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Amphiphilic Polymer Gel Electrolytes. 4. Ion Transport and Dynamics As Studied by Multinuclear Pulsed Field Gradient Spin-Echo NMR

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ABSTRACT: The transport dynamics in gel electrolytes based on amphiphilic polymers was found to be faster than in gel electrolytes based on corresponding nonamphiphilic polymers. The amphiphilic polymer studied was a polymethacrylate grafted with fluorocarbon and $(EO)_9$ side chains, and the nonamphiphilic one was a polymethacrylate carrying only $(EO)_9$ side chains. Self-diffusion coefficients of gel electrolytes based on the two polymers with different contents of 1 M lithium bis(trifluoromethylsulfonyl) imide (LiTFSI) salt in γ-butyrolactone were determined by ^{1}H, ^{19}F, and ^{7}Li pulsed field gradient spin-echo NMR spectroscopy. The polymer self-diffusion coefficients showed that the amphiphilic polymer molecules diffused faster than the nonamphiphilic ones and seemed more intramolecularly aggregated than intermolecularly. At electrolyte contents above 43 wt %, the ion conductivity of the amphiphilic polymer gel electrolytes was higher than for the corresponding gel based on the nonamphiphilic polymer under identical conditions, as measured by impedance spectroscopy. Moreover, the lithium ion diffusion coefficient in the amphiphilic gel electrolytes was found to be significantly higher than that for corresponding gels based on the nonamphiphilic polymer. The higher ethylene oxide content of the nonamphiphilic polymer decreased the mobility of the lithium ions due to cooperative coordination of lithium ions by ether oxygens in comparison with γ-BL. The TFSI anion diffusion was however approximately the same in the two gel systems. Consequently, the apparent lithium transference number (τ_+) of the amphiphilic gels was higher by almost a factor of 3 as compared to that of the gels based on the nonamphiphilic polymer. A splitting of the TFSI signal in the ^{19}F NMR spectra suggested that the TFSI anions in the amphiphilic polymer gels were partly present in a solvent-rich environment and partly associated with the aggregates formed by the fluorinated side chains. This kind of splitting was not observed in the spectra of the gels based on the nonamphiphilic polymer. The association of TFSI anions to the aggregated fluorinated side chains may thus also play a role in increasing the value of τ_+ for the amphiphilic polymer gels.

Introduction

The low ion conductivity of solid polymer electrolytes at ambient temperatures has so far limited the applications in, for example, small rechargeable lithium ion batteries in favor of polymer gel electrolytes. Polymer gel electrolytes are typically polymers swelled by electrolyte solutions, the latter consisting of a lithium salt dissolved in an anhydrous organic solvent. Among the archetypal polymer gel electrolytes are those based on poly(methyl methacrylate),[1,2] polyacrylonitrile,[3] vinylidene fluoride copolymers,[4] and polyether-based networks.[5−8] These systems have reached ion conductivties of ∼1 mS/cm at ambient temperatures. Gel electrolytes may also be designed using amphiphilic copolymers. Amphiphilic copolymers consist of both hydrophobic and hydrophilic chain segments combined in a single macromolecule and are typically found to aggregate and adsorb at interfaces, similar to smaller amphiphilic molecules.[9−11] These copolymers have received a lot of attention because of their application as gel-formers, rheology, or surface modifiers in a wide variety of areas.

In our effort to develop new polymer gel electrolytes for the use in lithium ion batteries, we have previously reported on the preparation and properties of amphiphilic polymer gel electrolytes based on semifluorinated graft copolymers.[12,13] The amphiphilic copolymers studied consisted of ethylene oxide (EO) side chains as the ionophilic part and fluorocarbon side chains as the ionophobic part. Ionophobic groups are, in contrast to the ionophilic groups, nonpolar and are insoluble in the electrolyte solution. This is analogous to the concept of hydrophilicity and hydrophobicity in water-containing systems. Under proper conditions, amphiphilic copolymers may, depending on the macromolecular structure, form gels by associating intra- or intermolecularly through the formation of ionophobic microdomains in the electrolyte solution. Interestingly, we have observed an increase in ion conductivity in gel electrolytes based on semifluorinated PEO graft copolymers as compared to that in corresponding gels based on PEO graft polymers without fluorocarbon groups.[12] In addition, it was observed that the ion conductivity increased with increasing fluorocarbon content for gels based on copolymers carrying $(EO)_9$ side chains.[13] The same study also demonstrated the importance of controlling the

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ionophobic–ionophilic balance of the amphiphilic copolymer in order to achieve phase stability of the gel electrolyte. In general, longer EO side chains increased the stability of the copolymer in the electrolyte solution, thereby preventing macroscopic phase separation. However, Raman spectroscopy revealed that lithium ions were strongly coordinated to EO chains above a critical chain length.[14] Fortunately, impedance spectroscopy measurements showed that the strong coordination of lithium ions to $(EO)_9$ side chains, in competition with the solvent, did not lead to a significantly lower ion conductivity. In view of the previously measured conductivities, it is important to gain knowledge concerning the mobility of the cations and anions, since the ion conductivity reflects the total mobility of both the cations and the anions. In particular, it is an advantage to have highly mobile lithium cations in relation to the anions in polymer electrolytes. The degree of cation mobility is commonly reflected by the apparent lithium transference number,[15] which is expected to be low in electrolytes based on EO-containing polymers with restricted lithium cation mobility. In other words, the ion conductivity is dominated by the anionic migration.

