Coordination of OH end-groups in the polymer electrolyte system LiX–PPG for X = PF_6^-, BF_4^-, ClO_4^-, $CF_3SO_3^-$, I^-, Br^- and Cl^-

Annika Bernson and Jan Lindgren*
Institute of Chemistry, Uppsala University, Box 531, S-751 21 Uppsala, Sweden
(Received 10 March 1944; revised 3 May 1994)

End-group coordination has been studied using poly(propylene glycol) with a molecular weight of 3000 (PPG(3000)) terminated with hydroxy groups. On dissolution of different lithium salts LiX in PPG(3000) for X = PF_6^-, BF_4^-, ClO_4^-, $CF_3SO_3^-$, I^-, Br^- and Cl^-, shifts of the OH stretching band were observed using Fourier transform infra-red spectroscopy. The size of the shift is dependent on the strength of the hydrogen bond formed between the OH group and the anion of the salt. A cation dependence of the OH stretching band was also found using KPF_6. There are two dominating coordination structures involving the OH groups present in the samples. One is a solvent-separated ion pair where the anion and cation are separated by an OH end-group, and the other is an OH group coordinated both to the cation of the salt and to an ether oxygen from the polymer.

(Keywords: poly(propylene glycol); infra-red spectroscopy; hydroxy end-groups)

INTRODUCTION

Significant ionic conductivity has been observed for polymer electrolytes based on poly(ethylene oxide) (PEO) or poly(propylene glycol) (PPG) complexed with inorganic salts[1]. This renders them suitable for a number of applications, e.g. as electrolytes in all-solid-state batteries. One important prerequisite for a fundamental understanding of the polymer electrolytes is a knowledge of the coordination relationships between the polymer and the salt and between the anions and cations of the salt. Good tools for obtaining this knowledge are infra-red and Raman spectroscopy; small changes in the local environments of the ions and the atoms of the polymer chain can be detected by these techniques.

Lately, low molecular weight polymers have been used as model systems for high molecular weight polymers. One advantage of the low molecular weight systems is that they are fully amorphous single-phase liquids, and therefore easier to handle during preparation and characterization[2,3]. For the long polymer chains of high molecular weight systems the coordination by the end-groups can be neglected as their number is very small compared to the number of ether oxygens in the chain. On the other hand, for short chains the number of end-groups becomes relatively large and their effect on the coordination has to be considered. Polymers that have been 'end capped' with non-coordinating CH_3 groups are commercially available for PEO systems, but so far PPG systems are primarily available with terminal hydroxy groups.

Hydrogen bonding and coordination of the OH group have been systematically investigated in, for example, water and alcohol solutions both experimentally and theoretically[4–6]. The conclusions from these studies are that (1) cation and anion coordination of the OH group lead to a downwards shift in frequency of the OH stretching band compared to the ideal gas-phase frequency ($\sim 3682\,cm^{-1}$ for methanol) and (2) simultaneous coordination of both the hydrogen and the oxygen of an OH group leads to a cooperative shift larger than the sum of the two individual shifts.

Cation dependent shifts of the OH stretching band have been observed using Raman spectroscopy on PPG(425) with dissolved MSCN (M = Li, Na and K)[7]. Also, anion coordination of the OH group for salts dissolved in PPG(4000) has been proposed by Schantz *et al.*[8].

This study concerns the OH groups in PPG(3000) and how they are affected by dissolving lithium salts LiX (X = PF_6^-, BF_4^-, ClO_4^-, $CF_3SO_3^-$, I^-, Br^- and Cl^-) in the polymer. Also, the coordination properties of the pure polymer were investigated for varying chain lengths.

