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Polymer electrolytes based on triblock–copoly(oxyethylene/oxypropylene/oxyethylene) systems

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Polymer electrolytes based on triblock copolymers of ethylene oxide (EO)/propylene oxide (PO)/ethylene oxide of moderate molecular weight and narrow block-length distributions, doped with $M(CF_3SO_3)_2$ and $M[N(CF_3SO_2)_2]_2$ (M = Mg, Ca, Sr and Ba), $LiCF_3SO_3$ and $LiN(CF_3SO_2)_2$ have been investigated using infrared spectroscopy, differential scanning calorimetry and conductivity measurements. The effects of varying the EO/PO block length, composition and temperature on the phase behaviour, ion-pair formation and conductivity of the polymer electrolytes have been studied. A two-phase microstructure has been observed. Ion pairing occurs for the triflate salts and the amount was found to be sensitive to the relative block sizes rather than the molecular weight of the copolymer. Copyright © 1996 Elsevier Science Ltd.

(Keywords: electrolytes; triblock copolymers; microstructure)

INTRODUCTION

The driving force behind the investigations done on ion-doped polymers (polymer electrolytes) has come from the possibility of using such materials in electrochemical devices and, in particular, as the basis of high energy/density all-solid batteries. Applied in power sources, the polymer electrolyte is required to have a high ionic conductivity. The conductivity depends directly on the aggregation and mobility of the ions present. Long-chain host polymers like poly(ethylene oxide) (PEO) show a tendency to form crystalline phases, where the conductivity is negligible compared to the amorphous polymer–salt fraction of the polymer electrolyte. In the amorphous phase the segmental motion of the polymer backbone is liquid-like.

It is therefore an important concern to minimize the presence of any crystalline phases. This has previously been achieved, for example, by using short PEO side chains grafted to a polymer backbone[1–6]. Work has also been done on low molecular weight diblock copolymers of PEO and poly(propylene oxide) (PPO) to introduce irregularities which inhibit crystallinity[7–9]. Triblock copolymers containing PEO–PPO–PEO have not been investigated, however, and the aim of the present work was to use these polymers to create a solid amorphous polymer electrolyte with suitable mechanical properties for use in a thin-film battery application. To achieve this, the block lengths have to be long enough to prevent a liquid electrolyte forming, yet short enough to prevent crystallization.

The polymers used here are linear triblock copolymers composed of two chemically different blocks, PEO and PPO, with the general formula $HO(C_2H_4O)_i(C_3H_6O)_j$-$(C_2H_4O)_iH$. These materials are commercially available under various trade names such as Pluronic® and Synperonic®, and the corresponding non-proprietary name is poloxamer. They are produced with different block lengths (EO_i–PO_j–EO_i, where i and j are the numbers of monomer units), which strongly influence the physical properties. This paper is based on the investigations of four different intermediate molecular weight triblock copolymers: P-85, F-88, F-108, and F-127. The names are based on the physical appearance in the pure form, paste (P) or flaked solid (F), on the molecular weight of PPO and the percentage PEO of the total copolymer weight.

Most work in the field of polymer electrolytes has dealt with monovalent ions and, in particular, with lithium ions. The present work is mainly focused on polymer electrolytes with alkaline earth triflate and imide salts, $M(CF_3SO_3)_2$ and $M[N(CF_3SO_2)_2]_2$ for M = Mg, Ca, Sr and Ba. The use of multivalent cations provides a possibility to study fundamental properties responsible for ion mobility in polymer electrolytes and might offer new technological applications where lower-cost materials and metals less reactive than lithium are desirable. We have investigated these salts, as well as $LiCF_3SO_3$ and $LiN(CF_3SO_2)_2$, in the triblock copolymers and compared the findings with the corresponding high molecular weight PEO solvent, using Fourier transform infrared (*FT*i.r.), differential scanning calorimetry (d.s.c.) and impedance spectroscopy.

EXPERIMENTAL

Preparation of the polymer electrolyte films

Polymer electrolytes of triblock copolymers or commercial PEO (^{L}PEO, $M_W = 4 \times 10^6$, BDH polyox 301)

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were prepared. The triblock copolymers Pluronics P-85 (average composition $EO_{26}-PO_{39}-EO_{26}$, molecular weight 4600 g mol^{-1}), F-88 ($EO_{103}-PO_{39}-EO_{103}$, 11 400 g mol^{-1}), F-108 ($EO_{132}-PO_{50}-EO_{132}$, 14 600 g mol^{-1}) and F-127 ($EO_{100}-PO_{65}-EO_{100}$, 12 600 g mol^{-1}) were obtained from the BASF Corporation, USA. Analytical gel permeation chromatography (g.p.c.) was used to determine the purity of the block copolymers. The amount of homopolymer impurity, the PEO–PPO diblock copolymer, was 14 wt%. The polymers were all end-capped by hydroxy groups and the molecular weights chosen were sufficiently large that the effect of end-group coordination of the ions could be neglected. End-group coordination has been found to be very substantial for low molecular weight PPO oligomers[10,11].

