

Coordination and conformation in PEO, PEGM and PEG systems containing lithium or lanthanum triflate

Annika Bernson and Jan Lindgren*

Institute of Chemistry, Uppsala University, Box 531, S-751 21 Uppsala, Sweden

and Weiwei Huang and Roger Frech

Department of Chemistry and Biochemistry, University of Oklahoma, Norman, OK 73019, USA

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The effect of chain length, cation type and polymer end group on the coordination and conformation in polymer electrolytes has been studied using high molecular weight poly(ethylene oxide) (PEO), poly(ethylene glycol) (PEG(400)) and poly(ethylene glycol)dimethyl ether (PEGM(400)) as polymers, with LiCF_3SO_3 and $\text{La}(\text{CF}_3\text{SO}_3)_3$ as salts. The experimental technique used has been Fourier transform infra-red spectroscopy. A coordination of nine to ten ether oxygens to the lanthanum ions has been found for the PEGM system by increasing the concentration of lanthanum triflate in the polymers and following the disappearance of the C–O–C stretching vibration of non-coordinated ether oxygens. The same coordination seems to be present also for the PEG and PEO systems. Conformational changes have been observed on addition of salt to the polymer, by following the disappearance of an absorption band at about 990 cm^{-1} , indicative of a *trans* conformation around the $\text{CH}_2\text{--CH}_2$ bond. For all three polymer types the *gauche* conformation is dominant at high salt concentrations. The OH end groups present in the PEG samples are important for the coordination in this system and both the cations and the triflate anions are coordinated by the OH groups to some extent.

(Keywords: coordination; conformation; end group)

INTRODUCTION

A large amount of work has been undertaken during the past decade in an attempt to increase the knowledge of the properties of poly(ethylene oxide) (PEO) and poly(propylene glycol) (PPG) electrolytes¹. The reason for the tremendous interest in these systems is that they are capable of significant ionic conductivities, making possible their application as electrolytes in solid state batteries. In spite of all the efforts made, a complete understanding of the interactions between the ions and the polymer has not yet been achieved. Model systems of low molecular weight polyethers are widely used to facilitate the studies, as these short-chain molecules create fully amorphous samples and thus single-phase systems, making preparations and systematic analyses easier^{2,3}. One fundamental question then arises: is a short-chain polymer a good model system for a long-chain polymer with the same monomer unit? In this study we try to address this question by comparing a long-chain polymer, PEO, with two shorter ones, poly(ethylene glycol)dimethyl ether (PEGM(400)) and poly(ethylene glycol) (PEG(400)). The difference between these two shorter polymers is that the PEG molecules are terminated by hydroxy groups whereas the PEGM

molecules are terminated by methyl groups. Earlier studies of lithium triflate dissolved in PPG have shown that the OH groups play a major role in the coordination⁴ and it is thus interesting to check whether this is also the case for PEO systems.

Several crystalline structures have been determined for PEO systems containing different salts. For all the structures investigated the cations are coordinated both to the anion and to the ether oxygens of the polymer. Chatani *et al.*^{5,6} found that Na^+ was coordinated to four ether oxygens for NaSCN-PEO_3 but only to three for NaI-PEO_3 . Recently, Bruce *et al.* have studied several thiocyanate salts and found that both K^+ and Rb^+ coordinate to five ether oxygens⁷, whereas in the structure of $\text{LiCF}_3\text{SO}_3\text{-PEO}_3$ the lithium ion is coordinated to only three ether oxygens⁸. This indicates that the coordination number is dependent on the radius of the cation used, and it is also expected that an increased charge would affect the coordination. The detailed conformation of the polymer chain for these crystalline complexes is different from the conformation in pure PEO. In crystalline PEO the internal rotations about the $\text{CH}_2\text{--O}$, O--CH_2 and $\text{CH}_2\text{--CH}_2$ bonds are *trans*, *trans* and *gauche*, respectively (denoted as *TTG*), forming a helical structure with 3.5 monomers per turn⁹. For most of the crystalline PEO–salt structures investigated the conformations are also *TTG* but with some of the *gauche* conformations in *gauche*(+) and others in *gauche*(–).

* To whom correspondence should be addressed

This creates a helix with a larger radius than in pure PEO. The question then arises: is this type of conformation also present in our amorphous systems?

In this study we try to answer the questions posed above using the polymers 'long-chain PEO', PEGM and PEG to illustrate the end group and chain length effects. Two different salts, lithium and lanthanum triflate, are used to observe the effects of charge and size of the cation.

EXPERIMENTAL

The triflate salt $\text{La}(\text{CF}_3\text{SO}_3)_3$ was prepared by dissolving La_2O_3 (Sigma, 99.9%) in aqueous HCF_3SO_3 (Aldrich, 98%) until a pH of around 5 was reached. The solution was filtered and then allowed to precipitate at $\sim 100^\circ\text{C}$. The resulting white salt was dried in a vacuum at 140°C . LiCF_3SO_3 (Aldrich, 97%) was dried in vacuum at 230°C .

Polymer electrolytes were made by dissolving stoichiometric amounts of PEO (BDH: $MW = 4 \times 10^6$), PEGM(400) (Polyscience) or PEG (KEBO: $MW = 400$) in anhydrous acetonitrile (Merck, spectroscopic grade) and salt in a mixture of acetonitrile and ethanol (Kemetyl: 99.5%). The two solutions were mixed and stirred overnight. For the PEO samples a thin layer of polymer solution was spread over a KRS5 (TlI+TlBr; Harrick) window, and the solvent was allowed to evaporate; for the PEGM and PEG samples, the solvent was first vacuum-evaporated and then a small amount of the quite viscous solution was spread over a KRS5 window. Both techniques gave films about $0.5 \mu\text{m}$ thick. The variation of the thickness of the films was about $\pm 8\%$, as measured using a microscope attachment focusing on different spots distributed over a 100 mm^2 sample area. The concentration of salt in the polymer will be referred to as n in this paper, where n denotes the ether oxygen to cation ratio.

