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Introduction

Polymer electrolytes are ionically conducting solid phases formed by the dissolution of salts in ion-coordinating macromolecules. Such materials are considered as replacements for conventional low molecular weight liquid based electrolytes for practical electrochemical devices such as power sources, variable transmission windows and displays. A handicap of these materials is that the room temperature conductivity is still too low for the applications envisioned. Therefore an understanding of the mechanism for ionic transport in polymer electrolytes would help to increase the conductivity.

Recently, the addition of a second, low molecular weight solvent (plasticizer) has been used to improve the conductivity in many systems. The mechanism by which this component enhances the conductivity is still not clear. Certainly its effect in most cases is not limited to the traditional decrease in \( T_g \), the temperature below which the polymer changes from the rubbery to the glassy state.

NMR represents a powerful tool for studying this transport mechanism since the relaxation rates of the ionic nuclei are closely related to molecular motion. Furthermore the fact that both ionic conducting species (Li\(^{+}\) and CF\(_3\)SO\(_3^-\) in our case) contain nuclei with a magnetic moment permit the separate study of the ion-mobilities.

Experimental

1. Sample Preparation

The polymer investigated was a random copolymer of ethylene oxide and propylene oxide (3:1 mol ratio) of molecular weight 5000g/mol (referred to as 3PEG5000) and bearing three terminal OH groups per molecule.

Samples were prepared by adding the LiCF\(_3\)SO\(_3\) (1 molal) and the desired concentration of plasticizer (dimethylformamide, DMF, and propylene carbonate, PC) to the dried, liquid polymer. To the resultant polymer solution was added a stoichiometric amount of hexamethylene disiocyanate and a small amount of Thorcat 535 catalyst for the crosslinking.

Samples were cast into 10 mm glass tubes and were subsequently removed after crosslinking was complete.

2. NMR-Measurements

\( ^7\text{Li} \) relaxation measurements were performed at 29.876 MHz on an upgraded Bruker CXP equipped with a superconducting magnet operating at 1.75T.

\( ^19\text{F} \) relaxation measurements were carried out on a laboratory-built NMR spectrometer operating at 13.65 MHz equipped with a 0.34T permanent magnet.

Standard pulse sequences were used for relaxation measurements with \( T_1 \) determined by inversion recovery. Data were collected over the temperature range 140 to 345K.

Results and Discussion

In figure 1 the relaxation time \( T_1 \) for the different plasticizer concentrations has been plotted against the reduced temperature.

![Figure 1. \(^{19}\text{F} \) spin lattice relaxation time for different plasticizer concentrations as a function of the reduced temperature.](image-url)
We can see, that for both plasticizers (DMF and PC), the increase in anion mobility by adding plasticizer corresponds rigorously to the decrease in $T_g$.

For a temperature below $T_g$ all the samples show a decrease in $T_g$ hinting at a second minimum. This effect can be explained as another relaxation mechanism taking over after the polymer chain motion freezes below $T_g$. A comparison of these results to a study of the pure salt carried out by Williams [1] indicates, that the first minimum is due to a homonuclear, intramolecular F-F dipolar interaction, whereas the second minimum corresponds to a lower Larmor frequency and must therefore be due to a heteronuclear interaction. This latter minimum is due to the F-H dipolar interaction modulated by the CF$_3$ rotation around the C-S bond. However for higher temperatures, where the first minimum occurs, $T_2$ and PFG measurements have shown [2, 3], that the triflate ion or aggregate is undergoing substantial translational motion, which is responsible for the relaxation of the $^{19}$F nuclei.

In the case of the $^{7}$Li relaxation time $T_1$, a plot against reduced temperature allows us to see, that the effect of either plasticizers, PC and DMF, on the cation mobility is not just related to the decrease in $T_g$ (see figure 2).

The DMF plasticizer causes the $T_1$ minimum to shift to lower temperatures, which means that the increase in mobility upon plasticizer addition is bigger for the cation than for the polymer. This is due to the fact, that the DMF solvates the Li ion and enables it to move faster. This also gives rise to an increase in the distance between the interacting nuclei, which leads to less effective relaxation. Therefore $T_1$ at the minimum becomes longer for the most plasticized sample.

Although PC like DMF causes a decrease in $T_2$, its effect on the microscopic cation mobility measured by NMR is opposite. PC, as a solvent of high dielectric constant, screens the Coulomb cation-anion interactions reducing in this way the number of ion pairs. Therefore the liberated cations are then more able to coordinate to the polymer oxygen atoms. This will explain the shorter relaxation time at the minimum upon PC addition. A greater cation-polymer interaction will restrict also the motions of both the polymer in the vicinity of the co-ordination site and the cation. That this restriction of mobility of the Li ions and also the polymer segments does not play a large role in the overall effect of plasticizer on $T_g$ is a reflection of the fact that the $T_g$ of the plasticized system is a result of the combined motional properties of all the components.

Conclusion

The incorporation of dimethylformamide (DMF) and propylene carbonate (PC) plasticizers results in a shift of the $T_1$ minima for both nuclei to lower temperatures indicating an increasing mobility consistent with a decreasing $T_g$ and higher conductivity. Both plasticizers enhance the anion mobility indirectly by increasing the segmental motion, whereas the effect on the cation varies with plasticizer and it is not merely determined by the change in $T_g$.

References