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Ion conducting electrolytes based on aggregating comblike poly(propylene oxide)

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Abstract

Solid and gel electrolytes based on comblike poly(propylene oxide) (PPO) have been prepared and studied. The polymer consisted of a polyethylene backbone densely grafted with PPO side chains terminated by hexadecanoyl chain ends. Analysis by impedance spectroscopy of the solid polymer electrolytes containing lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) salt showed ion conductivities of $10^{-5.5}$ S cm^{-1} at 20°C. The ion conductivity of polymer gel electrolytes containing 1 M LiTFSI in γ-butyrolactone (γ-BL) reached $10^{-3.0}$ S cm^{-1} at 20°C with 50 wt% of electrolyte solution added. Thermal analysis showed that the comblike PPO aggregated through microphase separation of the hexadecanoyl units in both the solid and the gel electrolytes. This microphase had multiple melting points in the temperature interval between −45 and 40°C. Furthermore, the crystallisation of γ-BL was greatly suppressed in gel electrolytes. A study of the gel electrolytes by FT-IR spectroscopy implied that the lithium ions were preferentially coordinated by the PPO grafts, and not by γ-BL.

Keywords: Comb polymer; Poly(propylene oxide); Gel electrolyte

1. Introduction

During the last two decades much research has been devoted to the developmental and fundamental new amorphous polymer materials containing different lithium salts. Many of these materials have been identified as potential candidates for electrolyte membranes for use in applications such as high energy density rechargeable batteries [1,2]. Examples of the polymer component in these materials include amorphous comblike copolymers consisting of short polyether side chains attached to different backbone polymers such as poly(ethylene oxide) [3,4], polystyrene [5,6], polyacrylate [7,8], polyphosphazene [9–11], polysiloxane [12,13], and polyitaconate [14]. Typically, these solid polymer electrolytes exhibit maximum ion conductivities of ~10^{-5} S cm^{-1} at room temperature, although higher values have recently been reported [15]. Unless the polymers can be applied as thin films, this level of conductivity is generally considered too low for use as electrolyte membranes in battery applications.

In order to improve the ion conductivity of the electrolytes, especially at room temperature and below, organic solvents are added to swell the polymers whereby gel electrolytes are formed. Often, the polymer components are employed as crosslinked networks to obtain gel electrolytes with sufficiently good mechanical properties [1]. In the ideal case, gel electrolyte membranes show a liquid-like ion conductivity while retaining the dimensional stability of a solid material. The organic solvents generally have high dielectric constants to ensure high levels of ion dissociation. They include γ-butyrolactone and various carbonates such as ethylene carbonate and propylene carbonate. The main challenges with the gel electrolyte concept today are to combine good mechanical properties and high ion conductivity, and to increase the solvent retention.

In a previous work, a number of high molecular weight poly(propylene oxide) (PPO) was prepared and characterised with the aim of preparing polymer electrolytes [16]. The polymers had a comblike architecture and were synthesised using an ethylene–vinyl alcohol copolymer as a macroinitiator for anionic graft polymerisation of propylene oxide. Hexadecanoyl chloride was subsequently used to cap the PPO chain ends. The polymers, thus, consisted of a polyethylene backbone polymer densely grafted with PPO chains terminated by hexadecanoyl chain ends (Scheme 1). The nature of the chain ends, hydroxyl or hexadecanoyl, was shown to have a large influence on the properties in solution. It was also found that the end capped polymers aggregated through phase separation of their hexadecanoyl

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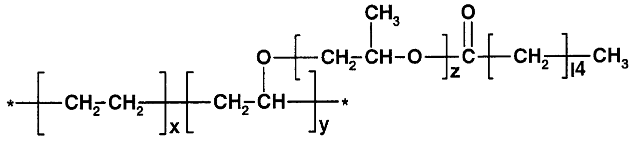

Scheme 1.

chain ends in the solid state. In this way, physically crosslinked polymer networks were formed.

The present investigation is focused on studying the comblike PPO as the polymer component in both solid and gel electrolytes. The solid electrolytes were composed of polymer and lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) salt, and the gel electrolytes, in addition, contained γ-butyrolactone. The phase behaviour of the electrolytes was studied by calorimetry, and the ion conductivity and ion coordination were investigated by impedance and FT-IR spectroscopy, respectively.