Aggregation behavior of macromolecules, as well as diffusion of ions and solvent molecules, is reflected in NMR chemical shifts, spin relaxation rates, and molecular self-diffusion coefficients measured by pulsed field gradient spin-echo based (PGSE) methods.[16−18] For example, ^{19}F chemical shifts are well dispersed and sensitive to the solvent environment, which makes it possible for NMR lines of difluoromethylene groups in an ionophobic polymer segment to be resolved in a spectrum.[19] Any presence of associated ionophobic side chains in the gel can therefore be identified. Recently, there have been several studies where PGSE NMR has been used to determine the dynamics of different liquid electrolytes[20] and gels based on polyethers[21−25] or poly(vinylidene fluoride).[26−28] In these studies, the self-diffusion coefficients of the solvent, as well as of the cation and anion of the lithium salt present in the gel electrolytes, were selectively measured by ^{1}H, ^{7}Li, and ^{19}F NMR.

The aim of the present study was to investigate the ion transport, phase structure, and the dynamics of two gel electrolyte systems, namely one based on a semifluorinated $(EO)_9$ graft copolymer and one based on a $(EO)_9$ graft homopolymer. We used ^{1}H, ^{7}Li, and ^{19}F NMR to investigate the self-diffusion of ionic species, solvent, and the polymers. The NMR measurements were complemented with calorimetry and impedance spectroscopy measurements.

Experimental Section

Gel Electrolyte Preparation. The synthesis and structural characterization of the grafted polymers have been reported previously.[12,13] The polymers used in this study were prepared by free radical polymerization, and their molecular data are presented in Table 1. The homopolymer, consisting of methacrylate backbones carrying $(EO)_9$ side chains, was denoted FA0, and the amphiphilic graft copolymer, consisting of methacrylate backbones carrying $(EO)_9$ side chains as ionophilic groups and fluorocarbon side chains as ionophobic groups, was denoted FA77.[29] Polymer films were cast on glass plates from toluene solutions. The solvent was first allowed to evaporate at room temperature, and then residual solvent was removed by vacuum-drying of the films for 48 h. The polymer films were vacuum-dried for another 24 h before transfer into a glovebox filled with argon. Weighed pieces of the polymer films were transferred to glass ampules. Precise volumes of an electrolyte solution, consisting of 1 M LiTFSI salt in γ-butyrolactone (γ-BL), were then added, and the gels were allowed to homogenize at room temperature for 24 h. Volumes of electrolyte solution were added to give gel electrolytes with 50, 60, 70, 80, and 90 wt % of electrolyte solution. To the gels with low contents of electrolyte solution, i.e., 10, 20, and 35 wt %, extra LiTFSI was added to give a total oxygen-to-lithium ratio of 20. The total content of oxygen in the gel electrolytes included the oxygens of both the $(EO)_9$ side chain units and γ-BL. It should be noted that polymer FA0 contained more EO units than copolymer FA77. The LiTFSI salt (kindly supplied by the 3M Co.) and the γ-BL (Merck Selectipur, Battery Grade) were used as received.

Table 1. Molecular Data of the Polymers

	composition (wt %)[c]				
polymer designation	$(EO)_n$ MEMA[a]	DFHMA[b]	EO[c] (wt %)	M_n (kg/mol)	T_g (°C)
FA0	100	0	80	39	−63
FA77	24	76	20	48	−34

[a] $(EO)_n$ MEMA = $(EO)_n$ monomethyl ether methacrylate. [b] DFHMA = 1*H*,1*H*,7*H*-dodecafluoroheptyl methacrylate. [c] Evaluated by ^{1}H NMR spectroscopy.

NMR Measurements. NMR experiments were performed on Bruker DMX 200 and AMX 300 spectrometers operating at 200.13 and 300.13 MHz ^{1}H resonance frequencies. In all self-diffusion experiments, the stimulated echo pulse sequence was used.[30] The experiment consisted of a $90°-\tau_1-90°-\tau_2-90°-\tau_1-$signal, with one magnetic field gradient pulse of strength G and duration δ in each τ_1 period. The separation between the leading edges of the pulses was Δ. The gradients for the ^{1}H and ^{19}F experiments (performed on DMX200s) were generated in Bruker gradient probes with a maximum G of 9.5 T/m. For ^{1}H experiments to measure the solvent diffusion, δ was set to 0.5 ms, Δ to 21.6 ms, and G was stepped up linearly in 32 steps to the maximum available gradient strength (calibrated on samples with known diffusion coefficient). For polymer diffusion measurements, δ was set to 5 ms, Δ to 506.1 ms, and G was the same as above. ^{19}F NMR spectra (presented below) were recorded in the same probe. For the ^{19}F diffusion measurements of the polymer, δ was set to 2 ms, Δ to 200 ms, and G was varied in 16 equidistant steps from 0.1 to 5 T/m. The ^{19}F diffusion measurements of the anion were carried out with the same δ and Δ settings as above, and G was varied linearly from 0.1 to 5−7 T/m. The probe used in the ^{7}Li diffusion experiments (performed on AMX 300) was from Cryomagnet System (Indianapolis, IN). The parameters of these experiments were $\delta = 6$ ms, $\Delta = 250$ ms, and G was varied in 16 equidistant steps from 0.22 to 0.88 T/m maximum value.

