalline and amorphous distinct phases coexist, measurements of the free induction decay (FID) of ^1H and ^{19}F allow the determination of the relative proportion of these two phases as well as their own salt concentration. This was performed at various initial concentrations $1/n$ and for temperatures between 210 K and 380 K.

(ii) Measurements of the diffusion coefficients of the cationic and anionic species were made through the usual pulsed magnetic field gradient technique (PMFG) using a sequence described by Stejskal and Tanner [25]. Let τ be the time interval between the initial $\pi/2$ pulse and the π pulse, which is equal to the time interval between the π pulse and the echo signal. Denoting by $A(2\tau)$ and $A^*(2\tau)$ the amplitude of the echo in the absence and in the presence of the gradient pulses, one has for a nucleus with a gyromagnetic factor γ

$$\ln[A^*(2\tau)/A(2\tau)] = -\gamma^2 D g^2 \delta^2 (\Delta - \delta/3)$$

where g is the magnitude of the two gradient pulses, Δ the time interval between these pulses and δ their duration. The magnitude of the pulsed gradient field was varied between 0 and 600 G cm^{-1} . The two pulses were separated by a time Δ varying between 40×10^{-3} and 60×10^{-3} s, and were applied for $\delta = 5 \times 10^{-3}$ s. This allowed us to observe the attenuation of a spin echo amplitude over a range of about 30, providing a good accuracy (5%) for the determined values of the self-diffusion constants.

(iii) Measurements of the longitudinal relaxation times T_1 of the ^7Li in the amorphous phase were made with the usual inversion recovery sequence (π , τ , $\pi/2$).

2.3. Differential scanning calorimetry (DSC)

Differential scanning calorimetry traces were obtained using a Perkin Elmer DSC II instrument between 200 K and 400 K. The heating rates, either 10 or 20 K min^{-1} , displayed no noticeable differences in the thermograms.

3. Structural information

3.1. DSC

The DSC spectra of $(\text{PEO})_n(\text{LiTFSI})$ for $n = 6, 8, 10, 12$ and 30 between 200 and 400 K are shown in figure 1. In each case we used the following cycle: quenching at 320 K min^{-1} from room temperature down to 200 K, heating at a rate of 20 K min^{-1} to 400 K, fast quenching to 200 K and heating at the same rate of 20 K min^{-1} up to 400 K. For $n = 6, 8$ and 10 we show the two heating sequences, while for $n = 12$ and 30 only the first heating sequence is displayed, as no change was observed in the second one.

For $n = 6$, $n = 8$ and $n = 10$, the shape of the endothermic peak in the first heating process at 326 K is characteristic of the dissolution [26] of a crystalline part (the concentration of which will be determined by NMR—see subsection 3.2) into a purely amorphous phase. In the second heating process the endothermic event appearing at 246 K, 233 K and 231 K respectively is the signature of the glass–amorphous transition and corresponds to the glass temperature T_g . The absence of any event at higher temperatures shows that the recrystallization kinetics is very slow.