The PEGM samples containing large amounts of $\text{La}(\text{CF}_3\text{SO}_3)_3$ had to be freshly prepared because a brown sediment appeared if they were stored for more than 1 week at room temperature. The process was greatly accelerated by heat. These sediments also appeared in pure PEGM but only after storage for long periods (~ 1 year).

The polymers readily absorb water from the air and for that reason the samples were prepared and stored in a drybox (r.h. $\sim 3\%$). The Fourier transform infra-red (FTi.r.) measurements were made in a vacuum cell equipped with a heating element. Prior to the measurements, the samples were heated to 45°C and cooled while in place in the spectrometer to ensure that all water and solvent had evaporated. This was checked in the OH and CN stretching regions. The spectra of the samples were compared before and after heating and no deterioration, as discussed above, could be detected for these short heating periods.

Absorbance spectra were recorded on a Digilab/BioRad FTS-45 FTi.r. spectrometer in the range 400 – 4000 cm^{-1} with a spectral resolution of 1 cm^{-1} . The absorbance of the most intense band in the spectra was typically ~ 1.0 .

RESULTS

PEO, PEG and PEGM consist of the monomer unit

$(-\text{CH}_2-\text{CH}_2-\text{O}-)$, differing only in the chain length and end groups. We used PEO containing about 100 000 monomer units and both PEG and PEGM containing an average of nine monomers. For all three polymers there is a distribution of chain lengths. This probably has no effect on the results for the long-chain polymer systems but could be important for the short-chain ones. PEO and PEG are OH end-capped while PEGM is capped with CH_3 groups. At room temperature PEO consists of a mixture of a crystalline and an amorphous solid phase whereas PEGM and PEG are slightly viscous liquids. Dissolution of salt into PEO can create an amorphous solid or a mixture of crystalline and amorphous phases, while dissolution of salt into PEGM or PEG creates a slightly more viscous solution.

For pure polycrystalline PEO, a very strong absorption band is observed at about 1106 cm^{-1} at room temperature, corresponding to non-resolved antisymmetric and symmetric C–O–C stretching vibrations. This band is broadened but remains at the same position in melted amorphous PEO ($\sim 70^\circ\text{C}$), but on dissolution of $\text{La}(\text{CF}_3\text{SO}_3)_3$ the band is shifted to $\sim 1074 \text{ cm}^{-1}$, indicating that the ether oxygens have become coordinated¹⁰. A spectrum of pure PEGM or PEG is very similar to that of melted amorphous PEO, and on coordination of the ether oxygens an analogous shift of the 1106 cm^{-1} band, as in PEO, is observed. The C–O–C stretching region, $\nu(\text{COC})$, ranges from about 1050 to 1140 cm^{-1} , as shown in the overview spectrum in Figure 1.

The triflate ion was chosen as the anion for this study since its internal modes serve as a probe of its local environment, and several local environments have been proposed to occur in these types of polymer electrolytes. The free triflate ion is assumed to have the point group symmetry C_{3v} . The antisymmetric SO_3 stretching mode, $\nu(\text{SO}_3)_a$, belonging to the E irreducible representation is doubly degenerate, while the symmetric SO_3 stretching mode, $\nu(\text{SO}_3)_s$, belonging to A_1 is non-degenerate; both modes are infra-red active. These regions are found at about 1190 – 1340 cm^{-1} and 1000 – 1050 cm^{-1} , respectively, in the spectrum (Figure 1). In a previous model study¹¹ using CH_3CN as solvents, $\nu(\text{SO}_3)_a$ for a non-coordinated ('free') triflate ion was located at 1272 cm^{-1} . On coordination of the triflate ion to a cation, the degenerate $\nu(\text{SO}_3)_a$ band splits into two components, with the frequency difference dependent on the strength of the interaction. In the same study, the $\nu(\text{SO}_3)_s$ band

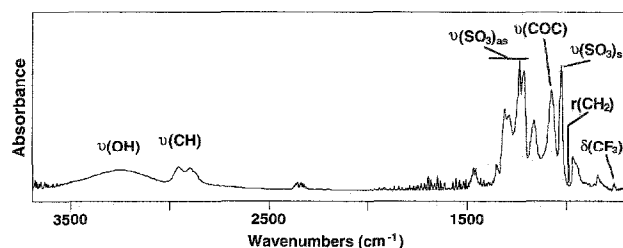


Figure 1 FTi.r. absorption spectrum of $\text{La}(\text{CF}_3\text{SO}_3)_3$ -PEG₁₀: an overview of the regions of interest. The OH stretching region, $\nu(\text{OH})$, at 3000 – 3600 cm^{-1} ; the C–O–C stretching region, $\nu(\text{COC})$, at 1050 – 1140 cm^{-1} ; the antisymmetric SO_3 stretching region, $\nu(\text{SO}_3)_a$, at 1190 – 1340 cm^{-1} ; the symmetric SO_3 stretching region, $\nu(\text{SO}_3)_s$, at 1000 – 1050 cm^{-1} ; the CH_2 rocking region, $r(\text{CH}_2)$ at $\sim 990 \text{ cm}^{-1}$, and the symmetric CF_3 deformation region, $\delta(\text{CF}_3)_s$, at 750 – 770 cm^{-1} .