The signal intensity of the echo I is given by

$$I = I_0 \exp\left(-(\gamma G\delta)^2\left(\Delta - \frac{\delta}{3}\right)D\right) = I_0 \exp(-kD) \qquad (1)$$

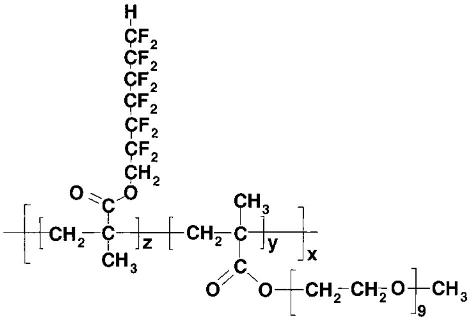
where I_0 is the echo intensity in the absence of gradients, γ the gyromagnetic ratio, and D the self-diffusion coefficient. The pulse sequence parameters are conveniently combined into the parameter $k = (\gamma G\delta)^2(\Delta - \delta/3)$. Equation 1 is valid for a freely diffusing monodisperse molecule. The diffusion coefficient of a polymer depends on the molecular weight. For a polydisperse polymer we have to account for a distribution of D, and I is given by

$$I = I_0\int P(D)\exp(-kD)\,\mathrm{d}D \qquad (2)$$

where $P(D)$ is the normalized probability density of D. $P(D)$ for polymers can often be described with a log-normal distribution:[31,32]

$$P(D) = (D\sigma(2\pi)^{1/2})^{-1}\exp(-{}^1/_2(\ln(D) - \ln(D_0))^2/\sigma^2) \qquad (3)$$

Scheme 1. Molecular Structure of the Semifluorinated Amphiphilic Graft Copolymer FA77



where the mass-weighted average self-diffusion coefficient $\langle D \rangle$ is given by

$$\langle D \rangle = D_0 \exp\left(\frac{\sigma^2}{2}\right) \tag{4}$$

and σ gives the width of the distribution. $\langle D \rangle$ is equivalent to the initial (low k) slope of a plot of ln I vs k.

Solvent diffusion was evaluated by using eq 1 with I_0 and D as adjustable parameters in a nonlinear fitting routine. ^{1}H polymer diffusion was evaluated by eq 2 with $P(D)$ given by eq 3 and treating I_0, $\langle D \rangle$, and σ as adjustable parameters.^{19}F polymer diffusion was evaluated by eq 1 on data obtained at low k values. The diffusion coefficients obtained in this way are equivalent to $\langle D \rangle$. The ^{19}F and ^{7}Li diffusion experiments to measure the TFSI anion and the lithium cation diffusion were evaluated by eq 1, as described above.

DSC Measurements. The thermal properties of the polymer gel electrolytes were studied with a Mettler DSC 30 equipped with a low-temperature cell under N_2 purge. The polymer gel electrolytes were weighed in aluminum pans, which were sealed in the glovebox under an Ar atmosphere before insertion into the DSC cell. The samples were annealed at 50 °C for 2 min and then cooled to −120 °C. After retaining the samples at this temperature for 2 min, they were heated to 40 °C. In a second temperature cycle, the samples were again cooled to −120 °C, retained at this temperature for 2 min, before finally heating them to 100 °C. The temperature scan rate was 10 °C/min in all cases. Glass transition temperatures (T_g) were evaluated from data obtained from the final heating scan.

Impedance Measurements. The conductivity of the gel electrolytes was measured by impedance spectroscopy. Samples were placed between two gold-plated stainless steel electrodes with a diameter of 20 mm, separated by two electrically insulating spacers of 250 μm. The measurements were carried out using a Novocontrol BDC40 high-resolution dielectric analyzer unit operating in the frequency range 0.1 Hz to 10 MHz at 100 mV ac amplitude and equipped with a Novocool cryostat. Data were measured during heating from −20 to 60 °C at 10 °C increments. Conductivities were subsequently evaluated using the WinDeta software from Novocontrol.

Results and Discussion

The molecular structure of the amphiphilic graft copolymer FA77 is shown in Scheme 1. As mentioned in the Introduction, FA0 had no fluorocarbon side chains and was primarily studied in order to compare the behavior and dynamics of gel electrolytes based on amphiphilic and nonamphiphilic polymers. First, the thermal properties of the gels are discussed on the basis of the results from the DSC analysis. Then, the diffusion of polymer and solvent molecules is discussed on the basis of the ^{1}H and ^{19}F NMR data obtained. Finally, the cation and anion mobility is discussed in terms of ion conductivity and self-diffusion coefficients.

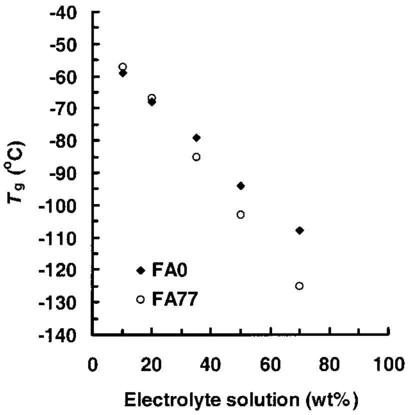


Figure 1. T_g's of gel electrolytes, evaluated by DSC, as a function of the concentration of electrolyte solution.

Thermal Properties. The glass transition temperatures of gels are linked to the mobility in the systems and are therefore an important complement to the conductivity and self-diffusion data. As expected, the glass transition temperatures (T_g) obtained from the final heating scan of the gel electrolytes based on FA0 and FA77 varied depending on the content of electrolyte solution (Figure 1). In general, increasing content of the electrolyte solution in the gel resulted in decreasing T_g. This can be explained by the low T_g observed for the electrolyte solution (1 M LiTFSI salt in γ-BL) at −140 °C.[33] The difference in T_g between the gels based on homopolymer FA0 and copolymer FA77 may be attributed to differences in chain conformation and phase structure of the polymers in the gels. The polymer chains in gels based on FA77 can be expected to be more aggregated, thus forming a more heterogeneous system at a microscopic level, as compared to the gels based on FA0. The FA0 polymer chains have a higher degree of interaction with γ-BL than that of FA77 because of their higher $(EO)_9$ content. Notably, no melting or crystalline transitions were observed for the gels during the heating and cooling scans. The crystallization and melting transitions of the neat electrolyte solution occur at −110 and −50 °C, respectively.[33] We have previously found that the $(EO)_9$ side chains of the homopolymer and the copolymers do not crystallize in the gel electrolytes,[13] and it is conceivable that the presence of the polymers in the gels depressed the crystallization of the electrolyte solution.

