

Diffusion and ionic conductivity in $\text{Li}(\text{CF}_3\text{SO}_3)\text{PEG}_{10}$ and $\text{LiN}(\text{CF}_3\text{SO}_2)_2\text{PEG}_{10}$

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Self-diffusion of the cation, the anion and the polymer chain in the low-molecular-weight polymer electrolyte systems $\text{Li}(\text{CF}_3\text{SO}_3)\text{PEG}_{10}$ and $\text{LiN}(\text{CF}_3\text{SO}_2)_2\text{PEG}_{10}$ has been studied as a function of temperature using nuclear magnetic resonance spectroscopy. The diffusion behaviour is very similar in the two systems, where the cation is diffusing attached to the polymer chain, while the anion is moving slightly decoupled. However, all species are slightly more mobile in $\text{LiN}(\text{CF}_3\text{SO}_2)_2\text{PEG}_{10}$ than in $\text{Li}(\text{CF}_3\text{SO}_3)\text{PEG}_{10}$, due to the plasticizing effect of the $\text{N}(\text{CF}_3\text{SO}_2)_2^-$ ion, which also explains the higher conductivity for the $\text{LiN}(\text{CF}_3\text{SO}_2)_2\text{PEG}_{10}$ system. The temperature dependence of the diffusion coefficients is of Arrhenius type while the ionic conductivity follows the Vogel–Tammann–Fulcher relation. The diffusion has been compared with the conductivity by applying the Nernst–Einstein relation: a slight discrepancy is found for $\text{Li}(\text{CF}_3\text{SO}_3)\text{PEG}_{10}$, while the agreement is very good for $\text{LiN}(\text{CF}_3\text{SO}_2)_2\text{PEG}_{10}$. Spin–lattice relaxation experiments have shown that the polymer chains undergo local conformational transformations, providing an additional diffusion mechanism for the ions. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

The ionic conductivity of polymer electrolytes¹ is due to transport of cations and anions in a polymer matrix. It is known that the ionic mobility is promoted by segmental motion of the polymer host and, therefore, ionic conductivity is mainly localized to the amorphous phase². However, the exact mechanism for the transport of ions is unclear and one important and experimentally accessible piece of information necessary to understand the mechanism, is diffusion data. Since the mobility of the ions depends on the local dynamics of the polymer chain segments, dynamic information is required for the polymer chain as well as for the ions.

The self-diffusion of polymer chains decreases with increasing molecular weight in, for example, pure poly(ethylene oxide) (PEO)^{3–5}, one of the most commonly studied host materials for polymer electrolytes. At low molecular weight the diffusion is described by the Rouse–Zimm model^{6,7}, predicting a self-diffusion coefficient inversely proportional to the molecular weight. Above the critical molecular weight for chain entanglement, diffusion is described by de Gennes' reptation model. In this model, each chain is confined to a tube formed by neighbouring chains and this leads to different molecular weight dependences of the diffusion inside the tubes and the overall diffusion⁸.

The diffusion of the polymer chains is reduced when a salt is dissolved in a polymer due to coordination of the cations to the polymer chains; more specifically to the

ether oxygens in the case of PEO. This has been observed for the polymer chains in PEO (molecular weight $MW = 8650$): when NaI was dissolved in the polymer the diffusion coefficient decreased as the concentration of NaI increased⁹. The activation energy for the diffusion process also increased with increasing NaI concentration, indicating an increase in the local viscosity upon coordination.

Ratner and co-workers¹⁰ have proposed a model for long-range transport of cations in polymer electrolytes based on cation percolation between different coordination sites along the polymer backbone. In this dynamic bond percolation theory, the available sites are constantly appearing and disappearing because of rapid conformational transformations of the polymer. Therefore, making and breaking of cation–ether oxygen bonds at a high rate is necessary for high cation mobility. This mechanism appears to be appropriate for the transport of Li^+ ions in high-molecular-weight $\text{LiCF}_3\text{SO}_3\text{PEO}_{20}$ systems¹¹. Armand has suggested that the cation–ether oxygen bond lability required for high cationic mobility is correlated to the cation–water exchange rate in aqueous solutions¹². As an example, Mg^{2+} –water exchange rates are several orders of magnitude lower than those of alkali metals and Mg^{2+} mobility in polymer electrolytes is indeed very slow¹¹. Cation mobility may also be a result of polymer diffusion¹¹, especially in low-molecular-weight systems below the critical entanglement limit.

The concentration of ion pairs and higher aggregates often increases with the salt concentration and this provides an additional mechanism for cation transport,

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based on cation transitions between different clusters. This model has been proposed for diffusion of Li⁺ ions in LiPF₆PMEO electrolytes¹³, where PMEО is oxymethylene-linked poly(ethylene oxide).

Determination of transport numbers for the cation and the anion in, for example, LiCF₃SO₃PEO₈ ($MW = 6 \times 10^5$)¹⁴ indicates that both cations and anions are mobile. The mechanism for the transport of anions is generally expected to be different from the transport of cations because of the much weaker interactions between the anions and the polymer chains, and because the anions are moving between local voids available in the structure¹⁵.