for the free ion was located at 1033 cm^{-1} ; this band was observed to shift to lower wavenumbers for $\text{Pb}(\text{CF}_3\text{SO}_3)_2$ dissolved in acetonitrile and PEO. Shifts of $\nu(\text{SO}_3)_s$ to higher wavenumbers have been observed for alkali-metal triflates dissolved in poly(propylene oxide) (PPO)^{12,13}, and simultaneous shifts to both higher and lower wavenumbers have been found for $\text{Yb}(\text{CF}_3\text{SO}_3)_3$ dissolved in PEO¹⁰. Gejji *et al.* have proposed that shifts to higher wavenumbers correspond to a monodentate coordination of the triflate ion whereas shifts to lower wavenumbers correspond to a bidentate coordination¹⁴. The $\nu(\text{CF}_3)_s$ and $\nu(\text{CF}_3)_a$ bands were located at 1224 cm^{-1} and 1157 cm^{-1} , respectively, for the free triflate ion¹¹.

Frech and co-workers have recently studied the effect of different solvents and cations on a mixed band, referred to as the $\delta(\text{CF}_3)_s$ band, in the region $750\text{--}770\text{ cm}^{-1}$ (Figure 1)^{15–18}. They found that this band is sensitive to environmental changes around the triflate ion, and therefore serves as a good complement to the SO_3 bands in determining the coordination of the triflate ions. Three bands are present in the $\delta(\text{CF}_3)_s$ region for lithium triflate dissolved in a PPO trimer: one small band at 752 cm^{-1} , assigned as 'free' triflate ions, a large band at 757 cm^{-1} , assigned as ion pairs, and another small band at 762 cm^{-1} , assigned as a higher aggregate ('aggregate 1')¹⁸.

Coordination

For a concentration study of $\text{La}(\text{CF}_3\text{SO}_3)_3$ in PEGM the largest spectral change in the polymer bands occurs in the $\nu(\text{COC})$ region (Figure 2). In this region the spectra of pure PEGM and the more dilute samples are dominated by an absorption band at 1106 cm^{-1} , corresponding to non-coordinated ether oxygens. With increasing concentration, a new band, corresponding to La^{3+} -coordinated ether oxygens, appears at 1078 cm^{-1} and at $n = 10$ this band is totally dominating. At higher

concentrations the 1106 cm^{-1} band has totally disappeared. These observations imply that all the ether oxygens are coordinated for $n = 9\text{--}10$ and higher concentrations.

A comparison of the spectra of $\text{La}(\text{CF}_3\text{SO}_3)_3\text{--PEG}_{10}$, $\text{La}(\text{CF}_3\text{SO}_3)_3\text{--PEGM}_9$ and $\text{La}(\text{CF}_3\text{SO}_3)_3\text{--PEO}_9$ shows that the $\nu(\text{COC})$ region is very similar for all three systems (Figure 3), implying that the observations made above are valid also for the PEO and PEG systems. A concentration study of the $\text{La}(\text{CF}_3\text{SO}_3)_3\text{--PEO}$ system shows that at concentrations lower than $n = 16$ the sample consists of two phases, one amorphous part containing $\text{La}(\text{CF}_3\text{SO}_3)_3$ and PEO, and one crystalline part containing pure crystalline PEO¹⁰. For this reason, only the samples of concentrations $n = 9$ and 16 are totally amorphous and therefore comparable to the other polymer systems. The $\text{La}(\text{CF}_3\text{SO}_3)_3\text{--PEG}$ system is totally amorphous and concentrations ranging from $n = 8$ to $n = 80$ were used.

Lithium triflate dissolved in PEO has previously been studied by Vallée *et al.* and a phase diagram is available¹⁹. It was found that at room temperature and up to $\sim 50^\circ\text{C}$ the samples with $n > 3$ contain both crystalline PEO and a crystalline complex, and no amorphous samples can be obtained for any concentration at room temperature. For PEG, on the other hand, amorphous solutions were obtained down to a concentration of $n = 5$ and for PEGM down to a concentration of $n = 20$. A sample of $n = 10$ has also been prepared for PEGM but some salt precipitated. Since the amount of crystals was small, the effect on the concentration was probably small.

For the concentration study of LiCF_3SO_3 in PEG, the changes in the $\nu(\text{COC})$ region are less than for lanthanum but at the concentration of $n = 5$ a new band can clearly be observed at about 1089 cm^{-1} , corresponding to lithium-coordinated ether oxygens (Figure 4).

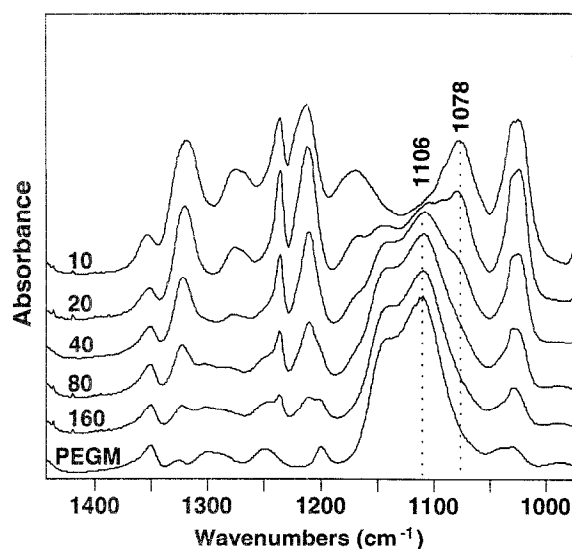


Figure 2 FTIR absorption spectra of pure PEGM and $\text{La}(\text{CF}_3\text{SO}_3)_3\text{--PEGM}_n$ for $n = 10, 20, 40, 80$ and 160 . The 1078 cm^{-1} band increases and the 1106 cm^{-1} band decreases with increasing concentration. In both the $\nu(\text{SO}_3)_a$ and $\nu(\text{SO}_3)_s$ regions, the amount of free triflate ions increases with increasing concentration