Polymer Diffusion. The polymer self-diffusion coefficients in the gels were measured by ^{1}H and ^{19}F PGSE NMR. The self-diffusion coefficients of the polymers in the gel electrolytes are presented in Figure 2. The self-diffusion coefficients of the FA77 copolymer (D^{H}_{FA77}), measured by ^{1}H NMR, were significantly higher for all electrolyte solutions as compared to that of the FA0 polymer (D^{H}_{FA0}). Further, it was observed that the self-diffusion coefficients obtained by ^{19}F NMR (D^{F}_{FA77}) were the same as D^{H}_{FA77}. The difference at 50 wt % of electrolyte concentration was within the error of the measurement. It can be expected that the polymer chains of FA0 are more expanded in the gels as compared to those of FA77. The fluorocarbon side chains of the latter polymer can be expected to associate, leading to lower hydrodynamic volumes of the polymer molecules, a reduced contact with the solvent, and thus faster diffusion. This accounts for the higher self-diffusion coefficients of FA77. The results also suggest that the aggregating behavior of the FA77 polymer had

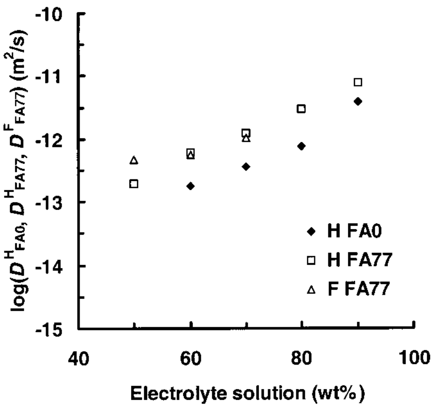


Figure 2. Self-diffusion coefficients of the polymers in the gels as measured by ^{1}H (H FA0 and H FA77) and ^{19}F (F FA77) PGSE NMR.

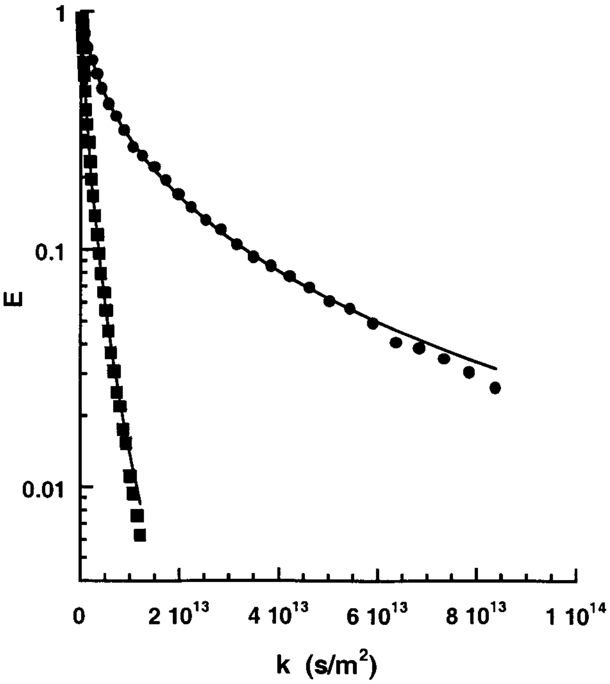


Figure 3. Echo intensities vs *k* (see Experimental Section) for the FA77 (squares) and FA0 (circles) gels containing 70 wt % of electrolyte solution. Included are the nonlinear least-squares fits of eqs 2 and 3 to the data.

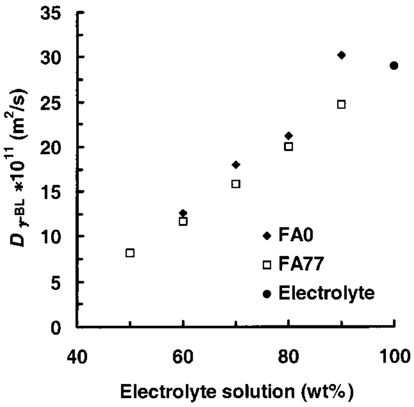


Figure 4. Self-diffusion coefficients of the solvent γ-BL in the gels and in the neat electrolyte solution, as measured by ^{1}H PGSE NMR.

a more intramolecular than intermolecular character at these concentrations of electrolyte solution. Intermolecular aggregates would, if present, hinder the translational diffusion of polymer molecules.

It can be seen in Figure 3 that the ^{1}H spin-echo attenuation was more curved for FA0 as compared to FA77. This was observed at all concentrations of electrolyte solutions. Polymers with a broad size distribution can show nonlinear echo decays at low polymer concentrations.[34] However, averaging processes led to a narrowing of the distribution of the self-diffusion coefficients and, consequently, less curved echo decays.[31] At concentrations higher than the overlap concentration of the system, intermolecular aggregation or entanglement of polymer chains may result in significantly curved echo decays, which are not related to any polymer size distribution.[32] Moreover, curvature in spin-echo attenuation data can also arise from restrictions in the diffusive polymer chain motion as well as from motions of the side chains.[35] However, the latter is not applicable in the systems of the present study since the rotational motion of the relatively short side chains is coupled to the backbone dynamics. The number-average molecular weights (M_n) of FA77 and FA0 were 48 and 39 kg/mol, respectively. GPC analysis of poly(methyl methacrylate) samples obtained by methanolysis of FA77 and FA0, respectively, showed that both the polymers gave equally narrow peaks in the chromatograms.[13] Because of the quite small differences in the molecular weights and polydispersities, it is not likely that the difference in echo decay curvature, shown in Figure 3, is influenced by these factors, independent of concentration. For these electrolyte concentrations, it is conceivable that the FA0 gels are above their overlap concentration and that the FA77 gels are below, due to the difference in the state of aggregation. This means that the polymer chains were entangled, and not aggregated, in the FA0 gels. Moreover, it shows that the amphiphilic graft copolymer chains in the FA77 gels were intramolecularly associated more than intermolecularly.