2. Experimental

2.1. Polymer preparation

Details of the preparation and structural characterisation of comblike poly(propylene oxide) have been reported previously [16]. In short, the polymers were prepared by first grafting an ethylene–vinyl alcohol (EVOH) copolymer with propylene oxide (PO), and then capping the terminal hydroxyl groups with hydrocarbon chains. More specifically, to produce the sample used in the present study, a pressure-sustaining reactor was charged with 1.80 g dried EVOH copolymer, 60 ml DMSO, and 90 mg NaH, and then carefully degassed. The EVOH copolymer had a molecular weight of 55 000 g mol^{-1} and contained 55 mol% vinyl alcohol units. An amount of 48.60 g of PO was charged to the reactor, and the grafting reaction was allowed to proceed at 80°C till all the monomer had been consumed. The product was purified by fractionation in water/methanol mixtures. In the next step, the hydroxyl chain ends of the polymer were capped by hexadecanoyl units by reaction with a 10% excess of hexadecanoyl chloride in toluene at 50°C. The polymer was purified by successive extractions in methanol/isooctane mixtures, and finally dried in vacuum. Analysis by ^{1}H NMR spectroscopy showed the average molecular weight of the PPO grafts to be 1500 g mol^{-1} and the PPO content to be 96 wt%. The proportion of the charged propylene oxide actually grafted onto the EVOH copolymer, that is the grafting yield, was 82%.

2.2. Electrolyte preparation

Solid polymer electrolytes were prepared by complexing LiTFSI, (Battery Grade, kindly supplied by the 3M Company) with comblike PPO under dry Ar-atmosphere in a glove box. The polymer was first dried at 60°C under vacuum for 3 days. Precise amounts of a solution of LiTFSI in dimethyl carbonate (Merck, Selectipur®, Battery Grade) were added to glass ampoules containing 300 mg of polymer to obtain electrolytes with the desired salt concentrations. The dimethyl carbonate was allowed to evaporate under Ar for two days at ambient temperature before the samples were transferred to a glass oven where the residual solvent was removed under vacuum at 60°C for 3 days. Salt concentrations were defined using the [Li]/[O] ratio, i.e. the number of lithium ions per coordinating PPO oxygens. Gel electrolytes were subsequently prepared by adding precise amounts of an electrolyte solution consisting of 1 M LiTFSI in γ-butyrolactone (γ-BL, Merck, Selectipur®, Battery Grade) to solid polymer electrolytes with [Li]/[O] = 0.050. In this way, gel electrolytes containing 50, 70, and 90 wt% of the electrolyte solution were prepared.

2.3. Impedance spectroscopy

The ion conductivity (σ) of the electrolytes was evaluated by measuring the temperature dependence of impedance spectra during heating from −20 to 100°C. Samples with a diameter of 18 mm and a thickness of 90 μm were sandwiched between two gold-plated stainless steel blocking electrodes spaced by a PTFE ring. The measurements were carried out using a computer controlled Novocontrol BDC40 high-resolution dielectric analyser equipped with a Novocool cryostat unit. Samples were analysed in the frequency range 10^{-1}–10^{7} Hz at 100 mV ac amplitude, and the conductivities were subsequently evaluated using the Novocontrol software WINDETA.

2.4. FT-IR spectroscopy

Spectra were recorded with a Bruker IFS66 FT-IR spectrometer using an overhead attenuated total reflectance (ATR) unit from Specac. The ATR unit was used with a zinc selenide crystal reflecting at 45°. The samples were prepared in the Ar-filled glove box by placing polymer electrolyte samples between the ATR crystal and a clean glass slide. Spectra of the samples were then recorded within 5 min after removal of the sample from the glove box. The spectral resolution was set at 2 cm^{-1}.

2.5. Calorimetry

The thermal properties of the neat polymer and the electrolytes were analysed with a Mettler TA 3000 DSC system under N_2 purge. Samples were placed in aluminium containers, which were sealed under Ar atmosphere. The samples were first cooled from 25 to −150°C at 10°C min^{-1}, and then heated to 60°C at the same scan rate. Glass transition temperatures (T_g) were evaluated from the heating scan.