EXPERIMENTAL

LiCl (Mallinckrodt; analytical reagent), $LiPF_6$ (Aldrich; 98%), $LiBF_4$ (Fluka AG; >98%), $LiCF_3SO_3$ (Aldrich; 97%), $LiClO_4$ (GFS; analytical grade), LiI (Merck; analytical grade) and LiBr (Merck; extra pure) were dried in a vacuum oven. Polymer electrolytes were then made by dissolving stoichiometric amounts of poly(propylene glycol) (PPG) (Aldrich; molecular weight of 3000) and the salt in anhydrous acetonitrile (Merck; spectroscopic grade) or anhydrous ethanol (Kemetyl; 99.5%). The solvent was first allowed to evaporate in a desiccator connected to a water suction pump. A small amount of

---

* To whom correspondence should be addressed

0032-3861/94/22/4848–04

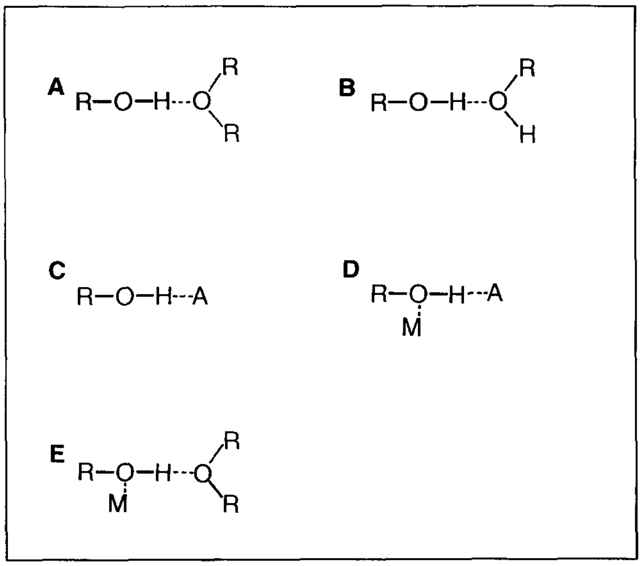

Figure 1 Different local structural arrangements discussed in the text (M = metal ion (cation), A = anion)

the viscous solution was then spread over a KRS5 (TlI + TlBr) (Harrick) or CaF_2 window. Salt and salt–cryptand complexes crystallized during this procedure in the polymer electrolytes $LiClPPG_{10}$ and $LiClPPG_{10}$-cryptand[211], respectively. Very thin polymer films were therefore cast directly from the acetonitrile solutions on a BaF_2 window to create supersaturated polymer films for these two blends. However, small amounts of crystals still existed in the samples, causing a lower and undetermined concentration. These samples were therefore used only in a qualitative way to localize the band positions in the OH stretching region. Since the polymer is not involved in the crystal formation, the spectra in the OH region were not affected by the presence of crystals. The preparation technique used for the two samples mentioned above gave very thin films ($\sim 0.05\,\mu m$), and therefore lower signal to noise ratios were obtained in the infra-red measurements for these two samples as compared to the other samples ($\sim 0.5\,\mu m$ thick). The concentration was 10 ether oxygens per metal ion for all samples in this investigation, except for the two samples discussed above.

The samples were prepared and stored in a drybox (relative humidity $\sim 3\%$) and the infra-red 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 when in place in the spectrometer to ensure that all water and solvent had evaporated. This was checked in the OH and CN stretching regions.

Absorbance spectra were recorded on a Digilab/BioRad FTS-45 Fourier transform infra-red (*FT*i.r.) spectrometer in the range 400–$4000\,cm^{-1}$ with a resolution of $8\,cm^{-1}$ (or $1\,cm^{-1}$ for a few of the samples). The absorbance of the OH stretching band was typically ~ 0.4.

RESULTS AND DISCUSSION

A downwards shift of $\sim 64\,cm^{-1}$ for the OH stretching band relative to the ideal gas-phase value is obtained on dissolution of the very weak hydrogen bond acceptor PF_6^- in methanol[9]. Dissolution of Cl^-, a very strong hydrogen bond acceptor, gives a shift of $\sim 411\,cm^{-1}$ for the same band. Shifts to lower wavenumbers of the OH stretching band have also been found on coordination by cations and organic molecules. In the present cases we can, therefore, expect OH stretching bands over a wide range of frequencies. In the following text we will discuss different local coordination geometries labelled **A**, **B**, **C**, **D** and **E** that refer to the schematic bonding situations shown in *Figure 1*.

