A novel solid polymer electrolyte: Synthesis and characterization

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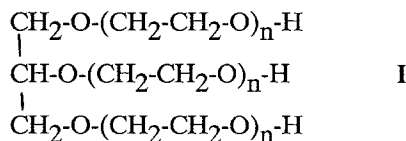
SUMMARY

A new polyether network was prepared using a polyethylene oxide (PEO) triol and a PEO diisocyanate, the latter component arising from the chemical modification of commercial PEO diamines. The physico-chemical properties of the network alone and with $LiClO_4$ were assessed in comparison with those of previously obtained structures. Ionic conductivities were found to be higher with this new system. Replacement of $LiClO_4$ by $LiN(CF_3SO_2)_2$ improved the conductivity further because of the plasticizing role of the imidic anion.

INTRODUCTION

Both laboratories involved in the present study have been engaged in investigations dealing with the use of polyether-based solid electrolytes (1,2). Different structures have been looked at in order to attain the most satisfactory performances, including networks. Thus, urethane or siloxane crosslinks were introduced among polyethylene oxide (PEO) chains to minimize crystallization and suppress creep. With the latter moieties some uncertainties remained as to the regularity of the structure and moreover no ionic solvation was provided by the Si-O bonds. With the urethane crosslinks, some stiffening of the networks was always observed as well as the onset of a barrier to ionic mobility (3). It seemed therefore interesting to try a new approach to PEO-based networks calling upon the reaction of a PEO triol with a linear PEO oligomer bearing terminal isocyanate groups. It was thought that such combination should yield structures with very low Tg and no local moieties capable of hindering ionic transport, thus giving the most favorable conditions for high conductivity.

EXPERIMENTAL

The PEO triol was kindly provided by DAI-ICHI KOGYO SEIYAKU COMPANY. It was dried under vacuum and characterized by elemental analysis, IR and NMR spectroscopy, vapour-pressure osmometry and GPC analysis. The structure of this oligomer corresponds to **I**:

$$CH_2\text{-}O\text{-}(CH_2\text{-}CH_2\text{-}O)_n\text{-}H$$
$$|$$
$$CH\text{-}O\text{-}(CH_2\text{-}CH_2\text{-}O)_n\text{-}H \qquad \textbf{I}$$
$$|$$
$$CH_2\text{-}O\text{-}(CH_2\text{-}CH_2\text{-}O)_n\text{-}H$$

with M_n = 2500 (VPO) and I_p = 1.2.

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The PEO diisocyanate **II** was prepared from the corresponding diamine (Jeffamine ED 600) kindly provided by TEXACO CHEMICAL COMPANY. This commercial compound was characterized as indicated above for **I**: M_n = 600 (VPO), I_p = 2.8 and average amine functionality 2.0. Its reaction with phosgene generated from bis(trichloromethyl)carbonate in the presence of triethylamine (4) in refluxing CH_2Cl_2 proceeded smoothly to give a diisocyanate, M_n = 900 and average functionality 2.0 (as determined by reaction with diisopropylamine). The fact that M_n was higher than expected is due to some condensation of an NCO terminal group with an unreacted NH_2 to give a diisocyanate with double molecular weight and bearing a central urea group.

$$OCNCH(CH_3)\text{-}CH_2(O\text{-}CH(CH_3)\text{-}CH_2)_a(O\text{-}CH_2\text{-}CH_2)_b(O\text{-}CH_2\text{-}CH(CH_3))_cNCO$$
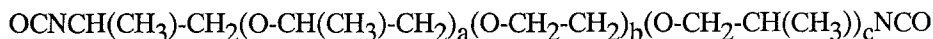
II

with a+c=2.5 and b=8.5.

Networks were prepared in a glove box by mixing **I** and **II** in stoichiometric amounts in methylene chloride (synthesis concentration 0.5 v/v) in the presence of traces of dibutyltin dilaurate. The well-stirred mixture was poured into a mould constituted by two polypropylene plates separated by a silicone-rubber joint at a distance of about 1 mm. The membranes was left at room temperature for several days to insure complete gelification (the reactivity of the aliphatic diisocyanate is considerably lower than that of aromatic homologues). They were then retrieved and placed under vacuum at about 70°C for several hours to remove the solvent. Thereafter they were stored in vacuo at 60°C. '

The inclusion of salts into the membranes was carried out by dipping them into an acetonitrile saturated solution of the desired salt and determining the extent of its diffusion by weighing the dried membrane.