The alkaline earth triflate salts were prepared by dissolving the metal carbonate ($MgCO_3$, Ventron; $CaCO_3$, $SrCO_3$, $BaCO_3$, Merck) in a slight excess of an aqueous solution of HCF_3SO_3. The $M(CF_3SO_3)_2$ (with M = Mg, Ca, Sr and Ba) solution was then filtered and precipitated at 100°C. The salts were finally dried in vacuum at 160°C for 48 h. $LiN(CF_3SO_2)_2$ was obtained from 3M Ltd and the alkaline earth imide salts were prepared as reported earlier[12].

Polymer electrolyte films with an ether oxygen/metal ion ratio (n) for $n = 6$–24 were prepared by dissolving the appropriate molar proportions of salt and monomer units of the polymer in anhydrous methanol (Merck, 'for spectroscopy'), and after sufficient mixing, the solutions were cast onto Teflon plates for the conductivity measurements, in aluminium pans for the d.s.c. measurements and on KRS-5 windows for the *FT* i.r. studies. The films were dried in vacuum at 95–100°C for a minimum of 48 h. All preparations and manipulations were carried out under an anhydrous nitrogen atmosphere ($H_2O <$ 1 ppm). Once dry and solvent-free, these films were stored at 25°C for at least a week and were not used until any crystallization was completed. From d.s.c. measurements we know that all films were totally amorphous, at least in the composition range $n = 6$–12, except those with magnesium and lithium triflate salts and alkaline earth triflate salts dissolved in PEO. The films intended for conductivity or d.s.c. measurements were normally 100–200 μm thick. The films to be used in the *FT*i.r. experiments were 10–20 μm thick (determined interferometrically) and their water content was checked from the O–H stretching bands.

D.s.c. measurements

Films of approximately 10 mg were sealed into 40 μl aluminium pans and transferred into a Mettler model DSC20 oven, connected to a Mettler TA4000 controller. During all thermal analyses, a flow of nitrogen was maintained over the perforated pan to keep away atmospheric moisture and remove any decomposition products. The samples were analysed between −150 and 200°C using a heating rate of 10°C min^{-1}.

Conductivity measurements

The conductivities of the polymer electrolytes were determined by a.c. impedance measurements over a frequency range of 2 MHz to 60 Hz with an applied signal of 10 mV by a Solartron 1260 frequency response analyser. Measurements were carried out in the temperature range 25–95°C at approximately 5°C intervals and controlled by a processor which also operates the frequency analyser and the data acquisition. Stainless steel electrodes were used in a closed cell filled with nitrogen, and thermostatically controlled by circulating water through the mounting stage of the cell. Only samples containing triflate salts have been investigated here.

FT*i.r. measurements*

The spectra were recorded on a Digilab-Biorad FTS-45 FT-IR spectrometer covering the range 400–4400 cm^{-1} with a resolution of 1 cm^{-1}. The KRS-5 window was enclosed in a vacuum cell equipped with a heating element. Spectra were recorded between 25 and 90°C.

RESULTS AND DISCUSSION

FT*i.r. spectroscopy*

The alkaline earth triflate polymer electrolyte systems. Poly(ethylene oxide) electrolytes. An overview of the spectra between 700 and 1400 cm^{-1} for the polymer electrolytes $M(CF_3SO_3)_2$ PEO_{12} for M = Mg, Ca, Sr and Ba (supercooled by melt quenching) is presented in *Figure 1*. Three regions of relevance to the coordination of the cation to the triflate ion are indicated: region 1 at 1230–1350 cm^{-1}, region 2 at 1020–1050 cm^{-1}, and region 3 at 745–770 cm^{-1}. The non-coordinated triflate ion is assumed to have point group symmetry C_{3v}. Two SO_3 stretching modes are observed, the doubly degenerate antisymmetric SO_3 stretching mode belonging to the E irreducible representation at ~1274 cm^{-1} (region 1) and the non-degenerate symmetric mode belonging to A_1 at ~1032 cm^{-1} (region 2). The non-degenerate CF_3 symmetric bending mode also belonging to A_1 is observed at 752 cm^{-1} (region 3).

When one of the oxygen atoms of the triflate ion becomes coordinated to a cation, the symmetry is lowered and the antisymmetric SO_3 mode splits into two components and the symmetric mode shifts to lower or higher frequency. For example, in $Ba(CF_3SO_3)_2PEO_{12}$ both coordinated and non-coordinated triflate ions occur. The antisymmetric stretching mode splits into two bands appearing at 1294 and 1249 cm^{-1}, indicating the presence of metal–ion coordinated triflate ions, simultaneously with the SO_3 stretching band at 1274 cm^{-1} from non-coordinated triflate ions.

As shown in *Figure 1*, a larger split of the antisymmetric stretching band is obtained if the radius of the alkaline earth metal ion is decreased, due to a stronger coordination by a smaller cation. The split, $\Delta\omega$, is 73 cm^{-1} for Mg^{2+}, 66 cm^{-1} for Ca^{2+}, 50 cm^{-1} for Sr^{2+}, and 45 cm^{-1} for Ba^{2+}. The value $\Delta\omega$ also depends on the charge of the coordinating cation as seen in *Figure 2*, where the split of the SO_3 antisymmetric stretching band is shown for several metal–triflate complexes in PEO and PPO known from literature[13–16], together with the current alkaline earth triflate complexes. The figure shows that $\Delta\omega$ is an approximately linear function of the charge to radius ratio. The largest deviations from this relation are observed when one component of the $\nu(SO_3)_a$ is close to the symmetric CF_3 stretching mode at ~1220 cm^{-1}. This band is insensitive to the cation type because the non-polar CF_3 end is not involved in strong bonding.

