Polymer Bulletin 17, 113–117 (1987)

Polymer Bulletin

Ionic conductivities and glass transition temperatures in poly(vinyl methyl ether)-salt mixtures

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SUMMARY

The solubility of a number of salts in poly(vinyl methyl ether) (PVME) was tested, and several gave homogeneous solutions over a range of concentrations. When dissolution of the salts occurred, the glass transition temperature of the mixture tended to rise, reflecting the solvation of the cations by the ether oxygens which also leads to crosslinking. Ionic conductivities (σ/Scm^{-1}) were measured for some of the mixtures but the level at room temperature was low. A rise in σ with increase in temperature was observed reaching 10^{-4} Scm^{-1} at 430K for PVME/$LiClO_4$ mixtures at a $[Li^+]/[O]$ ratio of 0.25.

INTRODUCTION

Since it was observed that poly ether/salt complexes had a potential use as solid electrolytes in batteries (ARMAND 1979 and 1983), interest has centred predominantly on systems involving poly(ethylene oxide). Conductivity levels in other polymer/salt complexes, such as poly(ethylene succinate) (DUPON et alia 1984; and WATANABE et alia 1984), poly(ethylene adipate) (ARMSTRONG and CLARKE, 1984), poly(ethylene imine) (CHIANG et alia 1986) and poly(alkylene sulphide)s (CLANCY et alia 1986) have also been measured but none are significantly better than poly(ethylene oxide). It has also been noted (ARMAND, 1983) that dissolution of salts in other poly ethers is less effective than in poly(ethylene oxide) and it was decided to examine the behaviour of poly(vinyl methyl ether) (PVME) in this respect. The solubilities of several alkali metal salts in PVME have been examined together with the consequential changes in the glass transition temperature (T_g) and the a.c. conductivity of the mixtures.

EXPERIMENTAL

Sample preparation. Poly(vinyl methyl ether) was purchased from Polysciences and fractionated. The sample used had $M_n = 27000$ and was dried under vacuum at 340-350K to remove all traces of water. Polymer/salt solutions were first prepared in dry methanol which was subsequently removed and the mixture was again heated to 350K under vacuum to remove water. The samples were transferred to a dry box containing the conductivity cell.

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A.c. conductivity. Measurements were made using a 1.59 kHz a.c. conductivity meter. The polymer/salt mixtures were sandwiched between two silver electrodes and contained within a Teflon ring to restrict sample flow during the heating cycle. The sample was allowed to equilibrate for 1 hour at each temperature before measuring the conductivity. This was repeated at intervals over the temperature range 290K to 430K.

Glass Transition Temperatures. The T_g of each polymer/salt mixture was measured by differential scanning calorimetry using a Perkin-Elmer DSC2 interfaced with an Apple II microcomputer. The T_g was taken as the mid point temperature of the base line shift recorded during the transition.

RESULTS AND DISCUSSION

A number of alkali metal salts have been found to be soluble in polyethers such as poly(ethylene oxide) and poly(propylene oxide), and it is accepted that the predominant interaction is between the cation and the ether oxygen. Studies on these and related structures (SHRIVER et alia, 1981) have led to the suggestions that the formation of such complexes is enhanced if the polymer has a high concentration of polar groups, has a low T_g and is sufficiently flexible to facilitate polymer/cation coordination. PVME satisfies most of these criteria; its repeat unit $-CH_2-CH(OCH_3)-$ contains an ether oxygen and it has a subambient T_g = 255K. The ability of the polymer to dissolve salts and form homogeneous, amorphous solutions is somewhat disappointing, however, as can be seen from Table 1.

TABLE 1

Solubility of alkali metal salts in PVME.

ANIONS	CATIONS		
	Li^+	Na^+	K^+
ClO_4^-	s	s	-
$CF_3SO_3^-$	s	n.s.	n.s.
I^-	s	n.s.	n.s.
Cl^-	n.s.	n.s.	n.s.
BF_4^-	s	-	-

s - soluble; n.s. - non soluble

With the exception of $NaClO_4$ (and this is a very borderline case) the PVME appears capable of solvating only the Li^+ cation. The ability of PVME to dissolve salts is also reflected in the change in T_g of the polymer/salt mixtures with increase in the amount of salt dissolved. Complexing of the cation by the polymer probably involves intermolecular interactions which form crosslinks in the system. These restrict molecular motion and raise the T_g of the mixture. This is shown in Figure 1 where the PVME/$LiClO_4$ system exhibits the largest increase,

ΔT_g = 60K at a ratio of $[Li^+]/[O]$ ∿0.3. The ΔT_g values for other polymer/salt solutions are smaller and for the PVME/NaClO$_4$ system ΔT_g is only 6K. This suggests that very little cation complexation occurs and that the salt exists predominantly in the form of ion pairs.