The pure polymer

A study of the dependence on chain length of the OH stretching band was performed to determine the coordination properties of the pure polymer. Poly(propylene glycol) with molecular weights of 4000, 3000, 2000, 1000, 725 and 425 was studied and some of the results are presented in *Figure 2*. The OH stretching region $\nu(OH)$ (at about 3100–$3650\,cm^{-1}$) has almost the same appearance for PPG(3000) and PPG(4000), with a large absorption band at $3485\,cm^{-1}$. In the spectra for the shorter polymers, this band is broadened and shifted to lower wavenumbers. It is likely that the $3485\,cm^{-1}$ band corresponds to hydroxy groups coordinated by ether oxygens (**A**; *Figure 1*); for the shorter polymers with a larger fraction of OH groups, a new band at lower wavenumber appears, corresponding to OH groups hydrogen bonded to other OH groups (**B**; *Figure 1*). Since for PPG(4000) and PPG(3000) the bands have practically the same appearance, the OH groups in both these samples coordinate essentially only to ether oxygens. The small band at $\sim 3200\,cm^{-1}$ appearing in the spectrum of PPG(4000) has been assigned as an overtone band[10], and the shoulder at $\sim 3590\,cm^{-1}$ was found in the present study to be independent of temperature and therefore assigned as a combination band.

Coordination of ions

Structure C coordination. Studies of pure anion–polymer interactions are enabled by the use of a cryptand with a 'cage' of suitable size to encapsulate a cation. Cryptand[211] has an optimal size for the encapsulation of Li^+ ions and we dissolved this cryptand together with LiCl in PPG(3000) to study the $OH \cdots Cl^-$ interaction. A comparatively sharp absorption band assigned to this coordination (**C**) was found in the spectrum at $3258\,cm^{-1}$

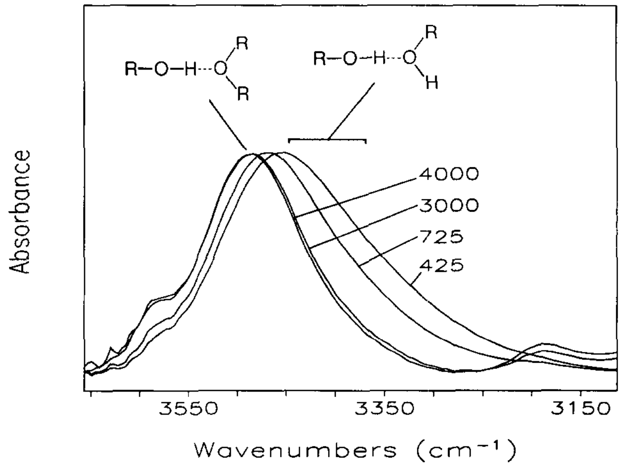

Figure 2 *FT*i.r. absorption spectra for pure PPG polymers with molecular weights of 4000, 3000, 725 and 425. The spectra are scaled to the maximum absorption in the region shown

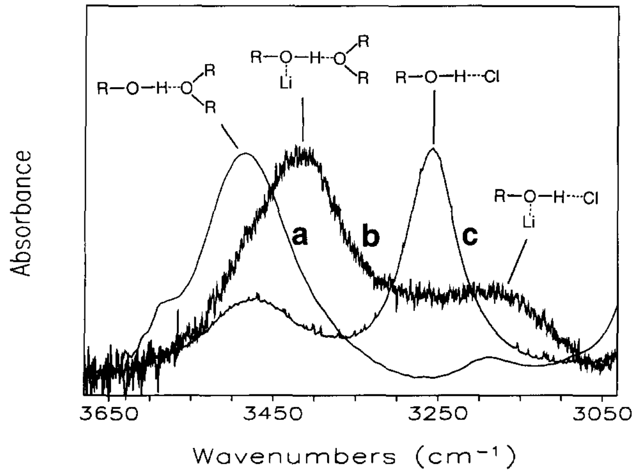

Figure 3 *FT*i.r. absorption spectra for (a) pure PPG(3000), (b) LiClPPG(3000)$_{10}$ and (c) LiClPPG(3000)$_{10}$cryptand[211]. The spectra are scaled to the maximum absorption in the region shown

(*Figure 3c*). An absorption band at ~3485 cm^{-1}, also found in this spectrum, was assigned to **A**.