In this paper we report measurements of cation, anion and polymer chain diffusion in the low-molecular-weight polymer electrolyte systems LiCF₃SO₃PEG₁₀ and LiN(CF₃SO₂)₂PEG₁₀, using the static fringe field gradient nuclear magnetic resonance (n.m.r.) technique. We have also studied these systems by n.m.r. spin-lattice relaxation measurements for ¹H, ⁷Li and ¹⁹F and, in addition, the conductivity by impedance spectroscopy.

EXPERIMENTAL

Sample preparation

All measurements were made on the polymer electrolytes LiCF₃SO₃PEG₁₀ and LiN(CF₃SO₂)₂PEG₁₀, i.e. with 10 ether oxygens/Li⁺ ion. The electrolytes were prepared from LiCF₃SO₃ (Aldrich, 97%), dried at 150°C for 48 h, and from LiN(CF₃SO₂)₂ (3M) used as received. The dry salts were dissolved in anhydrous acetonitrile (Merck, for spectroscopy) and, after mixing the solution with PEG ($M_r = 400$, KEBO), the solvent was removed at reduced pressure using a water-suction pump. The polymer electrolyte solutions thus obtained were subsequently dried at 45°C for 1 h in a vacuum oven to remove any remaining water and solvent. Infra-red (i.r.) spectroscopy was then used to ascertain that the samples were dry. The samples were stored and handled in a glove-box with a relative humidity of 3%.

I.r. spectroscopy

I.r. spectra were recorded for LiN(CF₃SO₂)₂ in PEG(400) and in nujol on a Digilab/Biorad FTS-45 FTIR spectrometer. The samples were spread between two KRS5 windows and measurements were made between 25 and 100°C. The spectral range covered was 400–4000 cm⁻¹ with a resolution of 1 or 2 cm⁻¹.

N.m.r. spectroscopy

Self-diffusion coefficients were measured between 23 and 100°C, using the static fringe field gradient method¹⁶ on a Bruker MSL spectrometer equipped with a 7T magnet. In order to obtain a suitable, linear magnetic field gradient, the probehead was removed from the centre of the magnet and fixed with two metal guiding blocks attached to one of the legs of the magnet. This arrangement allowed us to place the probehead accurately in the same position and field gradient after each sample exchange. The field gradient was calibrated with water and was found to be 70 T m⁻¹. The diffusion of the polymer chain, cation and anion could be studied separately by choosing different spectrometer frequencies. ⁷Li measurements were performed at 45 MHz and ¹⁹F and ¹H at 114 MHz. The change from ¹⁹F to ¹H was

accomplished by shifting the probehead position by about 3 mm towards a lower field. Sample containers for the diffusion measurements were made by machining an axial slot in an Al₂O₃ rod, confining the sample to a 1 mm thick slice. The sample was then placed in the n.m.r. probe, with the slice orthogonal to the magnetic field gradient. In this way we maximized the sample volume while at the same time minimizing the interference between the ¹⁹F and ¹H signals. This interference would occur for a thicker sample because of the simultaneous excitation of ¹⁹F and ¹H nuclei in different parts of the sample that would be possible in the very large magnetic field gradient.

The n.m.r. diffusion experiment involved a 90° pulse applied at time zero, followed by a 180° refocusing pulse at a variable time τ , producing a spin-echo at time 2τ . The diffusion process was monitored by measuring the amplitude of the spin-echo as a function of τ

$$M(2\tau) = M(0) \exp\left(-\frac{2\tau}{T_2}\right) \exp\left[-\frac{2}{3}\left(\gamma\frac{\partial H}{\partial z}\right)^2 D\tau^3\right] \quad (1)$$

where γ is the gyromagnetic ratio, $\partial H/\partial z$ the static field gradient and D the diffusion coefficient. If $\tau \ll T_2$, then the decay of the spin-echo as a function of τ is only due to the diffusion process.

Spin-lattice relaxation times, T_1 , for ⁷Li and protons, were recorded on a Bruker MSL spectrometer as a function of temperature, at 117 and 300 MHz, respectively, and for ¹⁹F on a Varian XL-300 spectrometer at 282 MHz. All relaxation measurements were made with the inversion-recovery method. For the relaxation measurements, the polymer electrolyte samples were transferred to standard n.m.r. glass tubes, which were sealed in a glove-box to prevent absorption of water.

Ionic conductivity

A.c. impedance spectroscopy measurements were made between 23 and 90°C using a system based on a Solartron 1260 frequency response analyser. The samples were kept in a thermostated glass vessel with stainless steel blocking electrodes and the box containing the sample holder was continuously flushed with dry air to prevent water contamination.