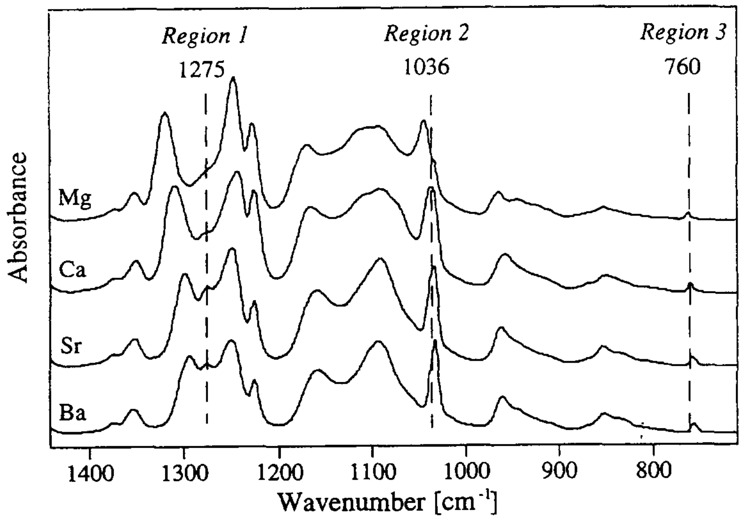

Figure 1 *FT*i.r. absorption spectra of $M(CF_3SO_3)_2PEO_{12}$ for M = Mg, Ca, Sr, Ba at 25°C

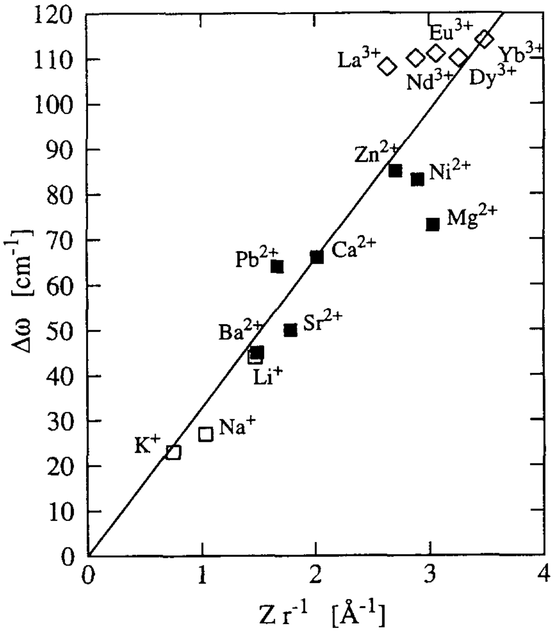

Figure 2 The split, $\Delta\omega$, of the antisymmetric SO_3 stretching mode of the triflate ion, coordinated by mono-, di- or trivalent cations as a function of Z/r (Z = charge, r = radius of the cation). Values of $\Delta\omega$ for Li^+, Na^+ and K^+ from ref. 13, Pb^{2+}, Zn^{2+} and Ni^{2+} from refs 14 and 15, and La^{3+}, Nd^{3+}, Eu^{3+}, Yb^{3+} and Dy^{3+} from ref. 16. The alkaline earth values are from the present work

It is clearly seen from *Figure 1* that, with increasing cation radius, the absorbance of the degenerate $\nu(SO_3)_a$ band at 1274 cm^{-1} (corresponding to 'free' triflate ions) increases at the expense of the split $\nu(SO_3)_a$ bands from the metal ion coordinated triflate ions. An analogous phenomenon can be observed in the symmetric SO_3 stretching region, where a shift of the band centre towards ~1032 cm^{-1} (the position for 'free' triflate ions) can be seen on increasing the metal ion radius. For samples with $n = 6$ an additional band is observed at higher wavenumbers, indicating the presence of clusters larger than ion pairs.

Ionic association in triflate systems can also be observed in the CF_3 symmetric deformation, $\delta(CF_3)_s$, region at ~752 cm^{-1} (region 3, *Figures 1*, *3* and *5*)[17]. The advantage of studying this band is that no PEO or other triflate bands interfere in this region. This region is shown in *Figures 3* and *5* for $Ba(CF_3SO_3)_2PEO_n$ for $n = 6$–16. The rather narrow mode at low salt concentration is clearly broadened on the high frequency side with increasing salt concentrations. The whole contour is fitted to Gaussian curves. The appearance of distinct components indicates a distribution of different triflate ion-containing species. For $n = 16$, the 'free' ion band at 752 cm^{-1} and the band assigned to ion pairs at 757 cm^{-1} are the most dominant.

Similar to earlier work done on $M[N(CF_3SO_2)_2]_2PEO_n$ for M = Mg, Ca, Sr and Ba[12] the C–O–C antisymmetric stretching mode, $\nu(COC)_a$, shifts from 1106 cm^{-1} to lower wavenumbers when salt is added (*Figure 1*). The largest shift is obtained for Mg^{2+} and the smallest for Ba^{2+}. An explanation for the different shifts is that the ether oxygens interact more strongly with a smaller cation, such as Mg^{2+}, leading to a larger shift of the C–O–C vibrational band. As seen from the undisturbed $\nu(COC)_a$, the amount of uncoordinated ether oxygens is higher for the smaller cations. This phenomenon was discussed in detail in ref. 12 and attributed to the lower number of ether oxygens coordinated for the smaller cations.