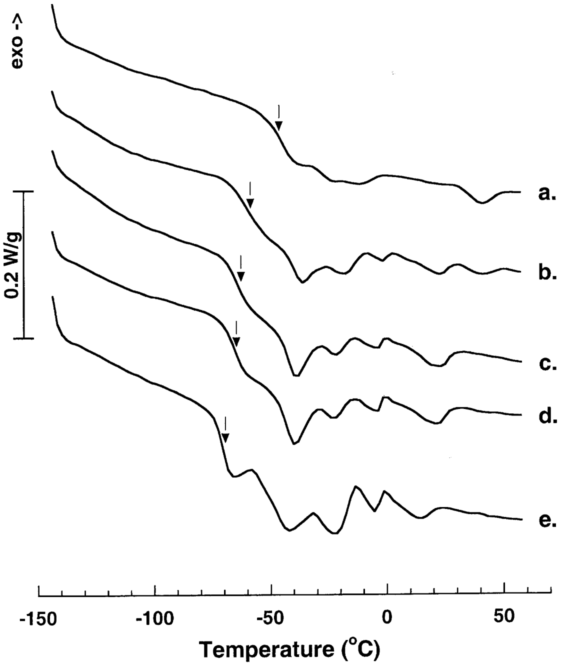

Fig. 1. DSC heating traces of polymer and solid polymer electrolytes based on comblike PPO with [Li]/[O] equal to: (a) 0.100, (b) 0.050, (c) 0.033, (d) 0.025, and (e) 0. Glass transitions are indicated by arrows. The electrolytes were cooled from 25 to −150°C prior to the heating scan. Scan rate: 10°C min^{-1}.

3. Results and discussion

3.1. Solid electrolytes

The solid electrolytes containing comblike PPO (Scheme 1) and LiTFSI appeared optically clear and, as expected, their viscosities increased with increasing value of [Li]/[O]. The phase behaviour of the electrolytes was studied by DSC. Fig. 1 shows the traces obtained when heating from −150 to 60°C. As seen for the neat polymer ([Li]/[O] = 0), the glass transition observed at −70°C was followed by multiple endothermic peaks between −45 and 15°C. These peaks were due to melting of the hexadecanoyl chain ends [16]. This is a strong indication that the hexadecanoyl chain ends were microphase separated from the PPO phase. Furthermore, the distribution of melting peaks suggested that the crystalline hexadecanoyl microphase domains had a broad size distribution. The reason behind this may be a broad size distribution in the molecular weight of the PPO grafts. Because of this, the hexadecanoyl chain ends may have different degrees of conformational mobility and freedom to form microphase domains.

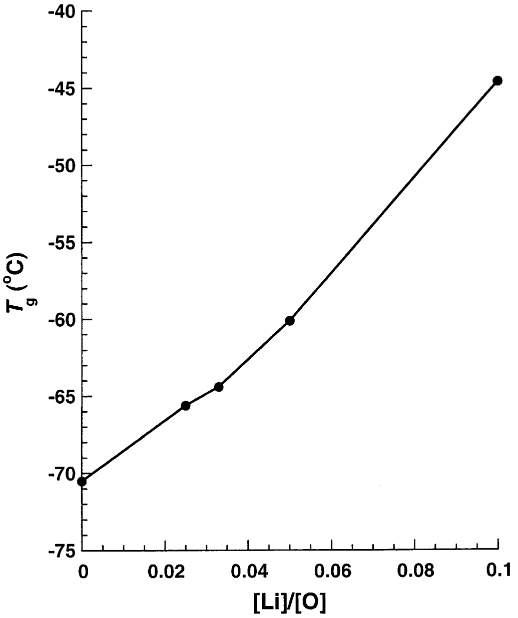

Fig. 2. Variation of T_g with the concentration of LiTFSI salt for the solid polymer electrolytes.