The difference in frequency between the OH bands for coordination geometry **C** for Cl$^-$ ions in PPG and methanol[9] is 13 cm^{-1}. On dissolution of tetrabutylammonium triflate in PPG, **C** is also present to a large extent, since the tetrabutylammonium ion is a large, bulky and relatively non-coordinating ion[11]. The difference between the **C** bands for triflate ions dissolved in PPG and in methanol[9] is also ~13 cm^{-1}. This suggests that a shift of 13 cm^{-1} to lower wavenumber is a good approximation for the position of the **C** band in PPG for most ions as compared with the results using methanol as solvent.

*Structures **D** and **E** coordinations.* Two OH stretching bands were found on dissolution of LiPF$_6$ and KPF$_6$ in PPG(3000), one shifted to higher wavenumber and another shifted to lower wavenumber as compared to the pure polymer band at 3485 cm^{-1} (*Figure 4*). The **C** band for PF$_6^-$ dissolved in methanol[9] is positioned at 3618 cm^{-1}, and therefore according to the discussion above the **C** band should be found at ~3605 cm^{-1} in PPG. In the spectra of KPF$_6$ and LiPF$_6$ dissolved in PPG(3000) the bands shifted to higher wavenumber are not positioned near 3605 cm^{-1}, but rather at ~3580 and ~3560 cm^{-1}, respectively. This observation, and the fact that the bands are cation dependent, suggests that these bands should be assigned as originating from metal ion coordinated OH groups. This prerequisite is fulfilled by both **D** and **E**. As pointed out earlier, coordination of a cation to an OH group leads to a downwards shift in frequency of the OH stretching band. This implies that the **E** band must be downwards shifted as compared to the **A** band. Therefore the bands at ~3580 and ~3560 cm^{-1} in the spectra of KPF$_6$ and LiPF$_6$ in PPG(3000) are assigned as **D** bands.

The other bands, shifted to lower wavenumbers as compared to the pure polymer case, are also cation dependent and are therefore assigned as corresponding to both metal ion and ether oxygen coordinated OH groups (**E**). This assignment is in agreement with earlier results[4–6] showing that cation coordination of the OH group induces a downwards shift of the OH stretching band.

The absorption band assigned to **E** is also found for LiCl dissolved in PPG (*Figure 3*), adding further support to the assignment since the position of the band is anion independent. In the spectrum of LiCl dissolved in PPG another band at ~3170 cm^{-1} is also found. Following our previous discussion, a logical assignment of this band is to a **D** band with both lithium and chloride ion coordinated OH groups, since the **D** band has to be positioned at a lower wavenumber than the corresponding **C** band.

The positions of the **D** bands for LiCl and LiPF$_6$ dissolved in PPG are separated by about 390 cm^{-1}. This large difference comes from the different abilities of the chloride ion and the hexafluorophosphate ion to act as hydrogen bond acceptors, and is in full agreement with the predictions made from the methanol results[9]. These two ions are the extreme cases in the present investigation and the **D** bands for the other anions will fall between them.

*Coinciding **D** and **E** bands.* For an anion with about the same acceptor strength as the ether oxygens in PPG, **D** and **E** should give OH stretching bands at the same wavenumber and only one band would be observed in the spectrum. This seems to be the case for the triflate ion. In the spectra of LiCF$_3$SO$_3$–PPG and KCF$_3$SO$_3$–PPG only one broad band is observed in each case (*Figure 5*). It is not possible from these bands alone to make any conclusions on the relative contributions from **D** and **E**. It has, however, been found that there is a preferred coordination by the Li$^+$ ion to the OH groups in these systems, and for LiCF$_3$SO$_3$PPG(3000)$_{10}$ all end-groups are found to be both cation and anion coordinated[11]. The bands at 3455 and 3485 cm^{-1} for KCF$_3$SO$_3$–PPG and LiCF$_3$SO$_3$–PPG, respectively, are thus related to **D**. For the samples containing hexafluorophosphate salts, bands are found at about the same positions as in the triflate cases (*Figure 5*), but these bands are related to **E** as discussed above.