Glass transition temperatures were determined by DSC. Dynamic mechanical properties were studied by viscoelasticity measurements. Electrical conductivities were obtained through the complex impedance method.

RESULTS AND DISCUSSION

Glass Transition Temperature

The Tg of the network without any added salt was -56°C. This value is lower than all values obtained for the POE-based networks bearing urethane crosslinks (5,6). Thus the use of PEO diisocyanates, which places the urethane moiety along the PEO chain and not at the branching point, results in a higher free volume due to less hindered segmental motions. The value is however slightly higher than that of siloxane-based PEO networks indicating that the rotational barriers have not been minimized entirely (3).

The introduction of $LiClO_4$ in the network gives a progressive increase in Tg as shown in Fig.1. This phenomenon had already been observed previously with polyether-based networks (2,5,6) and has been interpreted by the formation of ionic crosslinks induced by the dissolved salt interacting with the ether bridges of the chains. The Tg^{-1} vs salt concentration plot (Fig.1) gave moreover a straight line with a slope of 0.28 K^{-1} mol^{-1} dm^3 which is the same as that obtained previously for all PEO-based networks, independent of the crosslink agent. This agreement clearly confirms that the

reversible ionic crosslinking induced by the dissolved salt relates to the ether segments only. In conclusion, a gain in free volume was achieved with the new network, but its behaviour towards $LiClO_4$ was not altered by the change in structure (position of the urethane linkage).

Dynamic Mechanical Properties

Fig.2 shows the variations of the storage modulus E' as a function of temperature at 7.8 Hz for the saltless network and for a network containing a fairly high concentration of $LiClO_4$. Both systems gave the characteristic behaviour of polymeric elastomer, viz. the glassy state followed by the transition towards the rubbery state and finally the plateau proper to the latter condition with a drop in E' of about three orders of magnitude. Interestingly, the modulus at high temperature (rubber) is the same for both systems above about 40°C. This suggests that at around that temperature the ionic interactions with the ether groups which give physical crosslinks (see above) become negligible, i.e. the nature of the ionic aggregation changes as indeed already suggested (3) going from essentially quadrupoles to mostly dipoles (probably polymer-separated ion pairs).

A master curve was obtained by the usual superposition procedure, as shown in Fig.3. The values of the WLF constants (7) calculated from this, taking Tg as reference temperature, were $C_1 = 9$ and $C_2 = 90$ K.

The dynamic mechanical response of these new systems is entirely typical of amorphous elastomeric networks in that it follows a classical free volume behaviour.

Ionic Conductivity

Fig.4 shows the dependence of electrical conductivity upon temperature in a typical Arrhenius plot for networks containing $LiClO_4$. As for most of our previous work, the non linearity of these plots indicates that free-volume considerations apply here rather than classical activation parameters. Thus, as already pointed out in detail for other networks (2), the ionic movements inside these elastomeric materials are governed by the segmental motions of the polyether chains. It was to be expected that this basic feature would not be altered qualitatively by a structural change such as that implemented in this work, viz. the displacement of the urethane linkages from the branching sites to the middle of the PEO chains. Treatment of the conductivity data according to the WLF equation yielded the characteristic constants $C_1 = 10$ and $C_2 = 50$ K, in good agreement with the corresponding values obtained from the dynamic mechanical study detailed above.