A broad size distribution of the molecular weight of the PPO grafts is expected because the secondary hydroxyl groups of the EVOH copolymer were used to initiate the grafting. The addition of PO to these secondary hydroxyl groups leads to the formation of PPO grafts terminated by secondary hydroxyl groups. Consequently, the acidities, and thus the reactivities, of the initiating EVOH hydroxyl groups and the propagating PPO hydroxyl groups were of the same order during the grafting process. This situation results in a broad size distribution of the PPO grafts [17]. In a previous work, ethylene oxide was grafted from poly(4-hydroxystyrene) [5]. In this case, a narrow size distribution in the molecular weight of the resulting poly(ethylene oxide) (PEO) grafts is expected because of the high acidity, and reactivity, of the phenolic hydroxyl groups of poly(4-hydroxystyrene) in comparison with the primary hydroxyl groups of the PEO grafts. Electrolytes based on these comb-shaped polyethers had a hexadecanoyl phase which showed a single narrow melting peak at −10°C during analysis by DSC, indicating the presence of quite small domains of uniform size [18]. The presence of free, unattached hexadecanoyl segments can be expected to have a large influence on the crystallisation and melting behaviour. However, it was concluded that the samples were free from impurities in the form of hexadecanoic acid or hexadecanoyl chloride because neither absorbance from carboxylic acid at 1710 cm^{-1}, nor absorbance from acid chloride at 1800 cm^{-1} was detected by FT-IR.

As expected, the glass transition temperatures (T_g) of the electrolytes increased after additions of LiTFSI salt. The values are plotted as a function of the salt concentration in Fig. 2. The background for this behaviour is the formation of transient crosslinks because of intra- and intermolecular coordination of ether oxygens with lithium ions [2]. It was also noted that the melting enthalpy, proportional to the crystallinity, decreased with increasing salt concentration. The most probable reason for this was the increase in the viscosity of the electrolytes as the salt concentration was increased.

The temperature dependence of the ion conductivity (σ)

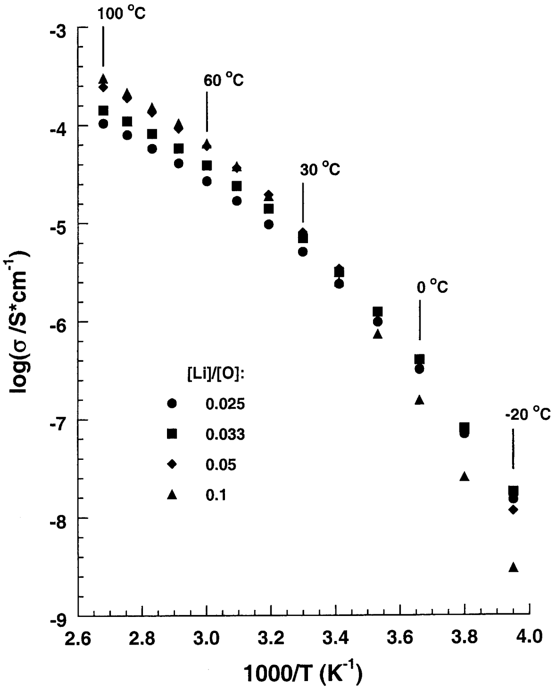

Fig. 3. Arrhenius conductivity plots for solid polymer electrolytes based on comblike PPO at different salt concentrations. The conductivities were evaluated by impedance spectroscopy during heating from −20 to 100°C.

was evaluated by impedance spectroscopy in the range −20 to 100°C. Fig. 3 shows the results obtained as Arrhenius plots for the solid polymer electrolytes. As anticipated, the shape of all the curves agreed well with the generally observed temperature dependence of amorphous polymer electrolytes, [1,2] and also with what has been previously shown for aggregating polyethers similar to the polymer in the present investigation [18]. This is indeed a strong indication that the ions were transported through segmental motions of the PPO grafts. Consequently, the ion conduction behaviour was well described by WLF or VTF equations [1,2]. The value of σ at 20°C was approximately $10^{-5.5}$ S cm^{-1}, showing a slight optimum at [Li]/[O] between 0.033 and 0.050. At temperatures below 20°C, the electrolyte with [Li]/[O] = 0.100 had the lowest value of σ. It is commonly observed that electrolytes with high salt concentrations have low conductivities at low temperatures because the presence of the salt decreases the segmental mobility, and thus increases T_g (Fig. 2). At temperatures above 40°C, on the other hand, the electrolyte with [Li]/[O] = 0.100 had the highest value of σ.