Triblock copolymer electrolytes. Infrared spectra of the pure copolymers together with spectra of PPO ($M_W = 4000$) and PEO are shown in *Figure 4*. All the spectra look very similar with a dominating C–O–C stretching band centred at 1106 cm^{-1}. All bands from the anions discussed above and below fall in regions with a small absorption from the polymers. *Figure 5* shows $Ba(CF_3SO_3)_2[F\text{-}108]_6$ and $Ba(CF_3SO_3)_2[F\text{-}127]_9$ compared to the PEO and $Ba(CF_3SO_3)_2$ based polymer electrolytes at the same concentrations. The notation $[F\text{-}108]_n$ means an ether oxygen/metal ratio of n, where all the ether oxygens of the triblock copolymer are taken into account. For the polymer electrolytes based on the block copolymers the amount of ion pairs is higher, while the amount of higher aggregates is somewhat lower. This effect could be due to the large difference in molecular weight between PEO and the triblock copolymers. In the polymer electrolytes based on a triblock copolymer we have found that the number of ion pairs depends on the

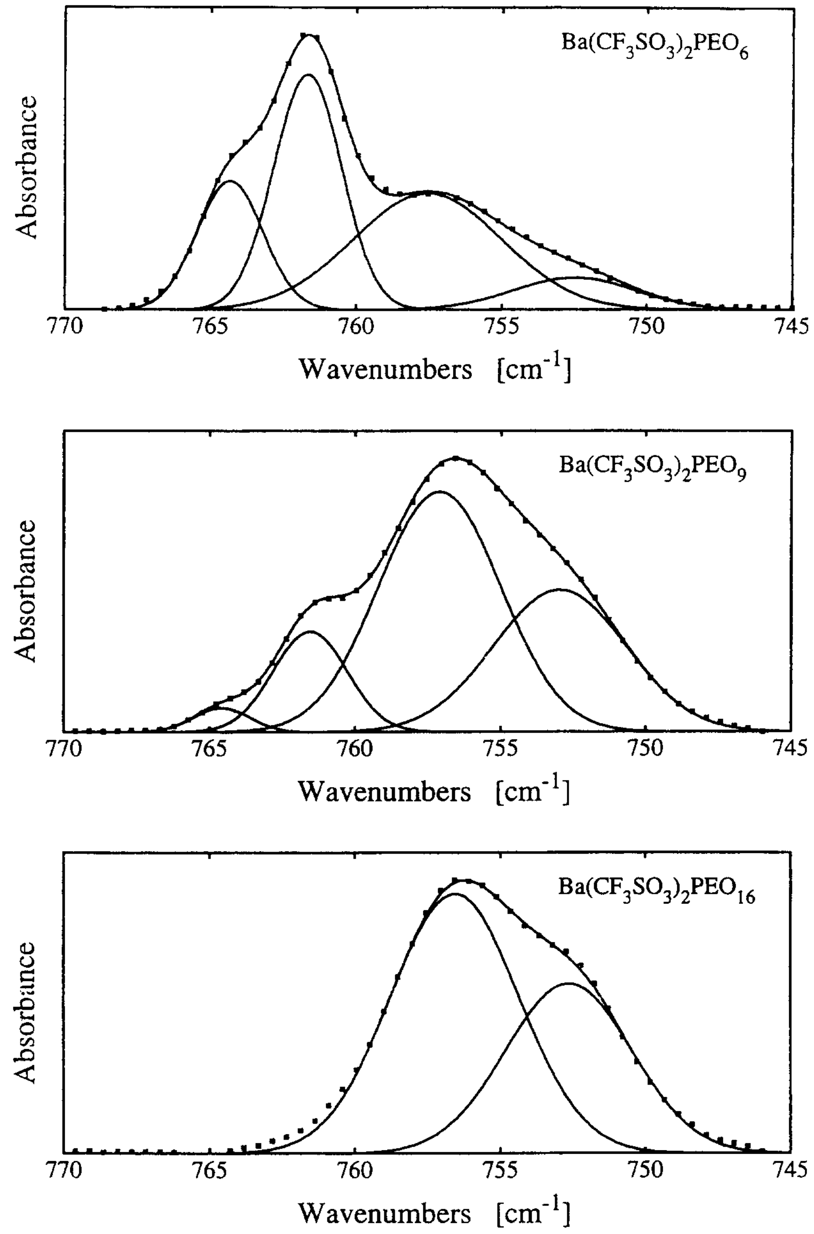

Figure 3 The CF$_3$ symmetric deformation mode at ~745–770 cm^{-1} of Ba(CF$_3$SO$_3$)$_2$PEO$_n$ for n = 6, 9 and 16 at 25°C. For these bands the solid lines correspond to the components of the Gaussian envelope fitted to the spectrum (dots). The components at ~752 cm^{-1} are attributed to 'free' triflate ions, the components at ~757 cm^{-1} to ion pairs, and those at ~762 cm^{-1} and ~765 cm^{-1} to higher aggregates