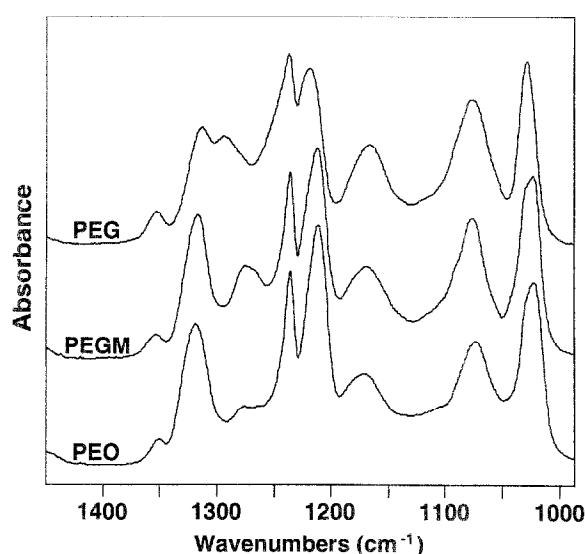


Figure 3 FTIR absorption spectra of $\text{La}(\text{CF}_3\text{SO}_3)_3\text{--PEG}_{10}$, $\text{La}(\text{CF}_3\text{SO}_3)_3\text{--PEGM}_9$ and $\text{La}(\text{CF}_3\text{SO}_3)_3\text{--PEO}_9$. The largest difference between the three polymers is observed in the $\nu(\text{SO}_3)_a$ region where two new bands, at 1293 and 1252 cm^{-1} , are observed for PEG but not for PEO and PEGM

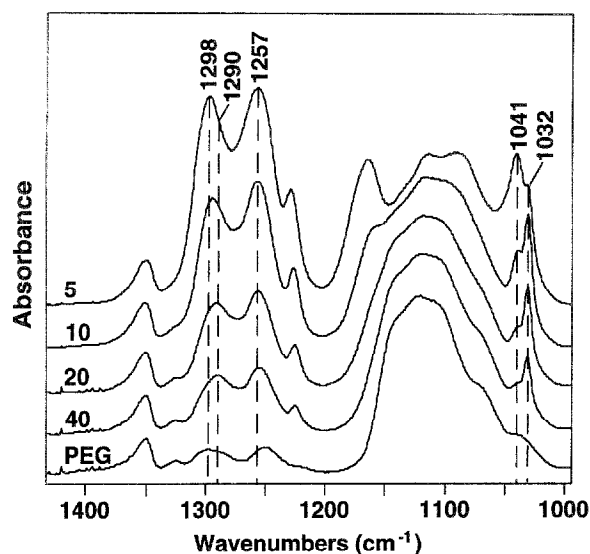


Figure 4 FTIR absorption spectra of pure PEG and $\text{LiCF}_3\text{SO}_3\text{-PEG}_n$ for $n = 5, 10, 20$ and 40 . A new band in the $\nu(\text{COC})$ region at about 1089 cm^{-1} , and a shift of the 1290 cm^{-1} band to 1298 cm^{-1} in the $\nu(\text{SO}_3)_a$ region are observed with increased concentration

Conformation

The conformation of the crystalline PEO chain is *TTG*, as pointed out in the Introduction. On melting of the polymer some of the $\text{CH}_2\text{-CH}_2$ *gauche* conformations change to *trans*. This is indicated by the growth of a CH_2 rocking band, $r(\text{CH}_2)$, at about 990 cm^{-1} , corresponding to *trans* conformations²⁰. For both pure PEGM and PEG, an analogous *trans* band is present at room temperature.

In Figure 5 the 990 cm^{-1} band can be clearly observed in the spectrum of pure PEGM. As $\text{La}(\text{CF}_3\text{SO}_3)_3$ is dissolved in the polymer the band decreases, and at a concentration of $n = 10$ it has almost disappeared. This implies that at a concentration of $n = 10$ almost all the $\text{CH}_2\text{-CH}_2$ dihedral angles have *gauche* conformation. The same result can be observed for the PEO and PEG

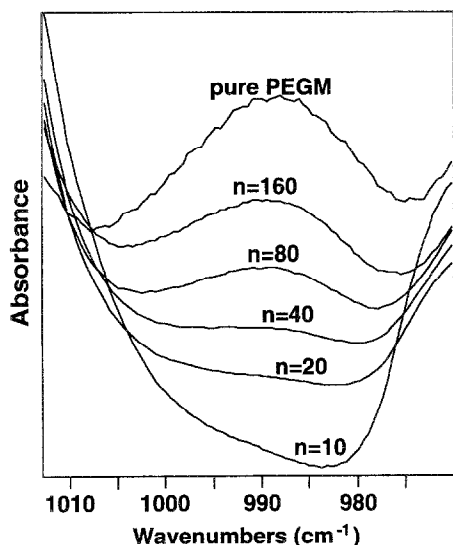


Figure 5 FTIR absorption spectra of the CH_2 rocking band of pure PEGM and $\text{La}(\text{CF}_3\text{SO}_3)_3\text{-PEGM}_n$ for $n = 10, 20, 40, 80$ and 160

samples where the 990 cm^{-1} band has totally disappeared for a concentration of $n = 9$ and 10 , respectively.