RESULTS AND CONCLUSION

I.r. spectroscopy

I.r. spectroscopy measurements have shown that no free CF₃SO₃⁻ ions exist in LiCF₃SO₃PEG₁₀ at any temperature¹⁷. The CF₃SO₃⁻ ions appear to be coordinated to Li⁺ ions forming so-called contact ion pairs and further to the chain ether oxygens via the Li⁺ ions. This system also contains solvent-separated ion pairs where an oxygen of the CF₃SO₃⁻ ion is hydrogen bonded to an OH end group of the PEG chain and an Li⁺ ion is coordinated by the oxygen of the same OH group. The number of contact ion pairs increases with increasing temperature, while the number of separated ion pairs decreases. The interaction between the CF₃SO₃⁻ ion and the Li⁺ ion in the contact ion pair appears to be stronger than the interaction between the CF₃SO₃⁻ ion and the OH end group in the solvent-separated ion pair, since the splitting of the degenerate bands for asymmetric SO₃

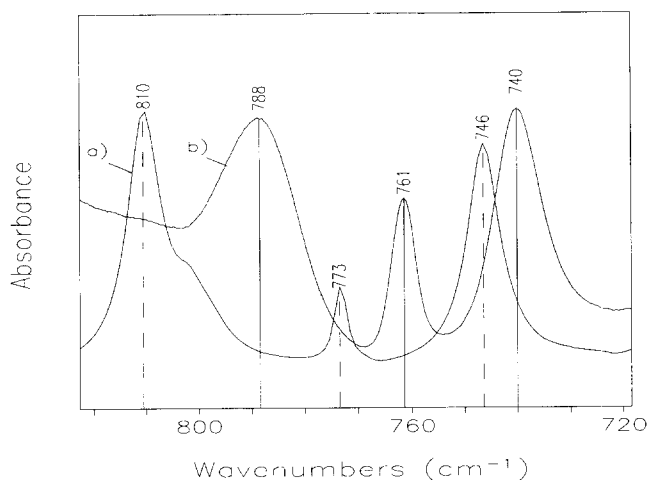


Figure 1 FTi.r. spectra at 25°C for (a) LiN(CF₃SO₂)₂ dissolved in nujol and (b) LiN(CF₃SO₂)₂PEG₁₀

vibrations increases with temperature¹⁷, i.e. when more contact ion pairs are formed.

The situation is somewhat different in the system LiN(CF₃SO₂)₂PEG₁₀. The i.r. spectrum for this system at 25°C is very complex and contains many bands. We have focused on three bands found at approximately 700–800 cm⁻¹, see Figure 1. Recent *ab initio* calculations¹⁸ have shown that these three bands in the i.r. spectrum for N(CF₃SO₂)₂⁻ interacting with Li⁺ are associated with stretching vibrations involving sulfur. When the N(CF₃SO₂)₂⁻ ion is free the vibrational frequencies of these three bands are shifted to lower wavenumbers. The three bands found for LiN(CF₃SO₂)₂PEG₁₀ in this region at 740, 761 and 788 cm⁻¹ are downshifted compared with the corresponding bands at 746, 773 and 810 cm⁻¹ for LiN(CF₃SO₂)₂ dissolved in nujol (Figure 1), where the Li⁺ ions are bound to the N(CF₃SO₂)₂⁻ ions. It can be concluded from this that there are no direct bonds between the cation and anion in LiN(CF₃SO₂)₂PEG₁₀. However, the N(CF₃SO₂)₂⁻ is not necessarily totally free but can coordinate to the polymer chain, via the OH end groups.

Diffusion

Self-diffusion coefficients have been determined by fitting equation (1) to the measured decay of the spin-echo amplitude as a function of the variable time τ . In all experiments, both for LiCF₃SO₃PEG₁₀ and for LiN(CF₃SO₂)₂PEG₁₀, the signal decays exponentially with τ^3 , indicating a single diffusion coefficient for each species. Therefore, even though it is clear from the i.r. spectra that, for example, the CF₃SO₃⁻ ions exist in different bonding arrangements in LiCF₃SO₃PEG₁₀ (i.e. in contact ion pairs and in solvent-shared ion pairs) we observe no difference between their diffusion coefficients; this similarity between the diffusion coefficients is what would be observed if transformations between different species are fast on the time scale of the diffusion measurements.

Self-diffusion coefficients for Li⁺, CF₃SO₃⁻ and the polymer chain in LiCF₃SO₃PEG₁₀ between 23 and 80°C are presented in Figure 2. Irrespective of whether the diffusion rate is controlled by the mass of the diffusing species or by their effective diameter, the small and light