EO/PO ratio. For a given salt type and concentration the number of ion pairs increases for decreasing EO/PO ratio. Polymer electrolytes based on F-88 and F-108, which are equal in EO/PO ratio but differ in molecular weight, show equal amount of ion pairs. A reason for the increase in ion pairs on decrease of the relative amount of EO is probably a preference for the cations to be located on the PEO rather than the PPO block. The cations are expected to coordinate preferentially to the oxygens of the PEO chain since the solvating power of PEO is larger than that of PPO. Although PPO has the same spacing between ether oxygens as PEO, its solvating power is lower, due to the steric hindrance from the methyl groups and the lower concentration of solvating groups. The local salt concentration at the PEO chain increases the number of ion pairs to an amount which is higher than expected from the total ether oxygen/metal ratio. However, the number of ion pairs does not increase to the amount expected from the EO/metal ratio. The amount of ion pairs increases with temperature as reported earlier for triflate salts in PEO[15,18].

The alkaline earth imide polymer electrolyte systems. For polymer electrolytes containing M[N(CF$_3$SO$_2$)$_2$]$_2$ for M = Mg, Ca, Sr and Ba, and PEO or triblock copolymers within the range studied of $n > 9$, the S–N stretching band at ~740 cm^{-1} and the band at ~1355 cm^{-1} for ν(SO$_2$) vibrations were used as probes to detect ion–ion interactions. We have found earlier[6] that these bands are sensitive to ion-pair formation. No ion pairs were observed. For n = 9, the polymer electrolytes for M = Sr and Ba contain small amounts of ion pairs. This amount increases as the relative amount of PPO increases. However, the observed changes as a function of the EO/PO ratio are much smaller compared to those for the alkaline earth triflate salts.

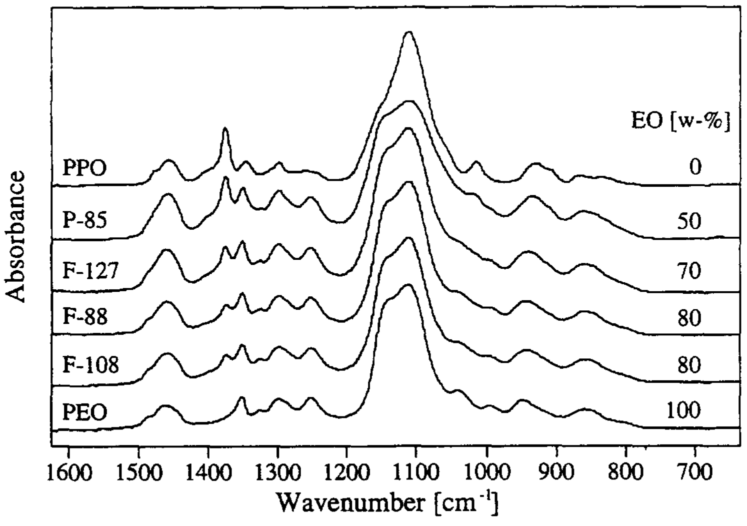

Figure 4 *FT*i.r. absorption spectra of the triblock copolymers P-85, F-88, F-108 and F-127, together with PEO at 90°C and PPO4000 at 25°C. The contribution of the EO units to the total molecular weight of the (co-)polymer is given in wt%

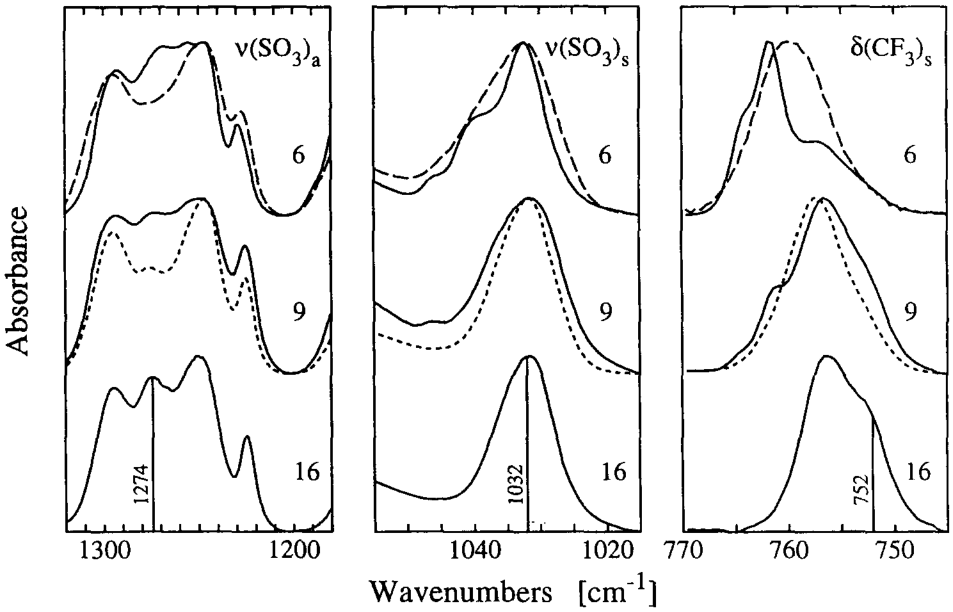

Figure 5 The SO_3 antisymmetric stretching mode, $\nu(SO_3)_a$, the symmetric SO_3 stretching mode, $\nu(SO_3)_s$, and the CF_3 symmetric deformation mode, $\delta(CF_3)_s$, for $Ba(CF_3SO_3)_2PEO_n$ for $n = 6$–16 (solid lines), $Ba(CF_3SO_3)_2[F\text{-}108]_6$ (dashed lines), and $Ba(CF_3SO_3)_2[F\text{-}127]_9$ (dotted lines)

The lithium triflate and lithium imide systems. As for the polymer electrolytes based on alkaline earth metal triflate salts and triblock copolymers, the samples made with $LiCF_3SO_3$ show ion pairing which increases on decreasing EO/PO ratio. The polymer electrolytes with $LiN(CF_3SO_2)_2$ and PEO or the triblock copolymers show no ion pairs for the concentration range studied, $n > 8$.