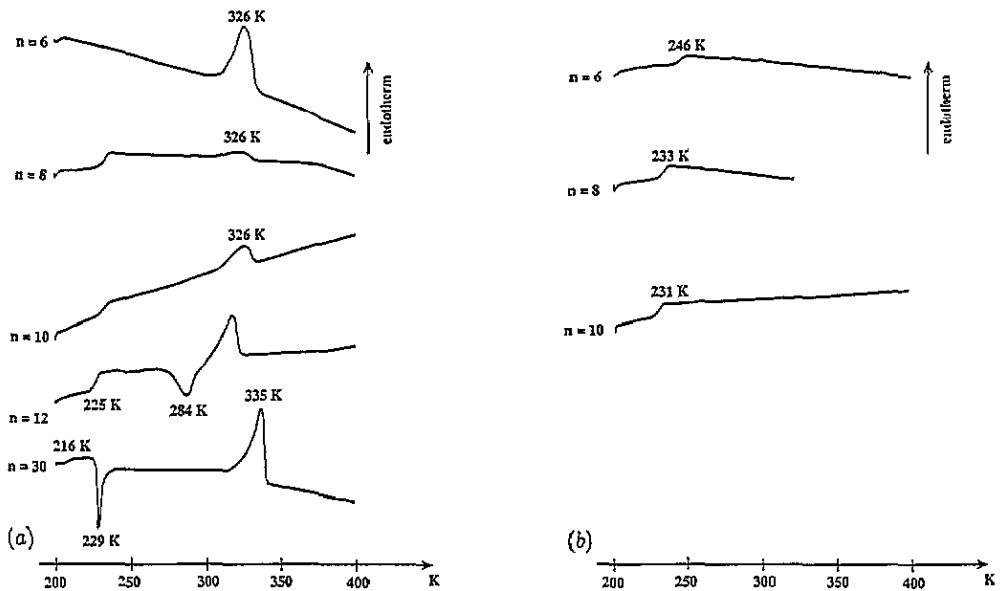


Figure 1. DSC traces for $(\text{PEO})_n(\text{LiTFSI})$. Heating rate, 20 K min^{-1} . (a) First heating sequence; (b) heating sequence following cooling at 320 K min^{-1} .

For $n = 12$ and 30 the glass temperature T_g clearly appears at $T_g = 225 \text{ K}$ and $T_g = 216 \text{ K}$ respectively, but in contrast to the previous case the exothermic peak at 284 K and 229 K shows that a recrystallization process occurs, as expected for low concentrations of LiTFSI. It should be noted that for $n = 30$, the endothermic peak at 335 K , corresponding to the transition to a pure amorphous phase, occurs at the same temperature as for pure PEO [7].

3.2. FID measurements

For liquids or polymers in the elastomeric phase, it is well known that after a $\pi/2$ pulse the resonance signal of a given species of nuclei, owing to transverse relaxation, freely decays according to an exponential law $G(t) \propto \exp(-|t|/T_2)$. $G(t)$ is the FID signal, which is the reduced autocorrelation function of the transverse magnetic moment operator [27]. In fact the observed signal decreases with a characteristic time T_2^* [28]

$$1/T_2^* = 1/T_2 + \gamma \Delta H_0 \quad (1)$$

where T_2 is the true transverse relaxation time essentially due, for $l = \frac{1}{2}$ spins, to dipolar interactions and ΔH_0 is the applied field inhomogeneity. In the elastomeric phase $\gamma \Delta H_0$ is not necessarily negligible and spin echo techniques must be used in order to measure $G(t)$. In the solid phase, $G(t)$ has usually a Gaussian time dependence and the corresponding linewidth is much larger than $\gamma \Delta H_0$. The FID signal can be directly observed after the $\pi/2$ pulse.

The function $G(t)$ was measured in the range 6×10^{-6} – 10^{-1} s. For such measurements, the recovery time of the NMR receiver was $5 \mu\text{s}$.

In the case of a semicrystalline compound, $G(t)$ can be written as

$$G(t) = G_c(t) + G_e(t)$$

where $G_c(t)$ and $G_e(t)$ stand for the contribution of nuclei in the crystalline (or glass) and elastomeric (amorphous) phases. As $G_c(t)$ and $G_e(t)$ decay according to very different time scales, it is possible to separate the relative number of the resonant nuclei belonging to the different phases from the ratio

$$\frac{G_i(0)}{G(0)} = N_i / \sum_i N_i \quad (2)$$

where N_i is the number of nuclei belonging to the phase i . This procedure can be used provided that the spin-lattice relaxation time in the elastomeric phase is not too short, otherwise the measurement of $G_e(t)$ is spurious.