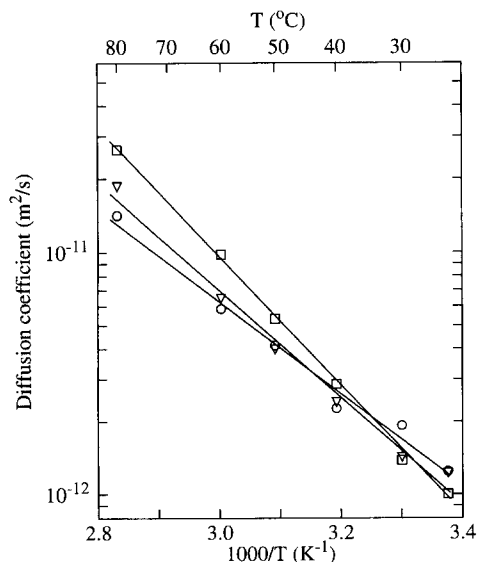


Figure 2 Temperature dependence of the diffusion coefficients for Li⁺ (O), CF₃SO₃⁻ (□) and polymer chains (▽) in LiCF₃SO₃PEG₁₀

Li⁺ ion ($MW = 7$) would be expected to diffuse much more rapidly than the considerably heavier CF₃SO₃⁻ ion ($MW = 149$) or the PEG molecule ($MW = 400$), provided there is no strong interaction between the species resulting in a correlated motion. However, in the present case, the diffusion coefficients for the Li⁺ ions and the polymer chains are very similar and we conclude that the Li⁺ ions diffuse together with the polymer chains over the entire temperature range studied here. This behaviour is due to the coordination of Li⁺ ions to the ether oxygens within or between polymer chains. This is substantially different from the behaviour of high-molecular-weight polymer electrolytes. Shi and Vincent have shown that the Li⁺ diffusion coefficient drops rapidly with increasing molecular weight up to the critical entanglement limit¹¹. Above this molecular weight the Li⁺ diffusion is approximately constant and is dominated by cation percolation between polymer chain oxygens, promoted by segmental motion; the long-range diffusion of the polymer itself plays an insignificant role.

At room temperature the diffusion coefficient for the CF₃SO₃⁻ ions is very close to that of the polymer chains and of the Li⁺ ions, but at higher temperatures the CF₃SO₃⁻ ions diffuse somewhat faster than the other species. A faster diffusion of the anions compared with the cations has been observed for similar systems^{13,14,19}, despite the fact that in all these cases the anions are bigger than the cations.

Anions may be trapped between different polymer chains and, if so, they diffuse together with the chains as a unit although the interaction between the anion and the chain is rather weak. Since the diffusion of the polymer chains is increasing with increasing temperature, this will also result in a faster diffusion of the CF₃SO₃⁻ ions. However, we observe that the temperature dependence of the diffusion for the polymer chains and for the anions is different. Therefore, the diffusion of the anions is not only dependent on the polymer chain self-diffusion. One reason for the enhanced diffusion of the CF₃SO₃⁻ ions could be the increase of the free volume with increasing

Table 1 Activation energies (kJ mol⁻¹) for (a) diffusion evaluated from equation (2) and for (b) spin–lattice relaxation using equations (6) and (7)

	LiCF ₃ SO ₃	LiN(CF ₃ SO ₂) ₂
<i>(a) Diffusion</i>		
Polymer	42	43
Cation	36	39
Anion	54	50
<i>(b) Spin–lattice relaxation</i>		
Polymer	22	25
Cation	23	26
Anion	15	14

temperature, allowing the anions to move more freely and therefore faster.

The temperature dependence of the self-diffusion coefficients for both the ions as well as for the polymer chain is described well by the Arrhenius relation:

$$D = D_0 \exp\left(-\frac{E_A}{RT}\right) \quad (2)$$

A temperature dependence following the Arrhenius relation has been observed for the diffusion of anions and cations in LiCF₃SO₃PEO₈ ($MW = 6 \times 10^5$)¹⁴ and in LiCF₃SO₃PPO ($MW = 1.5 \times 10^6$)²⁰ as well as for the polymer chains in NaIPEO ($MW = 8650$)⁹. However, in LiPF₆PMEO¹³ the diffusion coefficient of the anions varies according to the Vogel–Tammann–Fulcher (VTF) relation^{21–23}

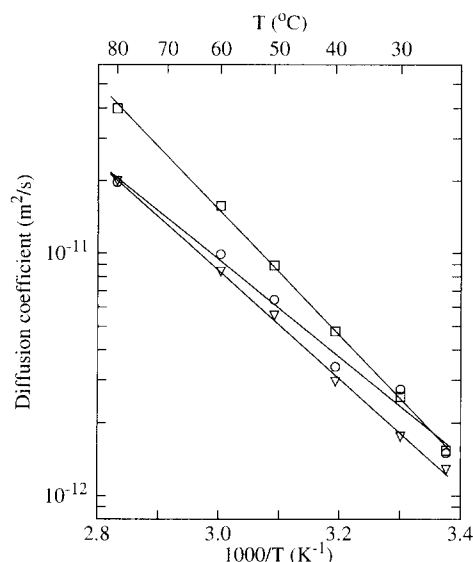
$$D = A_D T^{1/2} \exp\left[-\frac{E_A}{R(T - T_0)}\right] \quad (3)$$

where E_A is a pseudo activation energy related to the configurational entropy of the polymer chain and T_0 is related to the glass transition temperature. The diffusion coefficient of the cations in LiPF₆PMEO follows the VTF relation at low salt concentrations, but the Arrhenius relation at high salt concentrations.