The gradual decrease in intensity of the 990 cm^{-1} band is also found for LiCF_3SO_3 dissolved in PEG (Figure 6). The band is present down to a concentration of $n = 10$, but in the $n = 5$ sample it has disappeared. Using PEGM as the polymer, the highest concentration obtained is $n = 10$ and for this concentration the 990 cm^{-1} band can still be observed.

End group effects

OH stretching bands from the end groups are observed at $3000\text{--}3600\text{ cm}^{-1}$ for PEG (Figure 1). No such bands are observed either for PEGM, since no OH groups are present, or for PEO, which is actually terminated with OH groups although their number is extremely small ($2/(4 \times 10^6)$). Earlier studies of the $\text{LiCF}_3\text{SO}_3\text{-PPG}$ system have shown that both cation coordination and hydrogen bonding of the OH groups are important, and that both these types of coordination lead to shifts to lower wavenumbers of the $\nu(\text{OH})$ band⁴. On dissolution of lanthanum or lithium triflate in PEG, a clear shift in the $\nu(\text{OH})$ region can be observed for both ions. For pure PEG an OH stretching band is centred at 3455 cm^{-1} and on coordination to La^{3+} this band is shifted to 3245 cm^{-1} , whereas coordination to Li^+ only gives a shift to 3405 cm^{-1} . The coordination of the OH groups increases with increased salt concentration, but at the highest concentrations studied, non-coordinated OH groups still exist for both salts.

Comparison of the $\nu(\text{SO}_3)_a$ region between the three spectra in Figure 3 reveals a band at about 1293 cm^{-1} present for PEG but absent for the two other systems. A concentration study of $\text{La}(\text{CF}_3\text{SO}_3)_3$ in PEG shows that a second band, at about 1252 cm^{-1} , is also present in the PEG samples but not for the other two polymers (Figure 7). With decreasing concentration the intensities of these two new bands increase compared to the bands at 1314 and 1219 cm^{-1} . This indicates that there are two different splittings of the $\nu(\text{SO}_3)_a$ band, one large splitting of 95 cm^{-1} , also observed in the PEO

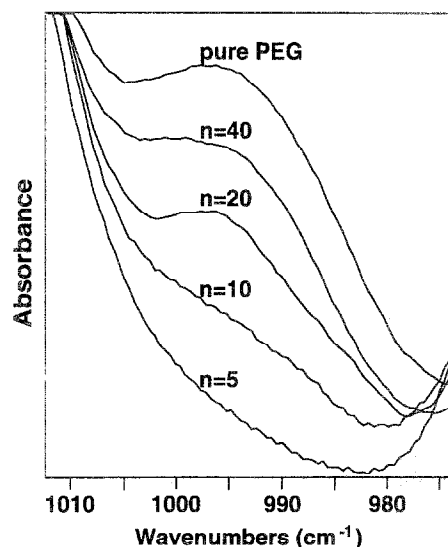


Figure 6 FTIR absorption spectra of the CH_2 rocking band of pure PEG and $\text{LiCF}_3\text{SO}_3\text{-PEG}_n$ for $n = 5, 10, 20$ and 40

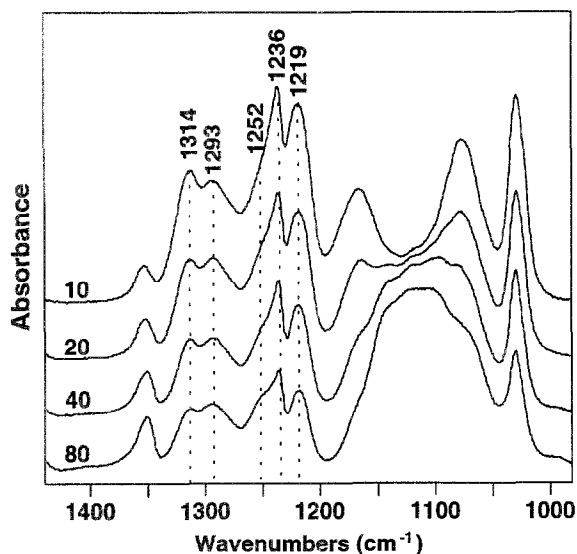


Figure 7 FTi.r. absorption spectra of $\text{La}(\text{CF}_3\text{SO}_3)_3\text{-PEG}_n$ for $n = 10, 20, 40$ and 80 . The intensity of the two bands at 1293 and 1252 cm^{-1} increases compared to the 1314 and 1219 cm^{-1} bands with decreasing concentration

and PEGM samples, and one smaller splitting of 41 cm^{-1} , unique to the PEG samples. The two different splittings imply that at least two different local structures for the triflate ion are present in the PEG samples. In the $\nu(\text{SO}_3)_s$ region, one broad band at about 1030 cm^{-1} is observed for all concentrations in the PEG sample, but for PEGM and PEO another band at about 1023 cm^{-1} is also present.