In a previous study, the ion conductivities of electrolytes consisting of aggregating combshaped polyethers and LiTFSI were evaluated [18]. These polymers, having a similar molecular architecture as the comblike PPO of the present study, were based on PEO and poly(ethylene oxide-*co*-propylene oxide), the latter containing 20 wt% propylene oxide. The values of σ were between $10^{-4.9}$ and $10^{-4.6}$ S cm^{-1} at 20°C, that is, one order of magnitude higher than for the PPO-based electrolytes. The reason for this is most probably the poorer ability of PPO to dissociate salt by forming ion–polymer complexes, as compared to PEO [13].

Alloin and Sanches have studied electrolytes based on chemically crosslinked PPO networks and LiTFSI [19]. At 20°C they measured $\sigma = 10^{-5.5}$ and $10^{-6.1}$ S cm^{-1} for networks having PPO chain segments of 2000 and 725 g mol^{-1}, respectively, between the crosslink sites. They explained the difference in σ as a consequence of the lower crosslink density of the network with the longer PPO moieties. In comparison, the values of σ for the network with 2000 g mol^{-1} between the crosslink sites were in level with the values measured for the aggregating comblike PPO in the present study, where the average molecular weight between the backbone and chain end was 1500 g mol^{-1}.

3.2. Gel electrolytes

Gel electrolytes were prepared by swelling solid electrolytes, having [Li]/[O] = 0.050, with various amounts of an electrolyte solution consisting of 1 M LiTFSI in γ-BL. In this way, gels containing 50, 70, and 90 wt% of electrolyte solution were prepared. An attempt to prepare a gel containing 30 wt% electrolyte solution revealed that the polymer was unable to host all of the solution. The system was phase-separated, and had a bottom phase of swollen polymer and a top phase of electrolyte solution. It can be envisaged that the degree of swelling of the comblike PPO is limited because the PPO chains between the backbone polymer and the hexadecanoyl chain ends become increasingly stretched when the amount of solution is increased. The situation is similar to the swelling of a chemically crosslinked network. This implies that the amount of electrolyte solution, which the comblike PPO can host may be increased by increasing the molecular weight of the PPO side chains.

Fig. 4 shows the DSC heating traces of the gel electrolytes. Two general observations were made as the concentration of electrolyte solution was increased. First, the glass transition temperature was lowered. This was expected because of the plasticizing effect of γ-BL. Second, the enthalpy of melting decreased. It was interesting to note that, estimating from the level of the decrease, this seemed to be purely an effect of dilution of the hexadecanoyl phase. Thus, the hexadecanoyl domains were not dissolved by the addition of the electrolyte solution, but remained to provide coherence to the gels. The DSC heating trace of the neat electrolyte solution is shown in Fig. 5. The curve showed a glass transition at −140°C, and an interval of crystallisation and melting transitions between −110 and −50°C. A comparison with the traces of the gel electrolytes shown in Fig. 4 showed that the crystallisation behaviour of the electrolyte solution was greatly depressed by the presence of the polymer in the gels. However, this may be largely a kinetic effect.

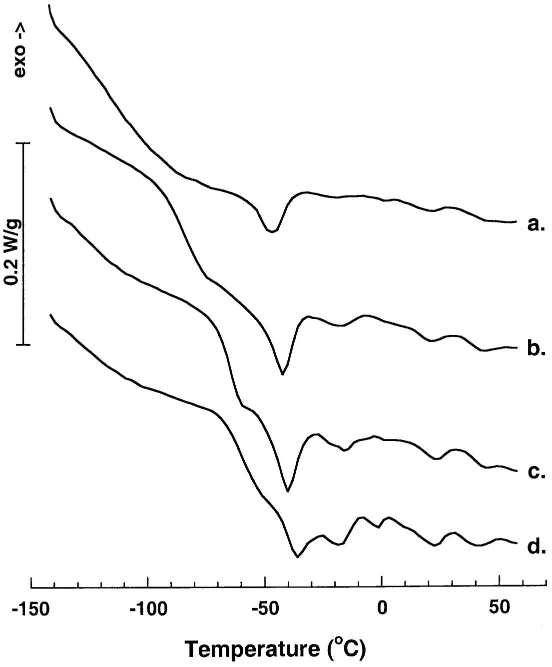

Fig. 4. DSC heating traces of gel electrolytes composed of 1 M LiTFSI salt in γ-BL and (a) 50 wt%, (b) 70 wt%, and (c) 90 wt% of comblike PPO. For comparison, the trace of the solid electrolyte with (d) [Li]/[O] = 0.050 is also shown. The electrolytes were cooled from 25 to −150°C prior to the heating scan. Scan rate: 10°C min^{-1}.