Activation energies for the self-diffusion have been evaluated from equation (2) and these energies are presented in *Table 1*. The activation energy for the diffusion of the CF₃SO₃⁻ ions is somewhat higher than for the Li⁺ ions and the polymer chains, which supports the idea that the diffusion mechanism for the anions differs from that of the cations and the polymer chains.

Closely the same behaviour is found for the system LiN(CF₃SO₂)₂PEG₁₀, *Figure 3*, where again the Li⁺ ions diffuse together with the polymer chains because of the coordination to the ether oxygens, while the N(CF₃SO₂)₂⁻ ions diffuse faster than the chains at higher temperatures. The difference in the diffusion rate between the N(CF₃SO₂)₂⁻ ions and the polymer chains is even more distinct than the difference between the CF₃SO₃⁻ ions and the polymer chains in LiCF₃SO₃PEG₁₀. The temperature behaviour of the diffusion coefficients for all species in LiN(CF₃SO₂)₂PEG₁₀ also follows the Arrhenius relation, equation (2), and gives activation energies, presented in *Table 1*, that are very similar to the activation energies found for LiCF₃SO₃PEG₁₀.

Even though the two systems LiCF₃SO₃PEG₁₀ and LiN(CF₃SO₂)₂PEG₁₀ are qualitatively very similar, the cations, anions and polymer chains are more mobile in the LiN(CF₃SO₂)₂PEG₁₀ system than in the

**Figure 3** Temperature dependence of the diffusion coefficients for Li⁺ (○), N(CF₃SO₂)₂⁻ (□) and polymer chains (▽) in LiN(CF₃SO₂)₂PEG₁₀

LiCF₃SO₃PEG₁₀ system. The large and flexible N(CF₃SO₂)₂⁻ ion acts as a plasticizer on the polymer matrix, giving a higher mobility of the polymer chains in LiN(CF₃SO₂)₂PEG₁₀ than in LiCF₃SO₃PEG₁₀. Also because of this the cations will be faster in LiN(CF₃SO₂)₂PEG₁₀, since the cations diffuse together with the polymer chains. This plasticizing effect will also influence the diffusion of anions, since anion diffusion is promoted by rearrangements of the polymer chains and therefore the N(CF₃SO₂)₂⁻ ions diffuse faster than the CF₃SO₃⁻ ions. The faster diffusion may also be a result of the bigger size of the N(CF₃SO₂)₂⁻ ion, producing more free volume in the system, because of more separated polymer chains. It is clear from i.r. data that there is a strong direct interaction between cations and anions in LiCF₃SO₃PEG₁₀ but not in LiN(CF₃SO₂)₂PEG₁₀; this is another source of the difference between these two systems.

The self-diffusion coefficient for the polymer chains is $8 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ in pure PEG(400) at 23°C and almost one order of magnitude smaller, $1 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ at 23°C, for the polymer chains in both LiCF₃SO₃PEG₁₀ and LiN(CF₃SO₂)₂PEG₁₀. Thus the diffusion of the polymer chains is drastically restricted when a salt is dissolved in the polymer. The activation energy for the diffusion of polymer chains is also much higher in the polymer electrolytes ($\sim 40 \text{ kJ mol}^{-1}$) than in the pure polymer (23 kJ mol^{-1})³.

Ionic conductivity

The temperature dependence of ΛT , where Λ is the molar conductivity for LiCF₃SO₃PEG₁₀, *Figure 4*, and LiN(CF₃SO₂)₂PEG₁₀, *Figure 5*, is distinctly non-Arrhenius. Instead, it can be described with the VTF relation

$$\Lambda = A_\Lambda T^{-1/2} \exp\left[-\frac{E_\Lambda}{R(T - T_0)}\right] \quad (4)$$

The VTF parameters E_Λ , T_0 and A_Λ were determined for the two systems by fitting the ionic conductivity to the VTF relation, and are presented in *Table 2*.

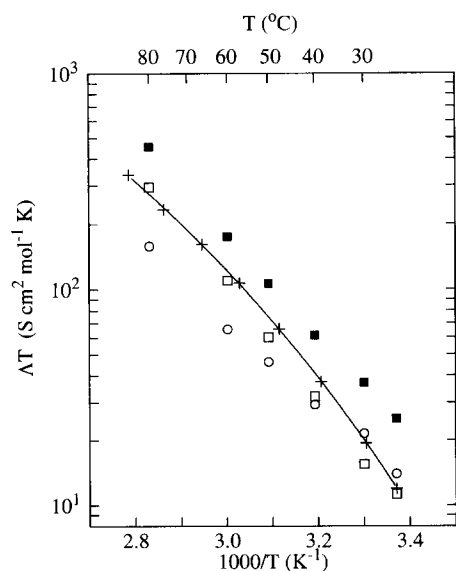


Figure 4 Ionic conductivity for LiCF₃SO₃PEG₁₀ (+). Conductivities have been calculated from equation (5) for Li⁺ (○) and CF₃SO₃⁻ (□). The sum of these conductivities is presented by (■). The solid line presents the least-squares fit to equation (4)