We applied this method to determine the fractions of protons ${}^1C = [{}^1G_c(0)/{}^1G(0)]$ and the fraction of fluorines ${}^{19}C = [{}^{19}G_c(0)/{}^{19}G(0)]$ in the crystalline phase in the compound $(\text{PEO})_n(\text{LiTFSI})$ with $n = 4, 8, 12$ and 20 . A typical FID signal of the fluorine ions for $n = 4$ at $T = 331$ K is displayed in figure 2. We obtain ${}^{19}C = 0.68$.

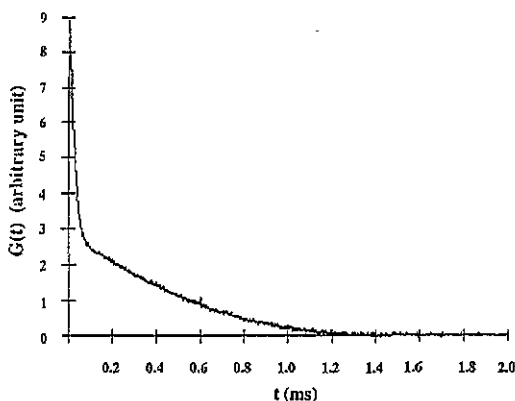


Figure 2. Fluorine FID signal at 80 MHz of semicrystalline $(\text{PEO})_4(\text{LiTFSI})$ at 331 K. The values of ${}^{19}G_c(0)$ and ${}^{19}G(0)$ are extrapolated taking into account the 10^{-5} s dead time of the receiver.

By definition one has

$${}^1C = {}^1N_c / {}^1N_t \quad {}^{19}C = {}^{19}N_c / {}^{19}N_t \quad (3)$$

where 1N_c and ${}^{19}N_c$ are the number of protons and ${}^{19}\text{F}$ in the crystalline phase while 1N_t and ${}^{19}N_t$ are the total numbers of these two species. Denoting by $1/n$ the number of cations per monomer unit, i.e. per four protons, and by $1/n_c$ the number of cations per monomer unit in the crystalline phase, we have

$$1/n = 4 {}^{19}N_t / {}^1N_t \quad 1/n_c = 4 {}^{19}N_c / {}^1N_c \quad (4)$$

Consequently

$$n_c = n {}^1C / {}^{19}C \quad (5)$$

Then from NMR measurements n_c can be determined for various values of n at different temperatures. The results are given in table 1.

It is striking that for $n = 4$, the crystalline phase concentration corresponds to a value $n_c = 3.5$ that is independent of the temperature, and identical to that found previously for the complex $(\text{PEO})_n(\text{LiCF}_3\text{SO}_3)$ [26]. This result may be compared with the seven EO units per whorl in the crystal of pristine PEO [29]. A 7:2 O/Li complex is however not consistent

Table 1. Values of n_c for $(\text{PEO})_n(\text{LiTFSI})$.

T (K)	$n = 4$	$n = 8$	$n = 12$	$n = 20$
293	3.5	8.0	14	32
305	3.5	7.0	11	32
315	3.5	5.7	melt	pure PEO
322	3.5	5.0	melt	pure PEO
331	3.5	melt	melt	pure PEO

with recent x-ray work [6], but consideration could be given to the possibility of pure PEO being intertwined with the 3:1 complex crystals, or at their fringes. On the other hand, for $n = 8$, the value of n_c decreases with increasing temperature. This is interpreted by the fact that the crystalline phase probably includes both pure PEO and complexed PEO with very close melting or interdissolution temperatures; then the endothermic peak observed by DSC around $T = 326$ K (see figure 1) is the superposition of the contributions of the two species. The decrease in n_c can be understood by the faster dissolution kinetics of pure PEO compared to that of the complex. For $n = 12$ we have the same process while for $n = 20$ the complexed crystalline phase disappears before that of pure PEO.

4. Diffusion coefficients

Diffusion is an important process associated with conductivity. In electrochemistry, the contribution of the different ions to the transport number is required and the relevance of this parameter for applications in electrochemical devices has been clearly shown by numerical modelling [30]. We used the PMFG technique (see subsection 2.2) to measure 7D and ${}^{19}D$ i.e. the absolute translational diffusion coefficients of ${}^7\text{Li}$ and ${}^{19}\text{F}$ containing species in the elastomeric phase of $(\text{PEO})_n(\text{LiTFSI})$ for $n = 6, 8, 10$ and 20 at various temperatures. The results are shown in figure 3.