For lithium triflate dissolved in PEG a shift in the $\nu(\text{SO}_3)_a$ region is also observed on lowering the concentration (Figure 4). For the $n = 5$ sample the split $\nu(\text{SO}_3)_a$ bands are found at 1298 and 1257 cm^{-1} . On dilution to $n = 40$ the 1298 cm^{-1} band shifts to 1290 cm^{-1} . This means that the frequency differences of the $\nu(\text{SO}_3)_a$ bands are 41 cm^{-1} for $\text{LiCF}_3\text{SO}_3\text{-PEG}_5$ and 33 cm^{-1} for $\text{LiCF}_3\text{SO}_3\text{-PEG}_{40}$. Also, the $\nu(\text{SO}_3)_s$ region is changing as the concentration is lowered for the $\text{LiCF}_3\text{SO}_3\text{-PEG}$ system (Figure 4). The absorption band at 1041 cm^{-1} is largest at the highest concentration and the band at 1032 cm^{-1} is largest at the lowest concentration. This type of behaviour is exactly analogous to that of the system $\text{LiCF}_3\text{SO}_3\text{-PPG}$, where the 1032 cm^{-1} band and the smaller set of split components was assigned to 'solvent-separated ion pairs' and the 1041 cm^{-1} band and the larger split components to 'contact ion pairs'⁴.

The $\delta(\text{CF}_3)_s$ region

Figure 8 illustrates the concentration dependence of the $\delta(\text{CF}_3)_s$ region for lanthanum triflate dissolved in PEGM. The large absorption band at 762 cm^{-1} is dominating the spectra for all concentrations, while the other band at 754 cm^{-1} is largest for the $n = 10$ sample and then decreases with both increased and decreased concentration. We assign the 762 cm^{-1} band to ion pairs and the 754 cm^{-1} band to free ions, following the discussion in refs 16–19. This would mean that the amount of free triflate ions is largest for a concentration of $n = 10$ and then decreases for both higher and lower

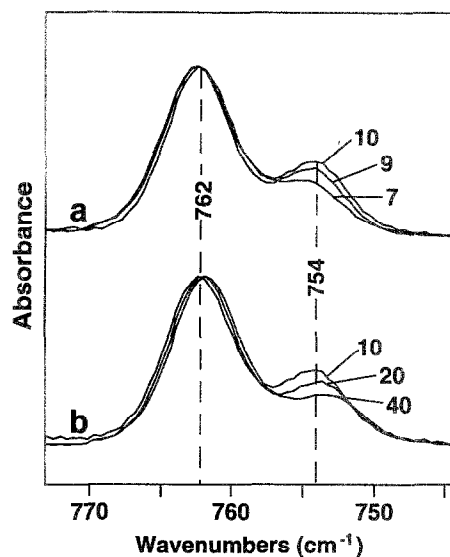


Figure 8 FTi.r. absorption spectra of (a) $\text{La}(\text{CF}_3\text{SO}_3)_3\text{-PEGM}_n$ for $n = 8, 9$ and 10 , and (b) $\text{La}(\text{CF}_3\text{SO}_3)_3\text{-PEGM}_n$ for $n = 10, 20$ and 40 . The absorption band at 754 cm^{-1} decreases with both increased and decreased concentration compared to $n = 10$

concentrations. The temperature dependence for the system $\text{La}(\text{CF}_3\text{SO}_3)_3\text{-PEGM}_{10}$, illustrated in Figure 9, shows that the amount of free triflate ions decreases with increasing temperature. This is also the case for the more dilute samples $n = 20$ and 40 . For the $\text{La}(\text{CF}_3\text{SO}_3)_3\text{-PEO}$ system, the 754 cm^{-1} band becomes larger, and consequently the amount of free triflate ions increases, when going from concentration $n = 9$ to 16 . This is the behaviour normally observed for these types of polymer electrolytes. For the PEG system the absorption bands in the $\delta(\text{CF}_3)_s$ region are very broad and, for that reason, of limited use in determining the coordination relations.

DISCUSSION

The information obtained from the different spectral regions will now be brought together into a unified picture of the local coordinations and conformations in the different systems.

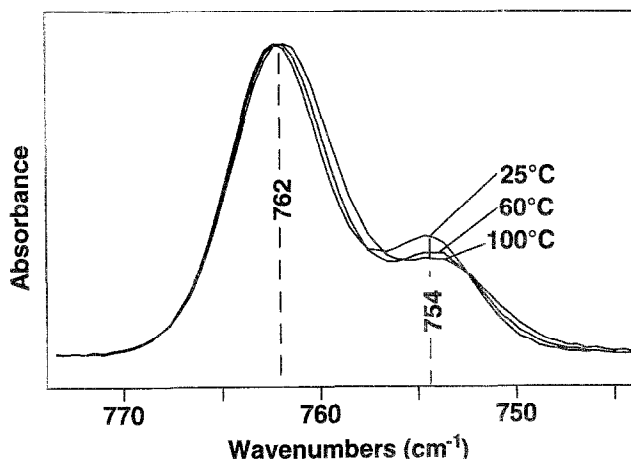


Figure 9 FTi.r. absorption spectra of $\text{La}(\text{CF}_3\text{SO}_3)_3\text{-PEGM}_{10}$ for temperatures of $25, 60$ and 100°C . The absorption band at 754 cm^{-1} decreases with increasing temperature