D.s.c. measurements

Triflate samples. D.s.c. thermograms for the polymer electrolytes based on the triblock copolymers and alkaline earth metal triflate salts show amorphous samples within the range $n = 6$–12 since they exhibit only glass transitions. Exceptions are polymer electrolytes with $Mg(CF_3SO_3)_2$ and $LiCF_3SO_3$ which are highly crystalline, probably due to the smaller cation radii of Mg^{2+} and Li^+. The PEO-based polymer electrolytes $M(CF_3SO_3)_2PEO_n$ for M = Mg, Ca, Sr and Ba, are highly crystalline. Incorporation of PPO subunits into PEO suppresses the crystallization of the PEO parts and leads to amorphous samples for Ca, Sr and Ba. Totally amorphous systems with magnesium and lithium triflate are not obtained with the triblock copolymers, although the crystalline points are largely reduced as compared to pure PEO. The amorphous fraction becomes larger on decreasing EO/PO ratio.

The pure triblock copolymers have crystalline parts with a melting temperature close to 60°C. The crystalline parts contain PEO as verified from comparisons of X-ray diffractograms taken of the block copolymers and PEO ($M_W = 4000$ and 4×10^6). Their amorphous parts show single glass transition temperatures (T_g, taken at the mid-point of the inflection) at −65.3°C (P-85), −59.9°C (F-88), −58.5°C (F-108) and −63.9°C (F-127). These

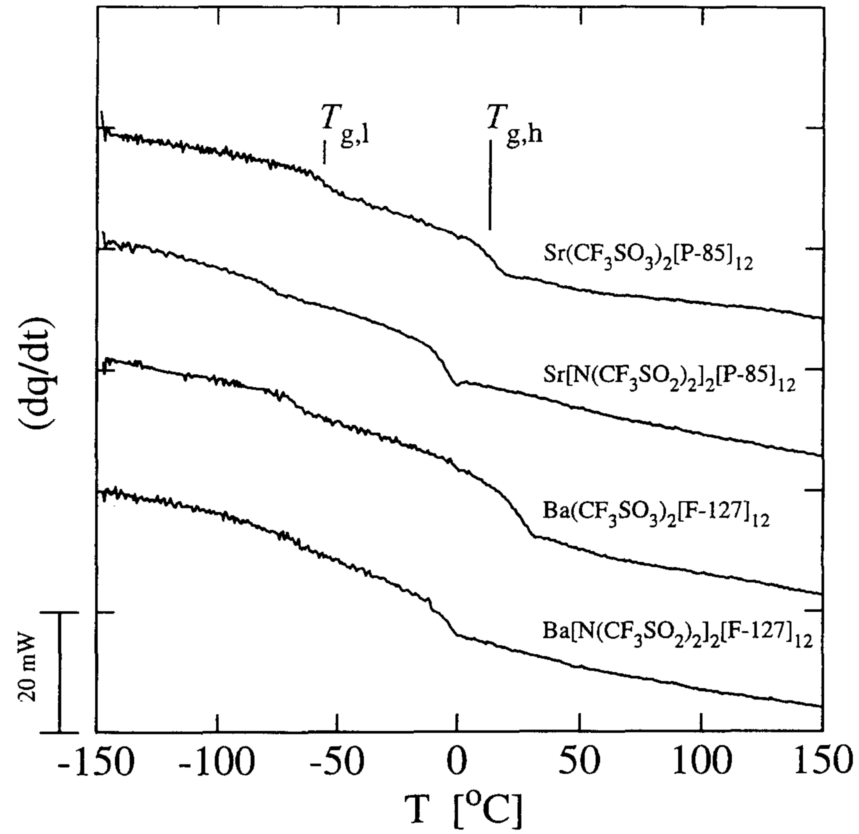

Figure 6 D.s.c. traces of $Sr(CF_3SO_3)_2[P\text{-}85]_{12}$, $Sr[N(CF_3SO_2)_2]_2[P\text{-}85]_{12}$, $Ba(CF_3SO_3)_2[F\text{-}127]_{12}$ and $Ba[N(CF_3SO_2)_2]_2[F\text{-}127]_{12}$ samples during the second heating cycle

glass transition temperatures reflect the dependence on the EO/PO ratio, the degree of crystallinity, and the total molecular weight of the polymer. The occurrence of one glass transition and its dependence on the EO/PO ratio indicate that the PEO and PPO constituents are mutually compatible and form one single amorphous phase.