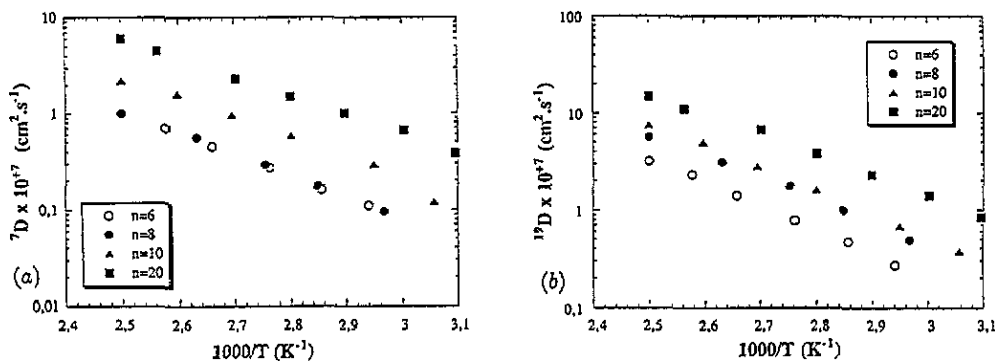


Figure 3. The temperature dependences of the diffusion constants 7D (a) and ${}^{19}D$ (b) in $(\text{PEO})_n(\text{LiTFSI})$ for $n = 6, 8, 10$ and 20 . Data were collected during a cooling cycle.

As in several other PEO complexes such as $(\text{PEO})_n(\text{LiC}_{p+1}\text{F}_{2p+3}\text{SO}_3)$, the diffusion constant ${}^{19}D$ of anion containing species is larger than 7D at any temperature and for all the n values investigated [20]. As the cations are more tightly bound to the PEO segments, their motions are more restricted than those of the anions. The curves of $\text{Log}(D)$ against $10^3/T$ are linear within the experimental error and we can extract activation energies 7E_A

and $^{19}E_A$ which are listed in table 2. This is in contrast with the two regimes observed by Arumagam *et al* [21] for LiPF₆. The activation energy 7E_A of the cations decreases slightly with increasing n , while the activation energy $^{19}E_A$ of the anions does not have a monotonic dependence on n .

Table 2. Apparent activation energies 7E_A and $^{19}E_A$ characteristic of the cationic and anionic species diffusion coefficients obtained from figure 3.

	$n = 6$	$n = 8$	$n = 10$	$n = 20$
7E_A (eV)	0.43	0.40	0.39	0.38
$^{19}E_A$ (eV)	0.49	0.40	0.45	0.43

From the above measurements, in table 3 the cationic transport numbers for various salt concentrations are compiled, assuming the validity of the Nernst–Einstein equation (cf discussion below)

$$t_+ = ^7D / (^7D + ^{19}D). \quad (6)$$

It must be stressed that these transport numbers are practically temperature independent and that t_+ is a minimum for $n = 8$.

Table 3. Cationic transport number for (PEO)_{*n*}(LiTFSI) complexes.

n	6	8	10	20
t_+	0.23	0.16	0.22	0.29

To compare the validity of the Nernst–Einstein equation in these compounds, we also calculate the conductivity σ_c ,

$$\sigma_c = Ne^2(^7D + ^{19}D)/kT \quad (7)$$

where N is the number of cations per unit volume

$$N = \rho N_A / (44n + 287)$$

N_A being the Avogadro number and $\rho = 1.3 \text{ g cm}^{-3}$.