Solvent Diffusion. The self-diffusion coefficient of γ-BL ($D_{\gamma-\mathrm{BL}}$) in the gel electrolytes was measured by ^{1}H PGSE NMR for gels containing 50−90 wt % of electrolyte solution. The $D_{\gamma-\mathrm{BL}}$ of the gels and the neat electrolyte solution are presented in Figure 4. Not surprisingly, $D_{\gamma-\mathrm{BL}}$ increased for the gels with increasing content of electrolyte solution. This result is in agreement with the measured T_g's of the gels, which decreased with increasing content of electrolyte solution (Figure 1). With the exception of the values at 90 wt % electrolyte solution, the difference in the values of $D_{\gamma-\mathrm{BL}}$ for the two systems was within the error of the measurements. The significant difference in $D_{\gamma-\mathrm{BL}}$ noted at 90 wt % added electrolyte solution, with $D_{\gamma-\mathrm{BL}}$ for the gel based on FA0 slightly higher than that of the neat electrolyte solution, may be explained by the preference of the lithium ions to be coordinated by the ether oxygens of the polymer side chains in competition with the γ-BL molecules.[36] Fewer ion−solvent complexes are formed when the polymer is present, resulting in more freely diffusing solvent molecules. The EO content in FA0 was significantly higher than in FA77, as seen in Table 1. However, at higher polymer concentrations, the coordination of lithium ions by the polymer seemed to be less important for the mobility of γ-BL, as seen in Figure 4, with values of $D_{\gamma-\mathrm{BL}}$ in the FA0 and FA77 gels due to a higher degree of polymer−solvent interaction. The measured $D_{\gamma-\mathrm{BL}}$ of the neat electrolyte solution and

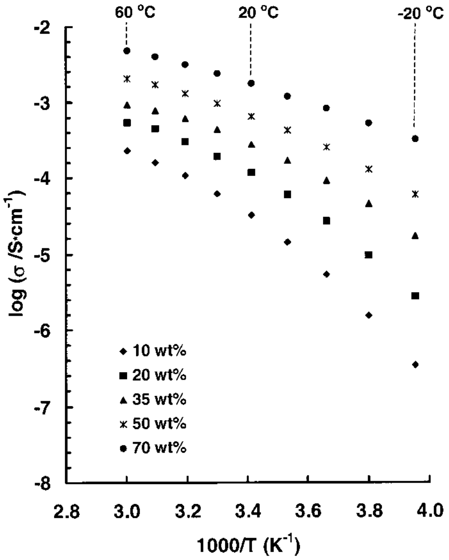


Figure 5. Arrhenius conductivity plots for gel electrolytes based on FA0 with different contents of electrolyte solution, as determined by impedance spectroscopy in the temperature range −20 to 60 °C.

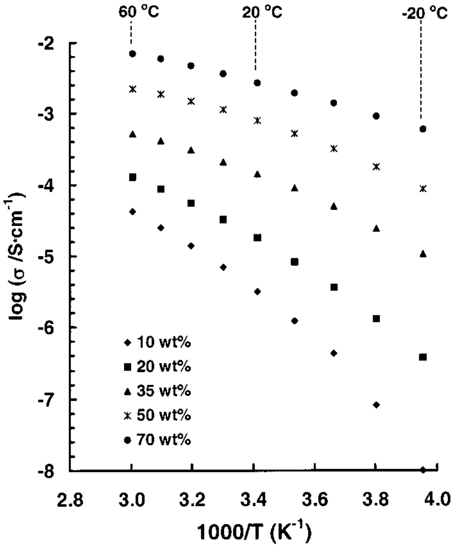


Figure 6. Arrhenius conductivity plots for gel electrolytes based on FA77 with different contents of electrolyte solution, as determined by impedance spectroscopy in the temperature range −20 to 60 °C.

neat γ-BL was 29 × 10^{-11} and 82 × 10^{-11} m^2/s, respectively. Previous investigators have reported values of $D_{\gamma\text{-BL}}$, 35 × 10^{-11} m^2/s,[22,23] in a electrolyte solution with the same salt concentration as in the present study and for neat γ-BL, 90 × 10^{-11} m^2/s.[20] For gels containing 20 wt % of poly(ethylene oxide) dimethacrylate (MW 4000) and 1 M LiTFSI in γ-BL, $D_{\gamma\text{-BL}}$ was measured to ~20 × 10^{-11} m^2/s,[22,23] which is similar to the values obtained in the present study. This value was measured both before and after cross-linking of the dimethacrylate.