The PEGM system

From the $\nu(\text{COC})$ region we learned that at $n = 9$ –10 and higher concentrations, all ether oxygens were coordinated for the $\text{La}(\text{CF}_3\text{SO}_3)_3$ –PEGM system. We can therefore conclude that each lanthanum ion has to coordinate nine to ten ether oxygens. This is also the number of ether oxygens present in one PEGM molecule, indicating the possibility that one PEGM molecule is coordinated to each lanthanum ion. If the concentration is further increased, beyond $n = 9$, the lanthanum ions would have to share polymer chains in order to be fully coordinated. The coordination of the triflate ion, on the other hand, is more complicated. From the behaviour of the $\delta(\text{CF}_3)_s$ region we saw that the amount of free triflate ions was largest for the concentration $n = 10$ and decreased for both higher and lower concentrations (Figure 8). The same behaviour can be observed for the $\nu(\text{SO}_3)_a$ and $(\text{SO}_3)_s$ regions where the 1272 and 1032 cm^{-1} bands, corresponding to free triflate ions, are largest for $n = 10$ and decrease on dilution, though the effects for these two regions are less obvious (Figure 2). We do not have a good explanation for this behaviour, but we believe that it is due to the combination of the PEGM molecules and a trivalent ion that is able to coordinate all the ether oxygens of the molecule. The results could be due to the distribution of chain lengths and might have been different if we had chosen a longer or a shorter polymer molecule. It is important to point out that although there are small changes in the amount of free triflate ions, most of the triflate ions are coordinated for all concentrations. This can be seen from the dominating 762 cm^{-1} band in the $\delta(\text{CF}_3)_s$ region (Figure 8) or the split $\nu(\text{SO}_3)_a$ bands (Figure 2). The temperature dependence for the system follows what has previously been observed for most triflate systems: a decreasing amount of free triflate ions on increasing temperature (Figure 9).

From the results presented above we can draw the conclusion that for the system $\text{La}(\text{CF}_3\text{SO}_3)_3$ –PEGM, each lanthanum ion has to have a coordination number of about 12, from nine to ten ether oxygens and two or three triflate ions. This is a large number, but not unreasonably high, since a coordination number of 12 has previously been reported for lanthanum ions encapsulated in a cryptand²¹.

In the Conformation section above, we noted that for $\text{La}(\text{CF}_3\text{SO}_3)_3$ –PEGM₁₀ almost all CH_2 – CH_2 dihedral angles had a *gauche* conformation. This is also the case for the crystalline PEO structure and for most of the known crystal structures of PEO–salt complexes, where there is a mixture of *gauche*(+) and *gauche*(–) conformations^{5–8}. Structures of complexes between salt and short-chain polyethers, comparable to PEGM, where one polyether molecule is wrapped around the cation, are also known^{22,23}. Inspired by these structures we have constructed a model complex between La^{3+} and one PEGM molecule (containing nine ether oxygens) where all CH_2 – CH_2 conformations are *gauche*(+ / –), most of the C–O conformations are *trans* and all ether oxygens are coordinated to the La^{3+} ion (Figure 10). In this model the PEGM molecule turns around the La^{3+} ion forming a helix, in which all the ether oxygens are pointing inwards. This also creates quite large spaces in which the triflate ions can be coordinated. The model was obtained

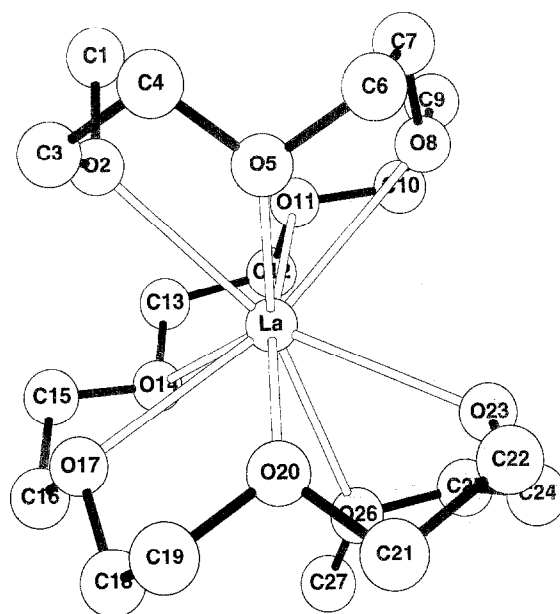


Figure 10 A possible model for coordination in the $\text{La}(\text{CF}_3\text{SO}_3)_3$ –PEGM system. Nine ether oxygens from one PEGM molecule are coordinated by one lanthanum ion

using the program PC-model²⁴; we forced the La–O distance to be ~ 2.7 Å and then let the program do an energy minimization. We used several different starting configurations for the PEGM molecule (*TTT*, *TTG*, *TTG*(–), *TTG*(+) etc.), but all the final structures were very similar. Only conformations involving one polymer chain were tried, since we believe that such a model is most likely considering the results in refs 22 and 23. But the possibility that several chains are involved in the coordination of one lanthanum ion cannot be excluded.

For lithium triflate dissolved in PEGM we cannot draw any conclusions as to the coordination number since no concentrations higher than $n = 10$ have been prepared; however, the crystal structure of LiCF_3SO_3 – PEO_3 probably gives a good indication of both the coordination and the conformation in this system. From the $\nu(\text{CH}_2)$ vibration at 990 cm^{-1} , it was observed that the amount of *trans* conformations decreases with increasing concentration of LiCF_3SO_3 , but they are still present for the highest concentration ($n = 10$). This is not surprising since the lithium ion is only thought to coordinate between three and six ether oxygens and consequently, even in a concentrated sample such as $n = 10$, about half of the ether oxygens are still uncoordinated.