By adding a salt to the copolymers, two glass transitions were observed in several cases, which means that the compatibility of the blocks is broken and a phase separation takes place (*Figure 6*). This phase separation is on a microscale only, since the blocks are chemically bonded which prevents the formation of large-scale domains. Totally transparent samples are found. The resulting two-phase network comprises a minor, low T_g, PPO block and a major, high T_g, PEO fraction. The low glass transition temperature is slightly lower than the single glass transition temperature of the pure copolymer and almost insensitive to the cation type and the salt concentration. Due to the lower solvating power of the PPO blocks (as discussed above), this lower T_g is assigned to a PPO microphase containing no or very little salt. The high glass transition temperature is sensitive both to the cation type and the salt concentration (a concentration-dependent T_g is common in polymer electrolytes). This high temperature glass transition is assigned to a PEO microphase with dissolved salt, where the cations are coordinated to the ether oxygens. A coordination of cations to the ether oxygens implies a slower average segmental motion of the polymer chains which increases the glass transition temperatures. For a given copolymer, doped with an alkaline earth triflate salt, the lowest value of the high T_g is reached for samples containing Mg^{2+}. For $M(CF_3SO_3)_2[F\text{-}127]_{12}$ and M = Mg, Ca, Sr and Ba, a variation of T_g from −5.8°C for Mg^{2+} to +24.8°C for Ba^{2+} is obtained. The reason for the lower T_g for Mg^{2+} is that a lower number of coordinated ether oxygens leads to a larger average chain mobility, as reported earlier[12]. Smaller cations are expected to coordinate fewer of the ether oxygens and therefore more ether oxygens will be left uncoordinated. This results in faster average segmental motion in the polymer and lowers the glass transition temperature.

Imide samples. When alkaline earth imide salts are present in the triblock copolymers, only a single glass transition is seen in most cases (*Figure 6*). We assume that the large anions hinder a system of separated microphases and retain a blending of the PPO and PEO fractions into a homogeneous phase. The trends in the positions of the glass transition temperatures (between −20 and −5°C) *versus* salt type, concentration and EO/PO unit ratio, are quite complex and cannot be explained solely on the basis of the number of coordinated ether oxygens and the interaction strengths between the cations and the oxygens. The T_g values for $M[N(CF_3SO_2)_2]_2PEO_n$ and M = Mg, Ca, Sr and Ba are somewhat lower compared to samples based on triblock copolymers with the same salt concentration.

Lithium samples. The samples composed of $LiCF_3SO_3$ and triblock copolymers showed crystalline contributions for the concentration range studied, $n = 6\text{–}16$. Inclusion of PPO blocks does not inhibit crystallinity

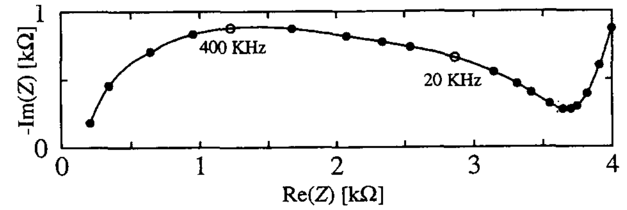

Figure 7 Complex impedance diagram of $Sr(CF_3SO_3)_2[F\text{-}88]_{12}$, sandwiched between stainless steel electrodes at 83°C

completely, in contrast to the case of the alkaline earth triflate polymer electrolytes. The amorphous part has a two-phase microstructure, as the samples exhibit two glass transitions. This two-phase microstructure is broken when $LiN(CF_3SO_2)_2$ is used as a salt. An amorphous region exists with only one glass transition for the composition $n = 6$–10, similar to that found for $LiN(CF_3SO_2)_2$ in PEO with a molecular weight of 4000 (ref. 19). However, the glass transition temperature is higher when triblock polymers are used.

Conductivity measurements

For polymer electrolytes based on alkaline earth metal triflates the complex impedance diagrams are measured for temperatures between 25 and 95°C. For temperatures above ~60°C the bulk semicircles in the impedance diagrams are considerably broadened and distorted (*Figure 7*). The bulk impedance appears to be a superposition of two semicircles with different time constants. We suppose that this profile is based on inhomogeneities due to the two-phase microstructure of the sample[20]. As mentioned in earlier sections, the samples contain salt-rich and salt-poor regions. For low frequencies the ionic current has to follow a rather tortuous path through the mosaic of the regions with least resistance, namely, the PEO-based microstructures. The conductivities are obtained by extrapolation of the linear response from the non-blocking electrodes to the Re(Z) axis.

In *Figure 8* the conductivities for the $M(CF_3SO_3)_2[F\text{-}108]_n$ and $M(CF_3SO_3)_2[F\text{-}127]_n$ samples with M = Mg and Ca and with compositions $n = 9$ and 12 are plotted as $\ln \sigma$ *versus* $10^3/T$. For amorphous samples based on triblock copolymers, the conductivity decreases for decreasing EO/PO ratio. The conductivities for the amorphous samples containing F-108 with M = Ca, Sr and Ba are higher compared to the samples containing F-127. This is shown in *Figure 8b*, where the conductivities of $Ca(CF_3SO_3)_2$ in F-108 and F-127 for compositions $n = 9$ and 12 are shown. The copolymer F-127 has a lower EO/PO ratio (and lower molecular weight) compared to F-108. The same dependence of the conductivity on the EO/PO ratio is found for the other copolymers studied, F-88 and P-85. A larger relative amount of EO units seems to increase the ionic conductivity.