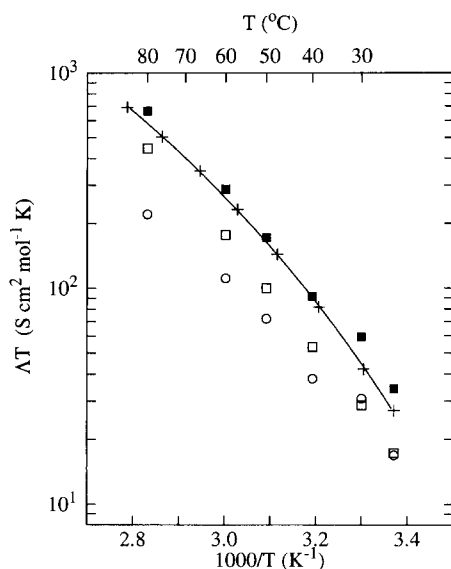


Figure 5 Ionic conductivity for LiN(CF₃SO₂)₂PEG₁₀ (+). Conductivities have been calculated from equation (5) for Li⁺ (○) and N(CF₃SO₂)₂⁻ (□). The sum of these conductivities is presented by (■). The solid line presents the least-squares fit to equation (4)

The ionic conductivity in LiN(CF₃SO₂)₂PEG₁₀ is higher than in LiCF₃SO₃PEG₁₀, over the whole temperature range studied. The N(CF₃SO₂)₂⁻ ion has a high flexibility and acts as a plasticizer²⁴, increasing the polymer chain mobility. Thus complexes containing N(CF₃SO₂)₂⁻ salt are expected to show a higher conductivity than the corresponding systems containing CF₃SO₃⁻ ions²⁵.

The self-diffusion and the conductivity data can be compared by application of the Nernst–Einstein equation:

$$\lambda_j = \frac{z_j^2 F^2}{RT} D_j \quad (5)$$

where λ_j is the contribution to the molar conductivity from the species j of charge z_j with a diffusion coefficient of D_j , and at temperature T .

Table 1 VTF parameters for LiCF₃SO₃PEG₁₀ and LiN(CF₃SO₂)₂PEG₁₀

	E_A (kJ mol ⁻¹)	T_0 (K)	A_A (S cm ² mol ⁻¹ K ^{1/2})
Li(CF ₃ SO ₃)PEG ₁₀	5.9	207	5640
LiN(CF ₃ SO ₂) ₂ PEG ₁₀	5.6	209	10502

We have transformed the diffusion coefficients for the anion and the cation into ionic conductivity using the Nernst–Einstein relation and the results are presented in Figures 4 and 5. The calculated conductivity for the individual species is lower than the measured total conductivity in LiN(CF₃SO₂)₂PEG₁₀. This is also the case for the calculated cation conductivity in LiCF₃SO₃PEG₁₀, while the conductivity for the anion is very close to the measured conductivity. However, the total conductivity is a sum of contributions from different kinds of charge carriers and, therefore, we have also included in Figures 4 and 5 the sum of the contributions from anions and cations calculated from the diffusion measurements. The calculated sum is higher than the conductivity measured by impedance spectroscopy for LiCF₃SO₃PEG₁₀.

Such a discrepancy between the experimentally determined conductivity and that predicted from self-diffusion data using the Nernst–Einstein relation is not uncommon. It has been explained by correlated motion of cations and anions in, for example, uncharged ion pairs contributing to the diffusion but not to the conductivity. It has been reported for LiPF₆PMEO¹³, (LiC_{p+1}F_{2p+1}SO₃)_xPEO¹⁹ for $x = 5$ and 7 , and for LiCF₃SO₃PEO ($MW = 600$)²⁶, amongst others.

However, the calculated sum of the contributions from the cations and the anions is very close to the measured conductivity in LiN(CF₃SO₂)₂PEG₁₀, where no ion pairs exist.

Spin–lattice relaxation

Spin–lattice relaxation measurements were performed separately on the cation, ¹⁹F in the anion and on the polymer chain protons in both polymer electrolytes, and are presented in Figures 6 and 7. In each of the three cases the relaxation could be described by a single exponential. The relaxation behaviour is very similar for the two different polymer electrolytes and a single relaxation rate maximum was observed for each of the three nuclei in both samples. A slight shift of the relaxation rate maximum towards higher temperatures was observed for protons and fluorine in LiCF₃SO₃PEG₁₀ compared with LiN(CF₃SO₂)₂PEG₁₀. The order is reversed for the Li⁺ relaxation maxima.