Ion Conductivity. The ion conductivities of the gel electrolytes were evaluated by impedance spectroscopy in the temperature interval −20 to 60 °C, and the results are presented as Arrhenius plots in Figures 5 and 6. The conductivity curves were convexly shaped, which usually indicates that the mobility of the ions is partly coupled to the mobility of the polymer segments in the gels.[15] At higher contents of electrolyte solution the conductivity curves become straighter, i.e., more Arrhenius-like, as the mobility of ions became increasingly coupled to the mobility of γ-BL. It can also be seen that the conductivity spanned over a wider range of values for the FA77 gels than for FA0 based gels. For the gels based on FA77, which contain below 40 wt % of electrolyte solution, the ion conductivities were lower than for the corresponding gels based on FA0. This observation is most probably due to the lower content of EO in the gels based on FA77, which lead to a significantly lower content of ion conductive phase at small additions of electrolyte solution. At 50 wt % of electrolyte solution, the conductivity was slightly higher for the FA77 based gel. A "crossover" in the conductivity, i.e., where the conductivities of the FA77 and FA0 gels were the same, was noted at approximately 43 wt % of electrolyte solution at 20 °C. The FA77 gel containing 70 wt % of electrolyte solution had an ion conductivity of approximately 3 mS/cm at room temperature, which is above the commonly stated lower limit of 1 mS/cm for practical use in battery applications. Previous investigations of polyether based gel electrolytes have also reported ion conductivities of around 3 mS/cm at room temperature.[5,22,37] The ion conductivity of the neat electrolyte solution has been measured to be ~9 mS/cm at room temperature.[20,33]

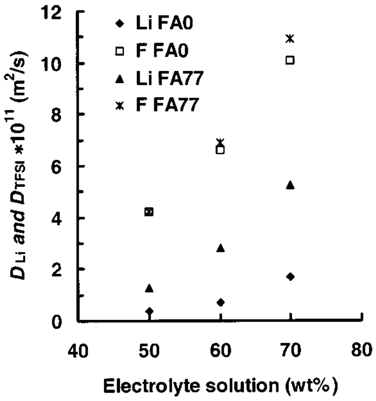


Figure 7. Self-diffusion coefficients of the lithium cations and TFSI anions in gels based on FA0 and FA77. The measurements were made by ^7Li and ^{19}F PGSE NMR.

Ion Diffusion. As mentioned in the Introduction, the mobility of the cation and anion of the lithium salt in gel electrolytes is an important subject to study. The self-diffusion coefficients of these ions were measured by ^7Li and ^{19}F PGSE NMR, and the results for both the FA0 and the FA77 gels are plotted vs the concentration of electrolyte solution in Figure 7. It should be noted that the measured D_{Li} and D_{TFSI} are weighted averages for all the species present in the gels containing Li and TFSI, respectively. This means, for example, that the measured D_{Li} will contain contributions from the diffusion of Li present in the form of free ions coordinated by γ-BL, free ions coordinated by EO side chains, ion pairs, and multiplets. Thus, changes in the diffusion coefficients reflect changes in mobility of the different species, changes in the degree of ion separation, and changes in the ion coordination in the gels.

As expected, the self-diffusion coefficients of both ions increased with increasing contents of electrolyte solution. The self-diffusion coefficients of the TFSI anion (D_{TFSI}) were higher than the lithium diffusion (D_{Li}) for all the measured electrolyte concentrations due to the more independent diffusion of TFSI anions, in contrast to the coordination of lithium cations by γ-BL molecules.

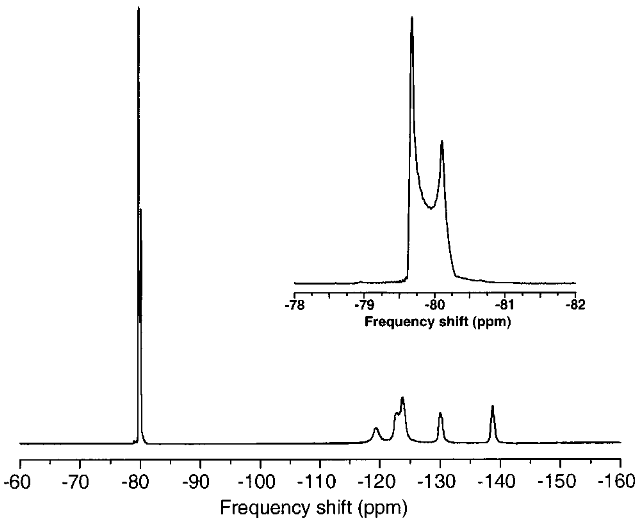


Figure 8. ^{19}F spectrum of the FA77 gel with 50 wt % of electrolyte solution, as recorded in a conventional single-pulse experiment. The broad peaks on the right-hand side in the spectra correspond to the signals from the fluorocarbon side chains attached to the backbone. The peak at the left was assigned to the TFSI anion, and the inset shows the expanded spectral region of this ion. As seen, the signal is split into two components, indicating two distinctly different environments of the TFSI anion.

This means that the lithium cation will diffuse together with the coordinated γ-BL as an entity. Further, D_{TFSI} was approximately equal in both gel systems. It was noted that D_{Li} was significantly higher for the FA77 based gel at all electrolyte concentrations as compared to the that of FA0 gel. As mentioned above, FA0 contained more $(EO)_9$ side chains than FA77, and lithium is coordinated preferentially by $(EO)_9$ segments in competition with the solvent in a gel electrolyte.[36] Therefore, the lower D_{Li} observed in the FA0 gels was partly an effect of the higher degree of lithium coordination by the $(EO)_9$ side chains as compared to that of the FA77 gels. Hayamizu et al. observed a large decrease in D_{Li} when adding 20% of a PEO oligomer to a solution of LiTFSI in γ-BL.[23] The observed changes in $D_{\gamma-BL}$ and D_{TFSI} were much smaller, and the authors concluded that the observed decrease in D_{Li} was a consequence of a strong coordination of the Li ions by the PEO, which was considerably less mobile in the system. The number of lithium ions per oxygen atom in the present gel electrolytes containing 70 wt % of electrolyte solution was 0.05 for the FA0 gel and 0.07 for the FA77 gel. However, the number of lithium ions per coordinating ether oxygens in the same gels was 0.11 for the FA0 polymer and 0.45 for the FA77 polymer.