An increase of the ionic conductivity with an increase in the relative amount of EO units is seen for the semicrystalline sample of $Mg(CF_3SO_3)_2$ in F-108 and F-127 for compositions $n = 9$ and 12, as shown in *Figure 8a*. Ion conduction takes place through the amorphous regions. The d.s.c. results show that polymer electrolytes of $Mg(CF_3SO_3)_2$ in F-127 contain lower fractions of crystalline regions compared to $Mg(CF_3SO_3)_2$ in F-108. The larger amorphous regions in samples containing F-127 result in higher ionic conductivities, as shown in *Figure 8*, despite the fact that within the amorphous regions the ionic conductivity is lowered by using a copolymer with lower EO/PO ratio.

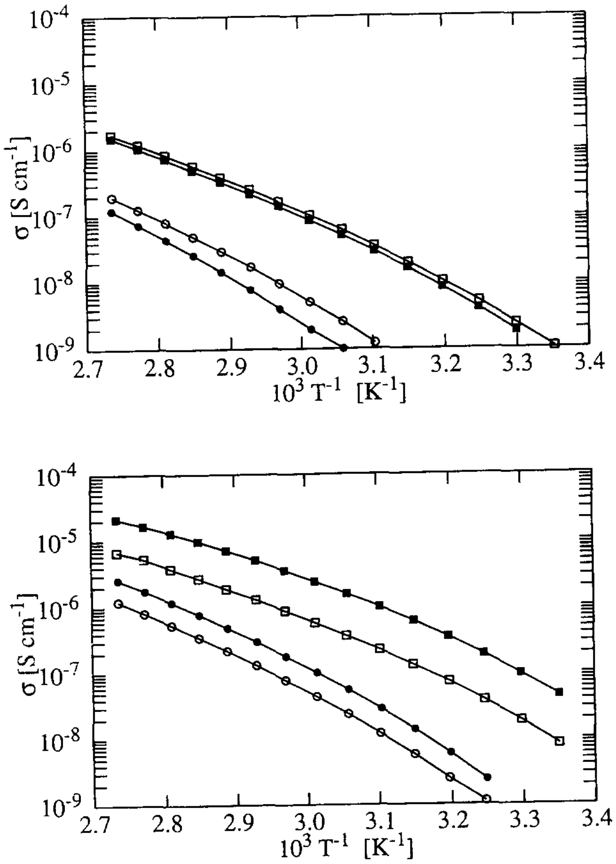

Figure 8 Logarithm of the total conductivity of $M(CF_3SO_2)_2[F\text{-}108]_n$ and $M(CF_3SO_2)_2[F\text{-}127]_n$ for M = Mg (a) and Ca (b). Compositions of samples containing the polymer F-108: $n = 9$ (●) and 12 (■). Compositions of samples containing the copolymer F-127: $n = 9$ (○) and 12 (□)

For the amorphous samples containing Ca, Sr and Ba and a given copolymer and composition range ($n = 6$–16), the highest ionic conductivities are obtained for samples containing cations with the smallest radii. This effect is correlated with the observations for the glass transition temperatures and can be explained by the number of ether oxygen atoms coordinated to the cations. The smaller cation coordinates fewer ether oxygens and, consequently, more uncoordinated ether oxygens will be left. This results in faster average segmental motion of the polymer chain, promoting the ion transport for the smaller cations. A higher ionic conductivity is obtained despite the fact that we observed a higher amount of ion pairs for smaller cations.

CONCLUSIONS

Polymer electrolytes have been formed by incorporating $LiCF_3SO_3$, $LiN(CF_3SO_2)_2$, $M(CF_3SO_3)_2$ or $M[N(CF_3SO_2)_2]_2$ (for M = Mg, Ca, Sr and Ba) in PEO–PPO–PEO block copolymers and compared with electrolytes based on high molecular weight PEO. It has been demonstrated that the incorporation of PPO blocks into PEO successfully suppresses the crystallization of the polymer electrolytes of alkaline earth triflate salts and imide salts and leads to improved conductivities. However, a too low EO/PO unit ratio decreases the conductivity. Hence the optimum EO/PO ratio is that which both maximizes the ionic conductivity and manages to suppress the crystallization. For the triblock copolymers complexed with triflate salts, a microphase separation of salt-rich PEO and salt-poor PPO fractions takes place. When the copolymers are complexed with imide salts, the phase separation is suppressed.

The differences between the conductivities of the triblock copolymers and the triflate-based electrolytes of the same composition (in the range $n = 6$–16) are caused by differences in the coordination number of the cation. The decreasing stability of the cation–polymer bonds for the larger cations leads to a higher conductivity, whereas an increased coordination number leads to a decrease in the polymer segmental motion and consequently to a decrease in conductivity. The difference in coordination number also explains why samples containing small cations have the lowest glass transition temperatures. The different glass transition temperatures of triblock copolymers complexed with imide salts cannot be explained by the coordination numbers of the cations only.

Details of the cation–anion interactions were studied by *FT*i.r. data. Ion pairs appear to play a minor role in the polymer electrolytes containing imide salts, although compositions of $n < 9$ were not considered in this work. Contact ion pairs have been observed in the samples containing triflate salts. The amount of ion pairs increases by increasing salt concentration, temperature, PEO/PPO segment ratio and decreasing cation size.

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