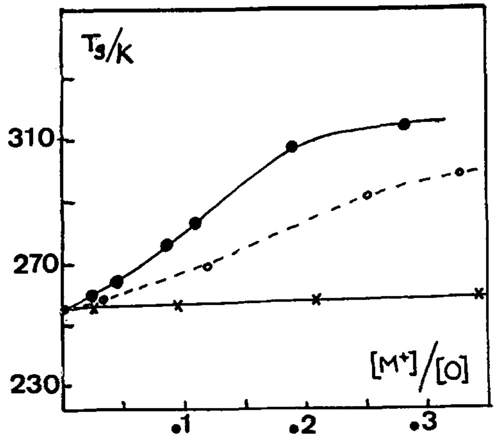

FIGURE 1 Variation of the glass transition temperatures of PVME when mixed with LiClO$_4$ (●), LiSO$_3$CF$_3$ (○) and NaClO$_4$ (x).

These trends are also indicative of the levels of conductivity observed in the mixtures.

At room temperature the conductivity (σ) is always less than 10^{-6}Scm^{-1} and only when temperatures exceed 360K does it rise above this level reaching 10^{-4}Scm^{-1} at 430K in the PVME/LiClO$_4$ mixture with a salt/polymer concentration of $[Li^+]/[O]$ = 0.25. In Figure 2 log σ is plotted against 1/T for $[M^+]/[O]$ ratios of 0.05 and in general

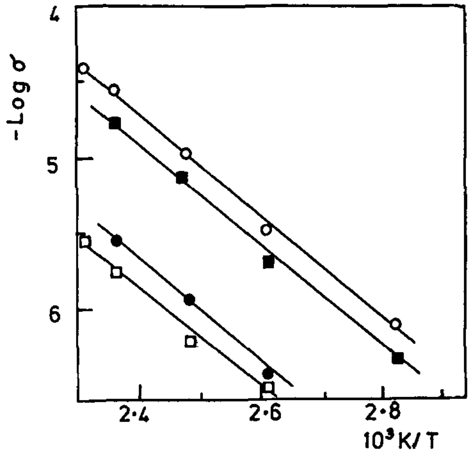

FIGURE 2. Arrhenius plots of log conductivity against reciprocal temperature for PVME mixed with LiClO$_4$ (○), LiI (■), LiBF$_4$ (●) and LiSO$_3$CF$_3$ (□).

higher conductivity levels are obtained for systems in which the elevation of the T_g is greatest. The plots are linear and appear to obey the Arrhenius relation, which is not a common feature of many other polymer/salt systems where distinctly curved plots have been obtained. The data all seem to have approximately the same slope and an average value of $\sim$64kJ mol^{-1} can be calculated for the activation energy.

In comparison with many other polymer/salt complexes which have been reported, the PVME systems are relatively poor both in the levels of conductivity achieved and in the ability to dissolve salts. These two features are of course related and the solubility characteristics are dependent on the structure of the polymer.

It has been demonstrated (SHRIVER et alia 1981) from spectroscopic considerations that the complexing of alkali metal salts with poly(ethylene oxide) results in the formation of a helical structure for the polymer which presents a cavity lined with ether oxygens to accommodate the cation. A molecular model of this type of structure is shown in Figure 3(a). If a section of PVME is modelled, it is soon obvious that only short sequences of ether oxygens can be formed, as shown in Figure 3(b), and then only with some difficulty. Further extension of the model to longer chain lengths shows that the oxygen sequence can be developed at most to five and that it is not possible to form a helical structure with an oxygen lined tunnel as in the case of poly(ethylene oxide). Complexing of the cations will then be less efficient because PVME cannot present the optimum environment to the ion.

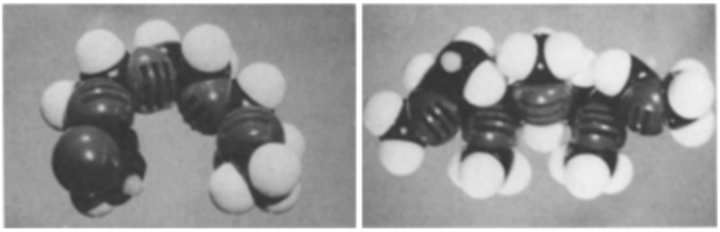
(a) (b)

FIGURE 3. Space filling models of short sections of (a) poly(ethylene oxide) and (b) poly(vinyl methyl ether).

The structure of poly(ethylene oxide)/$HgCl_2$ complex has been studied (IWAMOTO et alia 1968) and an extended zig-zag conformation of the polymer chain is proposed. The implication is that divalent or transition metal ions complex with an open chain structure to give intermolecular binding of the ions. Thus it might be more likely to occur in PVME and preliminary results indicate that $Ca(ClO_4)_2$ is easily dissolved in PVME and that ΔT_g is comparable to the PVME/$LiClO_4$ mixture. This point will have to be investigated more fully, but it is clear from the present data that it is unlikely that conductivity levels in PVME/salt mixtures will ever be as large as those in poly(ethylene oxide) or poly(propylene oxide) systems.

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Accepted December 8, 1986 C