The coordination of the triflate ions in several LiCF_3SO_3 –glyme systems has been investigated by Pedersen *et al.*²⁵ and Huang and Frech¹⁷ as a function of temperature and polymer chain length. In these systems, free triflate ions, ion pairs and ‘aggregates’ have been found. In our system LiCF_3SO_3 –PEGM_{*n*}, ion pairs are the dominant species for all concentrations, but lowering the concentration increases the amount of free triflate ions and increasing the concentration increases the amount of aggregates. The LiCF_3SO_3 –PEGM system does not show the strange concentration dependence found for the $\text{La}(\text{CF}_3\text{SO}_3)_3$ –PEGM system. This strengthens our suggestion that the unusual behaviour in

the latter system is due to the combination of PEGM(400) and a large trivalent ion.

The PEG system

The average PEG molecule contains eight ether oxygens and two OH oxygens. This is not very different from PEGM and therefore we believe that the general picture of the coordination and conformation is similar for the two systems. From the $\nu(\text{COC})$ region it was observed that for $n = 10$ the La-coordinated ether oxygens were totally dominant (Figure 6), but since no detailed studies around the concentration $n = 10$ have been performed for PEG, we cannot determine the exact coordination number. For the $\nu(\text{SO}_3)_a$ bands, two different splittings, one of 95 cm^{-1} and one of 40 cm^{-1} , were observed (Figure 6). Following the discussion in ref. 4 we conclude that the two different splittings come from contact ion pairs and solvent-separated ion pairs, respectively. A solvent-separated ion pair is an ion pair separated by an OH group; the lanthanum ion is coordinated to the oxygen of the OH group while the triflate ion is hydrogen-bonded to the OH group. The relative amount of solvent-separated ion pairs increases with decreasing concentration because the more dilute the sample is, the more OH groups are present per salt molecule. No help in determining the coordination of the triflate ions can be obtained from the $\nu(\text{SO}_3)_s$ and $\delta(\text{CF}_3)_s$ regions since only one broad band is observed in both these regions. However, since no $\nu(\text{SO}_3)_a$ band at 1272 cm^{-1} , indicative of free triflate ions, has been observed, we conclude that all triflate ions are coordinated, either in contact ion pairs or in solvent-separated ion pairs.

In the $\nu(\text{CH}_2)$ region, the *trans* band at 990 cm^{-1} decreases with increased concentration of $\text{La}(\text{CF}_3\text{SO}_3)_3$, and at a concentration of $n = 10$ the band has disappeared. This strengthens our statement that the bonding situation is very similar to that in PEGM. Since not all OH groups were coordinated at a concentration of $n = 8$, there is probably not space enough for both of the OH groups to be coordinated to the La^{3+} ion. We suggest that the eight ether oxygens and one of the OH groups from the PEG molecule are coordinated to the La^{3+} ion, forming a structure very similar to that presented in Figure 10.

For LiCF_3SO_3 dissolved in PEG, no further conclusions can be drawn than were already presented for the PEGM system, except that since not all ether oxygens were coordinated at a concentration of $n = 5$, the Li^+ ion is coordinating less than five ether oxygens in this system. A coordination of five to six ether oxygens by one lithium ion has previously been proposed by Huang *et al.*²⁶ for crystalline samples of LiCF_3SO_3 -diglyme at concentrations $n \geq 6$ and at low temperatures (below -80°C), but in these cases no triflate ions are coordinated to the lithium ion. In the crystalline structure of LiCF_3SO_3 -PEO₃, each lithium ion is coordinating three ether oxygens and two triflate ions⁸.

The PEO system

Since pure PEO is mainly crystalline at room temperature and crystalline PEO is found in most samples when salt is added, a detailed concentration study is not possible. The results obtained for the $\text{La}(\text{CF}_3\text{SO}_3)_3$ -PEO system (concentrations $n = 9$ and

16) indicate that the coordination and the conformation are very similar to those of the PEGM system. However, there is a very large difference in chain length between the two polymers. For PEGM, one molecule can be turned around the La^{3+} ion without the other molecules being affected, but for PEO each chain is very long, and when one part of the chain (containing nine to ten ether oxygens) is wrapped around the La^{3+} ion, neighbouring parts of the large molecule would be affected. This is a much more severe constraint than for PEGM, but since all ether oxygens are coordinated for $n = 9$ and no CH_2 - CH_2 *trans* conformations are observed, it is possible that a structure similar to that for PEGM (Figure 10) is obtained, but repeated along the whole PEO chain.

SUMMARY

In this work, PEO, PEG and PEGM have been compared and were found to be very similar in their coordination and conformation on dissolution of $\text{La}(\text{CF}_3\text{SO}_3)_3$ and LiCF_3SO_3 . Therefore we regard both PEGM and PEG as good model systems for long-chain PEO. One should, however, be aware of the differences.

On dissolution of $\text{La}(\text{CF}_3\text{SO}_3)_3$ into the polymer, a coordination of nine to ten ether oxygens for each La^{3+} ion is obtained for all three systems, with most of the triflate ions coordinated. Using PEG, the OH end groups coordinate both the cation and the anion of the salt, giving a slightly different behaviour as compared to PEO, but the coordination of the ether oxygens and the conformation of the polymer chain seems to be unaffected. One large difference, however, is that the solubility of a salt is larger for PEG than for both PEO and PEGM due to the presence of the OH groups.

A structure has been proposed for the PEGM-La^{3+} complex, where the polymer molecule is wrapped around the lanthanum ion forcing all ether oxygens to point inwards and coordinate to the lanthanum ion. For this structure the conformations around the CH_2 - CH_2 bonds are both *gauche*(+) and *gauche*(-) as in several of the crystal structures of PEO-salt complexes.

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