The ^{19}F spectrum of the FA77 gel containing 50 wt % of electrolyte solution, recorded in a conventional single-pulse experiment, is shown in Figure 8. The broad peaks on the right-hand side in the spectrum correspond to the signals from the fluorocarbon side chains attached to the methacrylate backbone. The broadening of the side chain signals reflected the slower molecular dynamics of the polymer segments, a consequence of being aggregated and attached to the polymer backbone. This effect is similar to those observed, for example, in micellar solutions of low molecular weight surfactants.[38,39] The narrow and intensive peak on the left-hand side arises from the TFSI anions. A remarkable observation is highlighted in Figure 8, where the spectral region of the signal of the TFSI anion is expanded. As seen, the signal was split into two components with different chemical shifts. Note that the separately recorded ^{1}H peaks of the solvent in the ^{1}H NMR spectrum recorded under identical conditions were a few hertz wide, and therefore magnetic field inhomogenities cannot explain this observation. Since the ^{19}F chemical shift is sensitive to the solvent environment,[19,40−44] the splitting indicated the presence of two different molecular environments for the anions. The exchange of anions between these environments must be slow on the time scale of $1/\Delta\nu \approx 10$ ms where $\Delta\nu \approx 80$ Hz (which corresponds to 0.4 ppm) is the frequency difference between the two observed peaks.[45] The splitting of the TFSI signal in the ^{19}F spectra was also observed in the FA77 gels containing 60 and 70 wt % of electrolyte solution. On the other hand, a single TFSI signal was observed in the spectra of the gels based on FA0. The latter observation suggested that in one of the two anionic environments in the FA77 gels the TFSI anions were surrounded by γ-BL molecules, and in the other, the anions were associated to the aggregates formed by the fluorinated side chains. Since ^{19}F chemical shifts of atoms solvated in fluorocarbon environments are typically lower than those in hydrocarbon environments,[44] the right peak in the inset of Figure 8 was assigned to anions associated to the aggregates. This implied that roughly one-third of the anions were associated to the fluorinated moieties of the FA77 copolymer.

In addition to the relative populations, the chemical shift difference between the two peaks carries information about the molecular environment of the anions close to the aggregated fluorocarbon side chains. A 1−2 ppm chemical shift difference, with respect to the solvent peak,[44] indicates a fully fluorinated environment for the anions. In the present case, however, the smaller (0.4 ppm) observed shift difference indicates that the environment of the anions associated to the aggregated fluorocarbon side chains has a substantial solvent character. In other words, it suggests that the anions are rather “loosely” associated to the aggregates or the aggregates are less dense than the micelles of fluorosurfactants. Finally, we note that, in the diffusion experiments presented above, the two peaks gave approximately the same diffusion coefficient, which can be explained by the time scale of the exchange of the anions between the two assumed environments. It falls between 10 ms (see above, from the frequency difference) and 1 s, which is the approximate time scale (see Experimental Section) of the diffusion experiments. Two distinctly different environments have previously been found in composite solid electrolytes, one being lithium in ionic clusters and the other being lithium solvated by a polyether.[46] A split signal in the ^{7}Li spectrum was not observed in the present study.

Fluorine-containing compounds are generally very hydrophobic. This is a consequence of the low surface free energies resulting from the small polarizability of fluorine and C−F bonds. If a polymer contains both fluorinated and nonfluorinated moieties, it will most certainly assemble at surfaces where it lowers the interfacial tension. However, not only polymer segments containing CF_n groups but also smaller compounds, such as fluorinated anions of lithium salts, are surface active. For example, Teeters et al. observed an enrichment of free trifluoromethanesulfonyl anions ($CF_3SO_2^-$) at the surface/air interface of an electrolyte based on tetra-

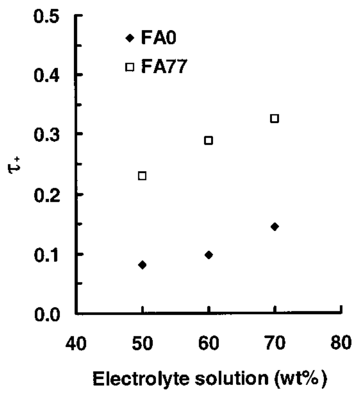


Figure 9. Apparent lithium transference numbers (τ_+) of the gels as a function of the content of electrolyte solution. The values of τ_+ were calculated on the basis of the self-diffusion data using eq 5.

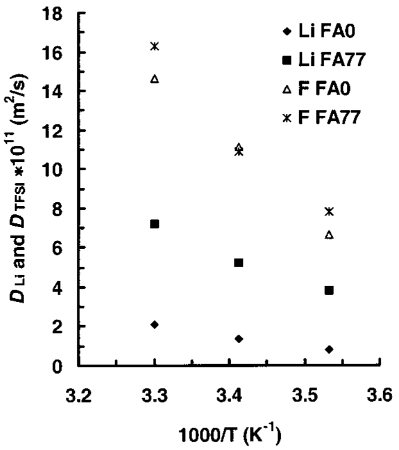


Figure 10. Self-diffusion coefficients of the lithium cations and TFSI anions in gels based on FA0 and FA77. The measurements were made by ^{7}Li and ^{19}F PGSE NMR.