General overview

A series of measurements was performed on the salts LiPF$_6$, LiBF$_4$, LiClO$_4$, LiCF$_3$SO$_3$, LiI and LiBr dissolved in PPG(3000) to give LiX PPG(3000)$_{10}$ (*Figure 6*). In these measurements we found successive downwards

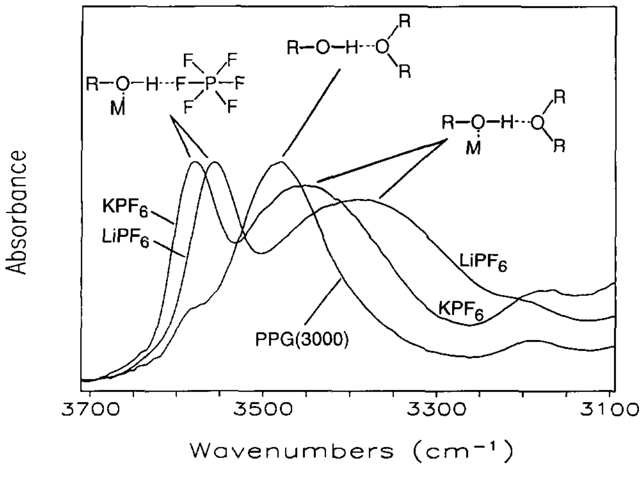

Figure 4 *FT*i.r. absorption spectra for pure PPG(3000), KPF$_6$PPG(3000)$_{10}$ and LiPF$_6$PPG(3000)$_{10}$. The spectra are scaled to the maximum absorption in the region shown

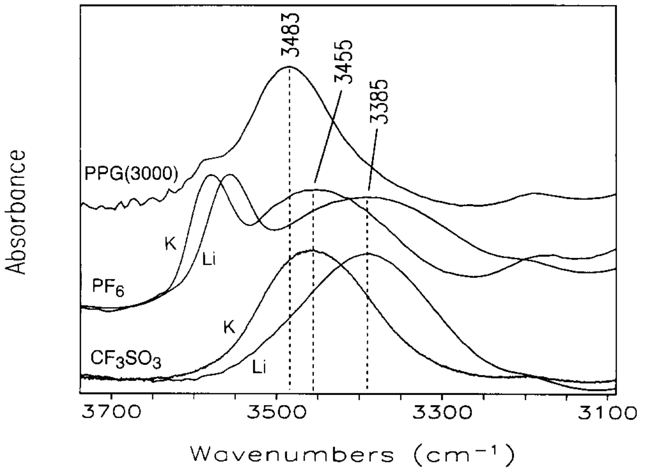

Figure 5 *FT*i.r. absorption spectra for pure PPG(3000), $LiPF_6PPG(3000)_{10}$, $KPF_6PPG(3000)_{10}$, $LiCF_3SO_3PPG(3000)_{10}$ and KCF_3SO_3-$PPG(3000)_{10}$