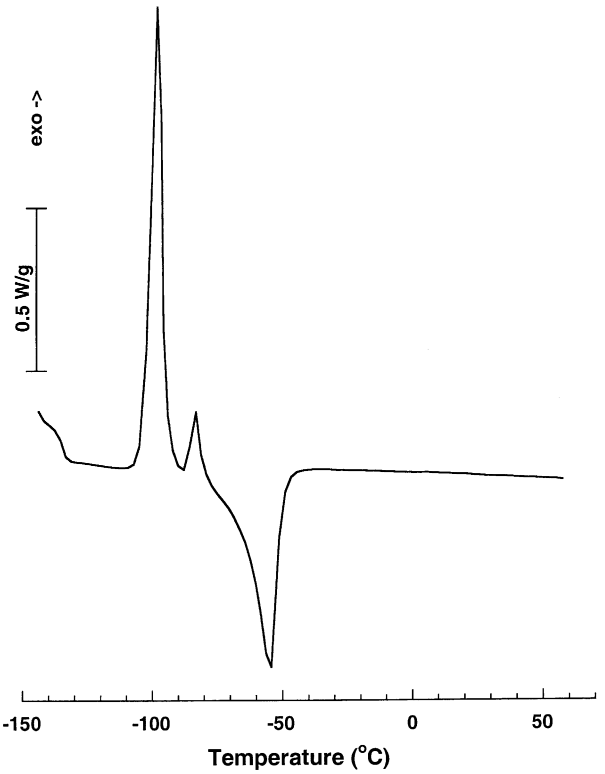

Fig. 5. DSC heating trace of 1 M LiTFSI salt in γ-BL. The solution was cooled from 25 to −150°C prior to the heating scan. Scan rate: 10°C min^{-1}.

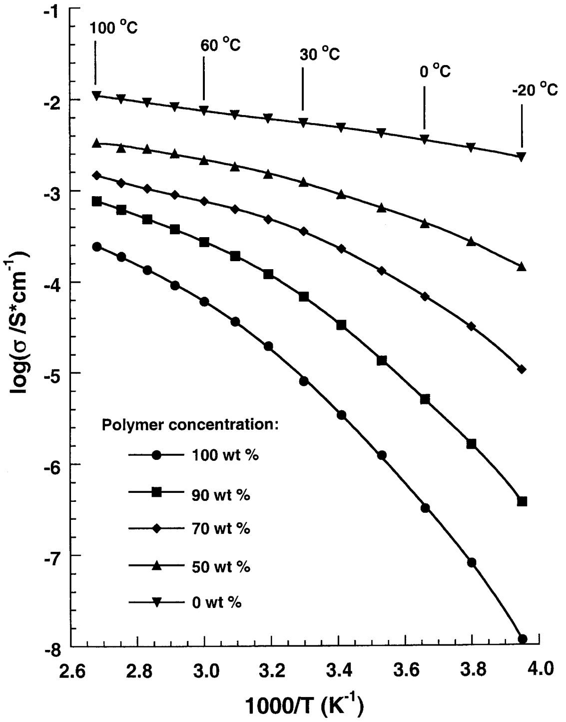

Fig. 6. Arrhenius conductivity plots for neat 1 M LiTFSI in γ-BL (0 wt% polymer), gel electrolytes containing various amounts of 1 M LiTFSI in γ-BL (50–90 wt% polymer), and a solid polymer electrolyte having [Li]/[O] = 0.050. The conductivities were evaluated by impedance spectroscopy during heating from −20 to 100°C.