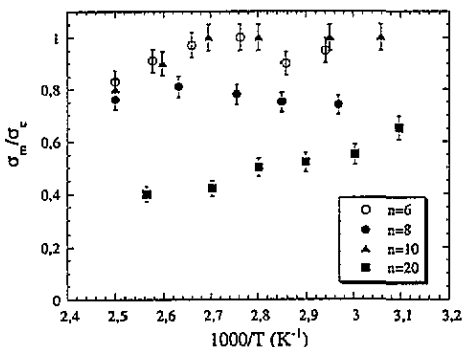


Figure 4. The temperature dependence of the ratio between the measured and calculated conductivity of (PEO)_{*n*}(LiTFSI).

From the experimental values of the macroscopic conductivity σ_m , we plot in figure 4 the ratio σ_m/σ_c against temperature for the various values of n . It can be seen that for

$n = 10$ this ratio remains constant and very close to unity, which means that the anions and cations are completely dissociated. For $n = 20$, however, the ratio is close to 0.5 and for this higher dilution of the complex a partial dissociation is now apparent, which suggests the validity of the redissociation process at high concentrations ('Coulomb fluid'). Furthermore, the highest absolute measured conductivity [14, 15] is obtained for $n = 10$, in agreement with the above remark. Again, these results are in sharp contrast with values of σ_m almost an order of magnitude lower than σ_c reported for the lithium hexafluorophosphate [21].

5. Relaxation times

The longitudinal relaxation rate $1/T_1$ of ^7Li nuclei was measured at a frequency $\nu = 95$ MHz as a function of temperature for $n = 4, 6$ and 8 . The results are shown in figure 5(a).

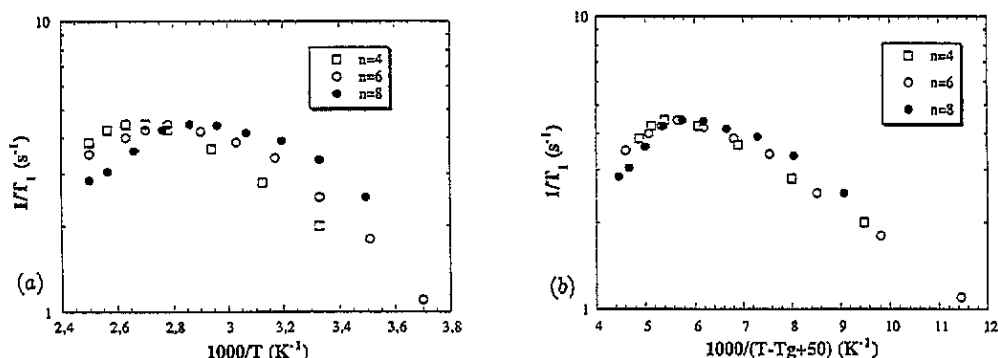


Figure 5. (a) The temperature dependence of the ^7Li relaxation rates of $(\text{PEO})_n(\text{LiTFSI})$ for $n = 4, 6, 8$ at $\nu = 95$ MHz; (a) the same according to the VTF model for $n = 4, 6, 8$, $T_g = 245$ K, 236 K and 231 K respectively.

It is known [31, 32] that the ^7Li relaxation process is dominated by the molecular reorientation through the modulation of the quadrupolar interaction by the fluctuations of the electric field gradient at the nuclear site. This has been demonstrated by complete deuteration of $(\text{PEO})_8\text{LiClO}_4$, which produces no measurable effects on the T_1 relaxation times of the ^7Li nuclei [31]. Furthermore, the above assertion was supported by second-moment calculations for both dipolar and quadrupolar interactions, which were compared to the observed linewidths in similar ionic conductor compounds LiCF_3SO_3 [32]. The magnetic dipolar interactions with the protons of the chains give a contribution to the ^7Li relaxation that is probably one order of magnitude lower than the quadrupolar contribution. It must be added, in comparing the $^7\text{Li}-^7\text{Li}$ and $^7\text{Li}-^1\text{H}$ dipolar relaxation processes, that the former is negligible because both the gyromagnetic factor and the concentration of ^7Li are much lower than those of protons.