Within the Bloembergen, Purcell and Pound model, the relaxation rate $1/T_1$ can be expressed in terms of the correlation time τ_c for the molecular motions modulating the nuclear spin interactions:

$$\frac{1}{T_1} = C \left[\frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right] \quad (6)$$

here C is a constant related to the mean-square amplitude of the fluctuating spin interactions causing the relaxation, ω_0 is the angular precession frequency of the observed spin species.

The correlation times derived from the experimental

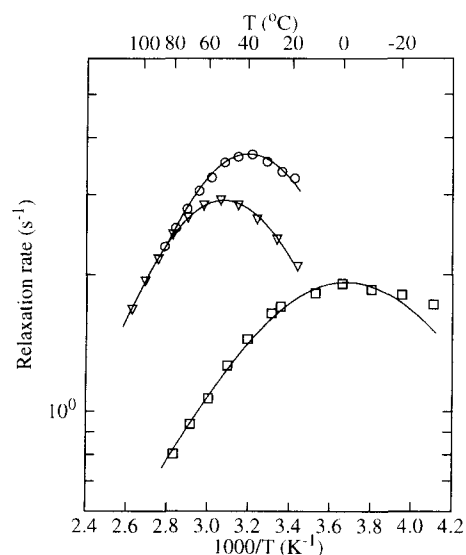


Figure 6 Spin–lattice relaxation rate, $1/T_1$, for Li^+ (O), CF_3SO_3^- (□) and polymer chains (∇) in $\text{LiCF}_3\text{SO}_3\text{PEG}_{10}$. The solid lines represent least-squares fits to equations (6) and (7)

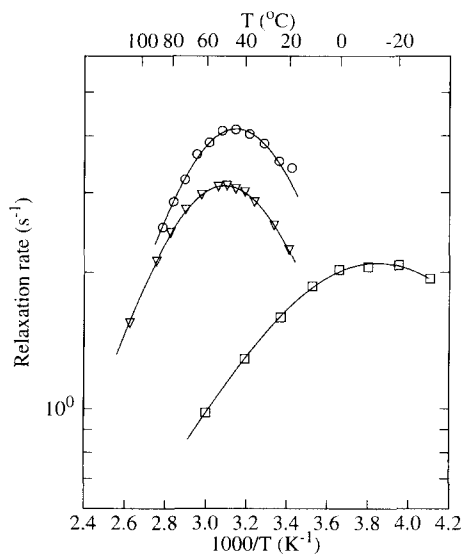


Figure 7 Spin–lattice relaxation rate, $1/T_1$, for Li^+ (O), $\text{N}(\text{CF}_3\text{SO}_2)_2^-$ (□) and polymer chains (∇) in $\text{LiN}(\text{CF}_3\text{SO}_2)_2\text{PEG}_{10}$. The solid lines represent least-squares fits to equations (6) and (7)

T_1 values via equation (6) can be fitted to the Arrhenius equation:

$$\tau_c = \tau_0 \exp\left(\frac{E_A}{RT}\right) \quad (7)$$

The activation energies for the mechanisms causing the relaxation can be calculated from equations (6) and (7) and are shown in *Table 1*. The activation energies derived from the relaxation data are much smaller than those extracted from self-diffusion experiments, especially for the CF_3SO_3^- ion and the $\text{N}(\text{CF}_3\text{SO}_2)_2^-$ ion. We therefore conclude that the spin relaxation must have some other source than translational diffusion. One possibility for both the ^7Li and the ^1H nuclei is that the spin relaxation is predominantly induced by conformational transformations of the polymer chain. Such conformational

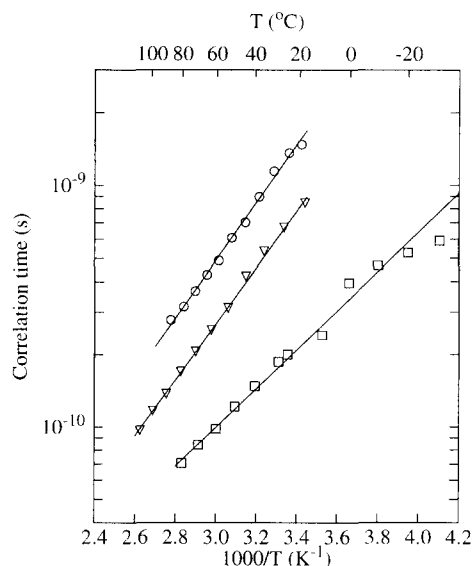


Figure 8 Temperature dependence of the correlation times for Li^+ (O), CF_3SO_3^- (□) and polymer chains (∇) in $\text{LiCF}_3\text{SO}_3\text{PEG}_{10}$ calculated from experimental T_1 using equation (6)

transformations would clearly modulate strongly the dipole–dipole interaction between protons and would therefore be a potential source of spin relaxation for the protons. However, also ^7Li – ^1H dipole–dipole interactions would fluctuate in a similar way. In addition to that, the probably quite strong electric quadrupole interaction between the ^7Li nucleus and the charge distribution of the PEG chain would also experience a similar random modulation as a result of the conformational transformations. Both of these fluctuating interactions involving the ^7Li nuclei will be quite efficient sources of ^7Li nuclei spin–lattice relaxation.