Arrhenius plots of the ion conductivity of the electrolyte solution, the gel electrolytes, and the solid electrolyte with [Li]/[O] = 0.050 are shown in Fig. 6. The temperature dependence of σ for the electrolyte solution followed an Arrhenius equation. As expected, σ for the gels increased progressively with increasing concentration of the electrolyte solution, and the temperature dependence changed gradually, from a VTF relationship for the solid polymer electrolyte, to a more Arrhenius-like relationship for the gels. The reason for this was that the transport of ions became less coupled with the segmental motions of PPO, as the electrolyte solution was added, and instead became increasingly coupled with the dynamics of the solvent. Typically, electrolytes have to possess values of σ exceeding ~10^{-3} S cm^{-1} at room temperature in order to be of interest for application in lithium polymer batteries. Inspection of Fig. 6 suggests that the PPO gels had to contain approximately 50 wt% of electrolyte solution to reach this value.

Aihara and coworkers have studied gel electrolytes based on chemically crosslinked PEO-networks containing 80% 1 M LiTFSI in γ-BL [20]. They measured σ of the neat electrolyte solution to be $10^{-2.1}$ S cm^{-1} at 40°C, and of the gel to be $10^{-2.6}$ S cm^{-1} at the same temperature. In comparison, the value of σ measured in the present study for the PPO gel containing 50% electrolyte solution was $10^{-2.8}$ S cm^{-1} at 40°C. The slightly higher σ measured for

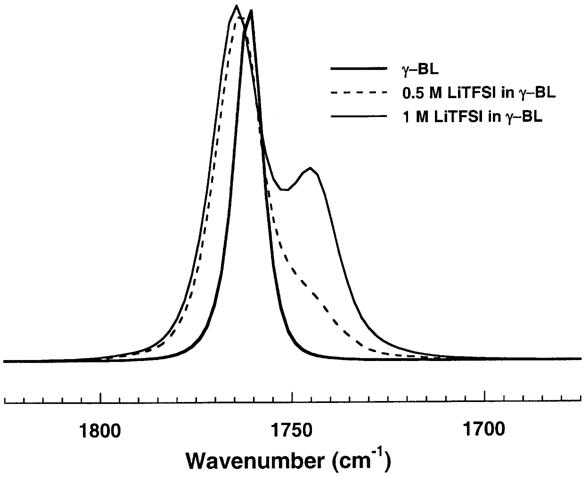

Fig. 7. FT-IR spectra showing the carbonyl region of neat γ-BL and LiTFSI dissolved in γ-BL at concentrations 0.5 and 1.0 M. The peaks are scaled to the same height for comparison.

the PEO based gel can, of course, be attributed to the higher content of electrolyte solution.

FT-IR spectroscopy is a useful tool for studying the immediate physical and chemical environment of a group in a molecule. For example, the vibration of carbonyl groups are known to be sensitive to their environment [21]. In order to extract information concerning the environment of γ-BL, and thus the ion coordination, the carbonyl region of γ-BL was studied in various gels and solutions of γ-BL, LiTFSI, and neat comblike PPO. Fig. 7 shows the carbonyl region of FT-IR spectra of neat γ-BL and of LiTFSI dissolved in γ-BL at 0.5 and 1 M concentration. The spectrum of neat γ-BL showed a single peak at 1760 cm^{-1}. As seen, addition of salt had a large effect on the carbonyl region. Two peaks were observed when the salt was present, the other at 1745 cm^{-1} and the other at 1765 cm^{-1}. Also, the peaks were significantly broadened after addition of salt. The peak at 1745 cm^{-1} increased, relative to the peak at 1765 cm^{-1}, when the salt concentration was increased. The peak at 1745 cm^{-1} was consequently assigned to carbonyl groups, which coordinated ions, while the peak at 1765 cm^{-1} was assigned to carbonyl groups of γ-BL molecules interacting with themselves. The solvation number of lithium ions by γ-BL was reported to be ~2.3 in dilute solutions [22,23].

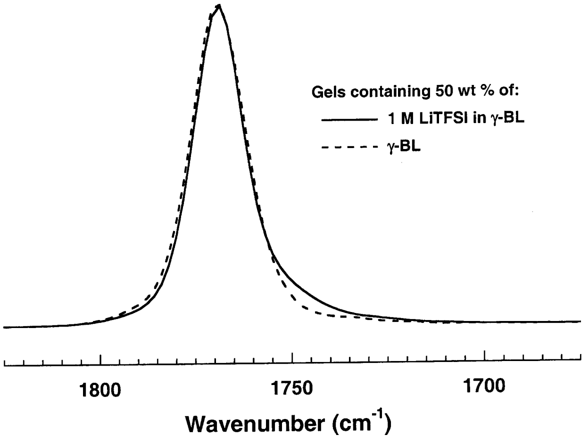

Fig. 8. FT-IR spectra showing the carbonyl region of gels containing 50 wt% γ-BL (no salt) and 50 wt% of 1 M LiTFSI in γ-BL. The peaks are scaled to the same height for comparison.