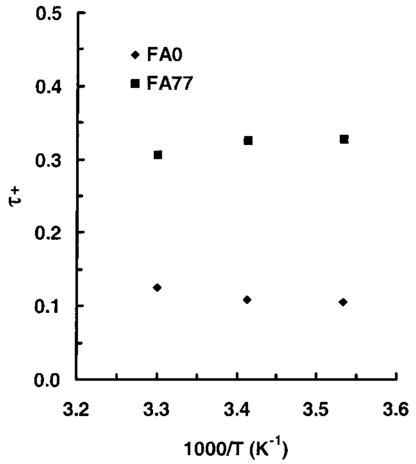


Figure 11. Apparent lithium transference numbers (τ_+) of the gels as a function of the temperature. The values of τ_+ were calculated on the basis of the self-diffusion data using eq 5.

glycol dimethyl ether.[47] In this case, the air surface was hydrophobic in comparison to the electrolyte solution. In the present study it may be expected that the fluorocarbon side chains, associated to form microdomains, have a considerable surface area toward the electrolyte solution in the gel. Consequently, it is likely that a fraction of the TFSI anions will associate to these microdomains.

It is of great interest to increase the lithium ion conductivity in polymer gel electrolytes for battery applications. One method that has been proposed is to entrap the anions of the salt and thereby facilitate the dissociation of ion pairs and multiplets in the gel electrolyte. In a study by Lee and co-workers,[48] CF_3SO_2 groups were substituted on cyclic aza-ether compounds to obtain an anion binding ligand. They found that the electron-withdrawing effect of CF_3SO_2 groups substituted on nitrogen atoms increased the concentrations of free ions, a result of the ion-pair dissociation effect of the aza-ether compounds, leading to increasing ion conductivity.[48] However, the authors did not specify whether the increase was due to increased anionic or cationic mobility. Furthermore, Tasaki et al. have performed molecular dynamics simulations on aza-ethers substituted with CF_3SO_2 groups in the presence of lithium hexafluorophosphate ($LiPF_6$) and ethylene carbonate (EC).[49] They proposed an ion dissociation mechanism where the PF_6^- anions were separated from the Li^+ to a larger extent with increasing size of the cyclic aza-ether.

It was concluded above that the fluorocarbon side chains of the FA77 copolymer associate, both intra- and intermolecularly, to form ionophobic microdomains in the gels. If the TFSI anions can adsorb to these microdomains, or be "captured" inside the microdomains, the mobility of the species in the gel would be affected. This may lead to an increased degree of dissociation of the lithium cation and the TFSI anion, which in turn would lead to higher lithium mobility.

Apparent lithium transference numbers (τ_+) were calculated on the basis of the self-diffusion data according to the equation[50]

$$\tau_+ = \frac{D_{\text{cation}}}{D_{\text{cation}} + D_{\text{anion}}} \tag{5}$$

We consider the calculated values of τ_+ to be apparent lithium transference numbers because they are based on data which are also dependent on the diffusion of uncharged species such as ion pairs, as mentioned above. From the data presented in Figure 9, it is observed that the τ_+ of the FA77 based gels were higher by almost a factor of 3 as compared to that of the FA0 based gels. It was also observed that the τ_+ increased with increasing electrolyte concentration. It is reasonable to assume that the interaction between the lithium ions and the ether oxygens of the EO segments in the polymer side chains influenced the value of τ_+, since the lithium coordinate to $(EO)_9$ side chains. It is also possible that the mobility of the TFSI anions is retarded through the association to the fluorocarbon side chains according to the discussion above.

The temperature dependence of the ion diffusion was studied in the temperature range from 10 to 30 °C for the gel electrolytes based on FA0 and FA77 containing 70 wt % of electrolyte solution. D_{Li} and D_{TFSI} as functions of temperature are presented in Figure 10, and the calculated τ_+ as functions of temperature are shown in Figure 11. As seen in Figure 10, the diffusion of the lithium cations and the TFSI anions increased with increasing temperature, as expected. The value of τ_+ was approximately constant for both gels (Figure 11). This indicated that the relation between the mobility of the ions, γ-BL, and the polymers was approximately the same in the rather small temperature interval studied. The activation energies (E_A) for the lithium diffusion were calculated to be 35 and 25 kJ/mol for the FA0 and the FA77 gels, respectively. The E_A for the TFSI anion diffusion was 28 kJ/mol (FA0 gel) and 26 kJ/mol (FA77 gel). The values of E_A calculated from conductivity data in the same temperature interval, obtained by impedance spectroscopy (Figures 5 and 6), were 24 and 22 kJ/mol for the FA0 and the FA77 gels, respectively. The activation energies obtained for the ion conductivity were, accordingly, at the same level as those obtained from the self-diffusion coefficients.

Conclusions

From self-diffusion coefficients measured by ^{1}H and ^{19}F PGSE NMR, it was concluded that the fluorocarbon side chains of the FA77 copolymer associated to form ionophobic microdomains in the gels. However, the data suggested that the aggregating behavior of the FA77 polymer had predominantly a more intramolecular than intermolecular character. It was observed that D_{Li} was significantly higher for the FA77 based gels at all electrolyte concentrations as compared to that of the FA0 gels. Further, the apparent lithium transference numbers (τ_+) of the FA77 based gels were higher by almost a factor of 3 as compared to that of the FA0 based gels. This effect was partly a result of the higher degree of lithium coordination by the $(EO)_9$ side chains of FA0 as compared to that of FA77. However, the ^{19}F NMR data suggested that the anions were partly associated to the aggregates formed by the fluorinated side chains. If the TFSI anions can associate to the microdomains formed in the FA77 gels, or be “captured” by the microdomains, the ion dissociation in the gel may increase. It is difficult to state the significance of the association of the anions to the fluorocarbon side chains from the data obtained in the present study, because of the different EO contents in the two polymers. The effect of the association of TFSI anions to the fluorinated microdomains on τ_+ will be investigated further in the near future.

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References and Notes

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