In principle the quadrupolar relaxation of a spin $I = \frac{3}{2}$ nucleus cannot be described in the usual form

$$d\langle M_z \rangle / dt = (1/T_1)(\langle M_z \rangle - M_0) \quad (8)$$

unless extreme narrowing conditions ($\omega\tau_c \ll 1$) are satisfied [27]. However, our measurements show a linear variation of $\text{Log}(M_0 - \langle M_z \rangle)$ with t in the whole investigated temperature range and even around the maximum of $1/T_1$ where, if we assume a simple single-exponential form $G(t) = \exp(-|t|/\tau_c)$ for the correlation function, $\omega\tau_c \approx 1$. The same feature was observed in LiCF_3SO_3 complexed in poly(propylene glycol) [32]. This

was explained by equality of the $\Delta m = \pm 1$ and $\Delta m = \pm 2$ transition probabilities W_1 and W_2 due to the quadrupolar interaction [33]. However this is a simple assumption; the reason for the observed behaviour of the longitudinal magnetization is not clear and may also arise from a distribution of correlation times leading to a different form of $G(t)$. It should be pointed out that despite the weak quadrupolar moment of ${}^7\text{Li}$ ($Q = 0.04$ barns), the quadrupolar coupling leading to the observed values of T_1 is of the order of 43 kHz, which is within the range of values found in other Li systems [34].

The behaviour of the relaxation times for different values of n may be unified in the amorphous phase if it is assumed that $1/T_1$ is proportional to a correlation time

$$\tau_c = \tau_0 \exp[B/k(T - T_0)] \quad (9)$$

where B is often referred to as the pseudoactivation energy and T_0 is the ideal glass transition temperature, which is typically taken to be $(T_g - 50)$ (K). This model (VTF) was introduced by Vogel–Tamman–Fulcher [35] and was applied with success to several amorphous polymers and particularly to $(\text{PEO})_n(\text{LiClO}_4)$ [31]. Consequently we plot in figure 5(b) the variation of $1/T_1$ with $1000/(T - T_g + 50)$ using the glass transition temperature T_g measured from the temperature dependence of the NMR linewidth of the protons. Indeed above T_g a sharp narrowing of the line is observed due to the onset of segmental motion of the chains. It can be seen that the three curves almost coalesce, giving satisfactory agreement with this model. This shows that the modulation of the quadrupolar interaction essentially depends on $T - T_g$ and not simply on the temperature, and that this mechanism is intimately correlated to the reorganization of the polymer chains.

6. Conclusions

We report here a rather complete description of the physical properties of $(\text{PEO})_n(\text{LiTFSI})$ complexes through a combination of techniques. DSC and NMR show that recrystallization kinetics are slow for $n \leq 10$ and that for $n > 4$ the crystalline phase includes two different defined complexes, in agreement with the phase diagram established for this system [4, 14]. The cationic transport numbers in the amorphous phase obtained through measurements of the diffusion coefficients are approximately 0.25. Furthermore, for $n = 10$, the ratio between the calculated and measured values of the conductivity is close to unity. The good agreement with the measured conductivity and that calculated from the diffusion coefficient is of extreme importance. Firstly, it justifies the use of NMR/PFMG for transport measurements in this system. Secondly, it reveals the outstanding properties of TFSI salts which seem to be dissociated in almost all conditions in donor solvents, almost irrespective of their dielectric constant. Yet, puzzling questions and food for thought remain: the diffusion coefficients yield straight lines on Arrhenius plots, but the total conductivities are VTF dependent. Furthermore good agreement with the latter model was obtained for the ${}^7\text{Li}$ relaxation rates in the complexes with $n = 4, 6$ and 8 , thus showing the importance of the glass temperature in the dynamic behaviour of the elastomeric phase. Possible parameters to take into consideration are the thermal expansion which does not play the same role for σ measured and for the 7D and ${}^{19}D$ evaluations.

Acknowledgments

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