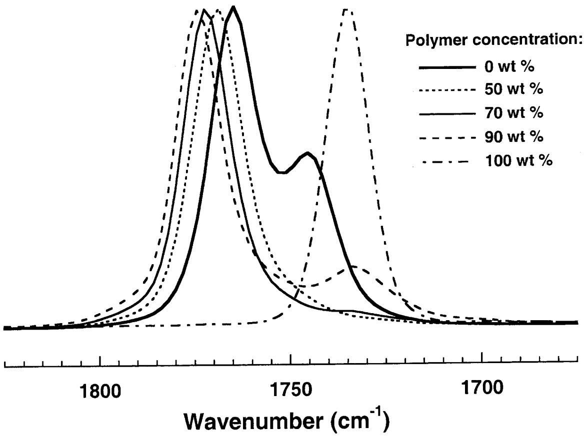

Fig. 9. FT-IR spectra showing the carbonyl region of neat 1 M LiTFSI in γ-BL (0 wt% polymer), gel electrolytes containing various amounts of 1 M LiTFSI in γ-BL (50–90 wt%), and neat comblike PPO (100 wt% polymer). The peaks are scaled to the same height for comparison.

Fig. 8 shows the carbonyl region of a gel containing 50 wt% γ-BL without salt, and a gel electrolyte containing 50 wt% of 1 M LiTFSI in γ-BL. As seen, the position of the peaks was the same in the two cases, that is, it was not affected by the presence of salt. However, a small shoulder of the peak of the gel electrolyte was observed at 1745 cm^{-1} indicating that a small fraction of the γ-BL was involved in ion coordination.

The carbonyl regions of 1 M LiTFSI in γ-BL (0% polymer), gel electrolytes containing various amounts of the electrolyte solution, as well as the neat comblike PPO, are shown in Fig. 9. Analysis of the electrolyte gels showed that the position of the carbonyl peaks was gradually shifted towards higher wavenumber as the concentration of polymer increased. This shift reflected the change in the chemical environment as the solvent concentration was decreased. In addition, it was observed that the height of the peak at 1745 cm^{-1} decreased sharply as the concentration of polymer was increased. This indicated that the ions were preferentially coordinated by the PPO side chains, as long as the polymer concentration was sufficiently high. Also, at high polymer concentrations a new peak could be observed at 1735 cm^{-1}. This peak originated from the carbonyl groups of the hexadecanoyl ester links, and appeared not to be shifted in comparison to the peak position of the neat polymer.

Hayamizu et al. used NMR spectroscopy to study the gel electrolytes based on crosslinked poly(ethylene glycol diacrylate) containing 80% of 1 M LiTFSI in γ-BL [20,22]. The authors found that the diffusion coefficient of the lithium ions in the gels was an order of magnitude lower, as compared to those in the electrolyte solution. The differences in diffusion of the anion and the solvent in the solution and in the gel, respectively, were much smaller. The authors concluded that there was a strong interaction between the lithium ions and the PEO chains in the gels. Although PEO can be expected to coordinate lithium ions stronger than PPO, it seems like there is a strong interaction between the both polyethers and the lithium ions in gel electrolytes containing LiTFSI and γ-BL.

4. Conclusions

This study showed that the comblike PPO aggregated in both solid and gel electrolytes. The employment of aggregating polyethers represents a new way of forming polymer electrolytes, where a polymer network is formed through microphase separation of the hydrocarbon chain ends. The ion conductivity of both solid and gel electrolytes compared well with that of similar electrolytes previously reported in the literature. In the present case, the hexadecanoyl microphase melted at temperatures between -45 and 40°C. By attaching longer hydrocarbon segments, having higher melting temperatures, at the chain ends it should be possible to increase the mechanical strength of the polyether network and the electrolytes.

Acknowledgements

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