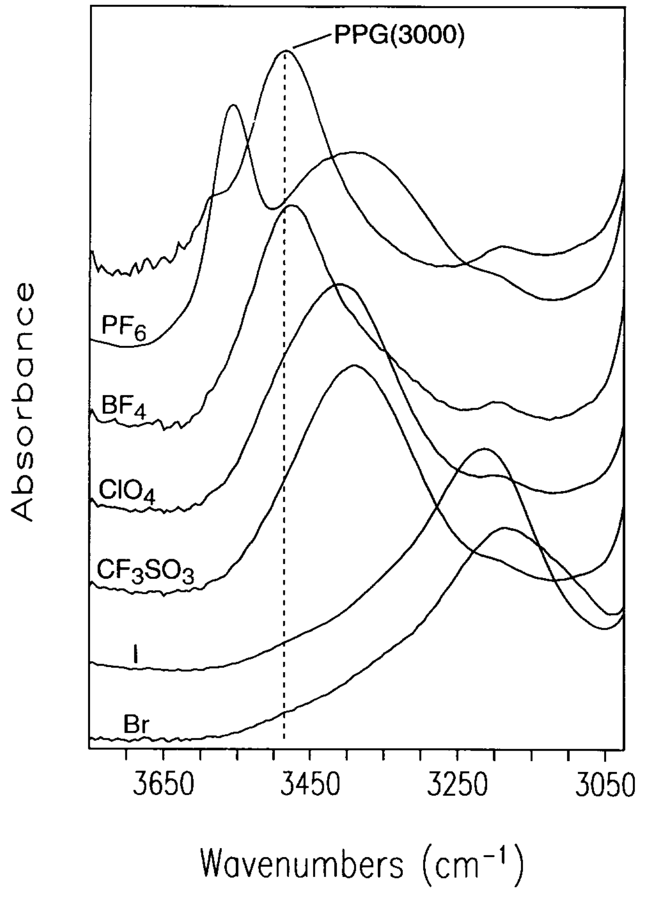

Figure 6 *FT*i.r. absorption spectra for pure PPG(3000) and $LiXPPG(3000)_{10}$, where $X = PF_6^-$, BF_4^-, ClO_4^-, $CF_3SO_3^-$, I^- and Br^-

shifts of the **D** OH stretching band. These shifts are, as discussed above, a measure of the relative hydrogen bond acceptor strengths of the anions. The ordering so obtained through the OH band shifts for these anions is exactly the same as was found in aqueous solutions[4]. In the cases where the acceptor strength is smaller for the anions than for the ether oxygens, two bands corresponding to **D** and **E** are obtained in the spectrum with the **D** band positioned at higher wavenumber. This is particularly obvious for $LiPF_6$, and can also be seen for $LiBF_4$ where a shoulder at $3385\,cm^{-1}$ corresponding to **E** occurs. On the other hand, for the cases where the acceptor strength is larger for the anions than for the ether oxygens, only one band corresponding to **D** is detected, as for LiI and LiBr. It has to be remembered, however, that the above observations are only valid for $LiXPPG(3000)_{10}$. The case of LiCl discussed earlier (*Figure 3*) is different since this sample has a lower and undetermined salt concentration owing to salt precipitation. In general, we expect an equilibrium situation between **D** and **E** to occur.

SUMMARY

Coordination of the OH end-groups of PPG on dissolution of a salt has been found to occur to a large extent, both by hydrogen bonding of anions and coordination of cations. The strength of the hydrogen bond formed between the anion and the hydrogen of the OH group determines which coordination structures are dominant in the sample. Solvent-shared ion pairs where the ions are separated by an OH group were present for all salts investigated and the position of the absorption band from this structure (**D**) is largely dependent on the hydrogen bond acceptor strength of the anion. For PF_6^-, a very weakly coordinating anion, this band is positioned at $3560\,cm^{-1}$, whereas for Cl^-, a strongly coordinating ion, the band is positioned at $\sim 3170\,cm^{-1}$ for lithium salts dissolved in PPG(3000).

ACKNOWLEDGEMENTS

This work was supported by grants from the Swedish Natural Science Research Council (NFR) and the Swedish Research Council for Engineering Science (TFR), which are gratefully acknowledged. We would also like to thank Dr Jörgen Tegenfeldt for fruitful discussions.

REFERENCES

1 MacCallum, J. R. and Vincent, C. A. (Eds) 'Polymer Electrolyte Reviews', Vols I and II, Elsevier, London, 1987 and 1989
2 Torell, L. M., Jacobsson, P. and Petersen, G. *Polym. Adv. Technol.* 1993, **4**, 152
3 Mendolia, M. S. and Farrington, G. C. *Electrochim. Acta* 1992, **37**, 1695
4 Bergström, P.-Å., Kristiansson, O. and Lindgren, J. *J. Phys. Chem.* 1991, **95**, 8575
5 Hermansson, K. and Olovsson, I. *Theor. Chim. Acta (Berlin)* 1984, **64**, 265
6 Kleeberg, H., Heinje, G. and Luck, W. A. P. *J. Phys. Chem.* 1986, **90**, 4427
7 Manning, J., Frech, R. and Huang, W. *Polymer* 1990, **31**, 2245
8 Schantz, S., Torell, L. M. and Stevens, J. R. *J. Chem. Phys.* 1991, **94**, 6862
9 Kristiansson, O. personal communication, 1994
10 Frech, R., Manning, J. and Black, B. *Polymer* 1989, **60**, 1785
11 Bernson, A. and Lindgren, J. *Polymer* 1994, **35**, 4842