The activation energies for ^7Li and ^1H relaxation are in the range 22–26 kJ mol^{-1} . It is interesting to note that these values are, indeed, not very far from the values 28 and 30 kJ mol^{-1} ascribed to the conformational transformations in high-molecular-weight amorphous and crystalline PEO²⁷.

The correlation times for the two systems $\text{LiCF}_3\text{SO}_3\text{PEG}_{10}$ and $\text{LiN}(\text{CF}_3\text{SO}_2)_2\text{PEG}_{10}$ are presented as a function of temperature in *Figures 8* and *9*. The Li^+ ion in the system $\text{LiCF}_3\text{SO}_3\text{PEG}_{10}$ has the longest correlation times over the entire temperature range. One possible explanation for the somewhat shorter correlation times for the polymer chain motion than for the motion of the lithium ions is that the fluctuations causing relaxation contain contributions not only from translational diffusion but also from conformational fluctuations in the polymer chain. It is also interesting to note that although the correlation times derived from ^1H and ^7Li relaxation data are distinctly different, they are associated with closely the same activation energy. This applies to both systems, and may suggest a coupling between the cation transport, polymer diffusion and polymer conformational transformations.

The ^{19}F nuclei are associated with much shorter correlation times and a distinctly smaller activation energy than the other species in the temperature range that has been studied and it is very likely that the process we are studying in the relaxation experiment is internal

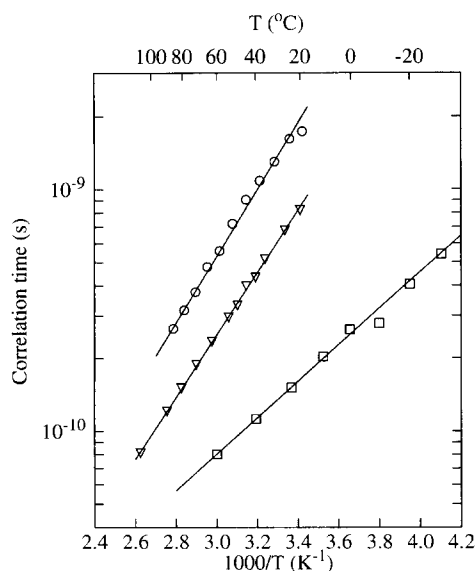


Figure 9 Temperature dependence of the correlation times for Li⁺ (○), N(CF₃SO₂)₂⁻ (□) and polymer chains (▽) in LiN(CF₃SO₂)₂PEG₁₀ calculated from experimental T_1 using equation (6)

rotation about the C–S bond or reorientation of the entire ion. This conclusion is supported by the magnitude of the measured ¹⁹F relaxation rate maximum, 1.9 and 2.1 s⁻¹ for LiCF₃SO₃PEG₁₀ and LiN(CF₃SO₂)₂PEG₁₀, respectively. If this relaxation is caused by the modulation of intramolecular ¹⁹F–¹⁹F dipolar coupling by tumbling of the anion, the constant C in equation (6) can easily be evaluated for a given intramolecular geometry²⁸, and from C the relaxation rate maximum can be calculated. Using an F–F distance of ≈ 2.2 we obtain a relaxation rate maximum of 1.8 s⁻¹, comparing well with the measured values.

The correlation time behaviour for the LiN(CF₃SO₂)₂PEG₁₀ system is very similar to that of the LiCF₃SO₃PEG₁₀ system, especially for the ¹H and ⁷Li nuclei, while the ¹⁹F correlation times are slightly shorter for the LiN(CF₃SO₂)₂PEG₁₀ system.

CONCLUSIONS

The cation transport is highly correlated with the polymer chain self-diffusion and the cations diffuse attached to the polymer host molecules in these low-molecular-weight systems. The diffusion mechanism for the anions is different from the cation diffusion mechanism, because of the much weaker interaction between the anions and the ether oxygens in the polymer chains. However, the anions are substantially bigger than the cations and may therefore be trapped in the polymer matrix. As a result of this, the anions do not easily move on their own and they diffuse together with chains, in spite of the weak anion–polymer interaction. In addition to the self-diffusion, the polymer chains are undergoing extensive conformational transformations. This local mobility of the polymer chains may be important for the enhanced anion diffusion observed at higher temperatures. Also, the cation mobility is coupled to the configurational changes as well as to the diffusion of

the polymer chains. It is also interesting to note that the conductivity predicted from the Nernst–Einstein relation is higher than the experimentally obtained conductivity for LiCF₃SO₃PEG₁₀, where ion pairs exist. The agreement is very good for LiN(CF₃SO₂)₂PEG₁₀, where no ion pairs have been detected.

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