Fig.5 shows the dependence of the ionic conductivity upon the $LiClO_4$ concentration for the present materials plotted at two constant free-volume fractions (T-Tg). A comparison with similar plots applied to the corresponding PEO-based networks bearing urethane crosslinks (3) reveals that the slope of the linear portion is close to unity in both instances. This implies that the relative abundance of the various ionic species resulting from the dissociation of $LiClO_4$ is also about the same in these systems, namely a predominance of dipoles (ion pairs) above about 40°C, as indeed suggested by the values of the storage moduli. When this comparison is applied to the actual magnitude of the conductivity, one notices that the present networks provide a more suitable environment for ionic transport since the conductivities are systematically higher for a given salt concentration at the same value of T-Tg. The gain is not trivial since between the most loose networks previously studied (3) and the present ones the conductivity increases by a factor of about four.
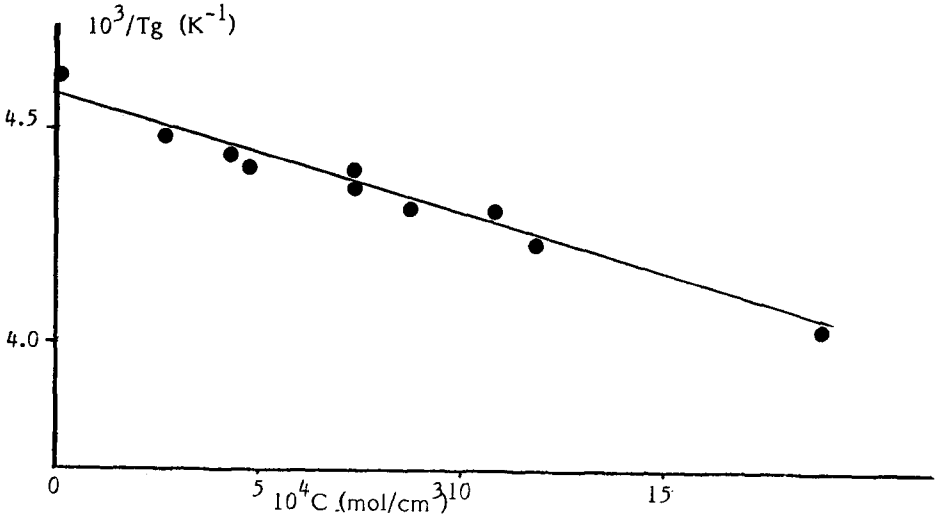
Fig.1. Dependence of Tg^{-1} on $LiClO_4$ concentration for the network (I + II).
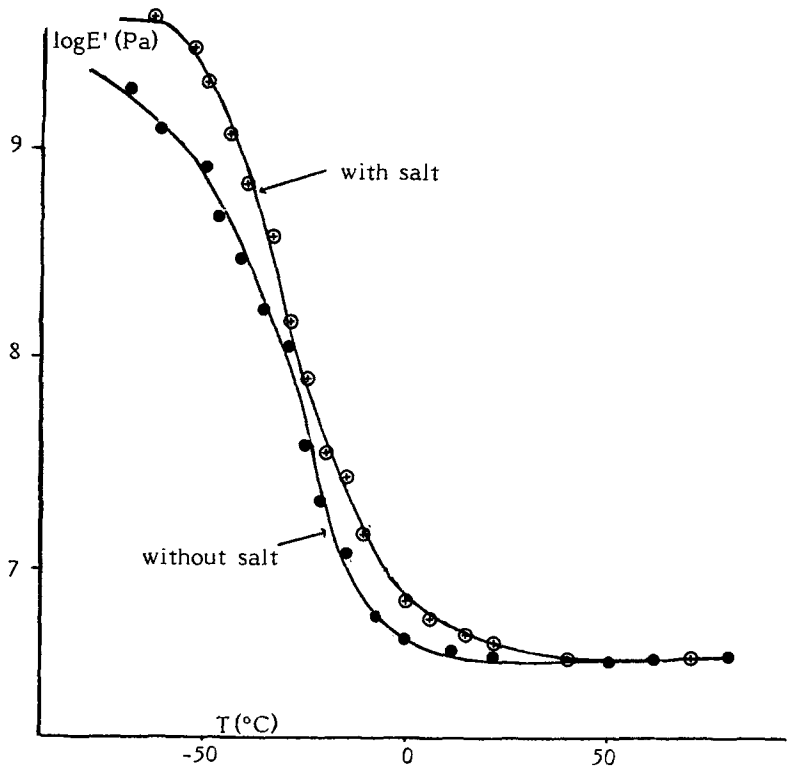

Fig.2. Variation of the storage modulus as a function of temperature at 7.8 Hz for network (I + II) as such and with $LiClO_4$ (2.2 mol dm^{-3}).
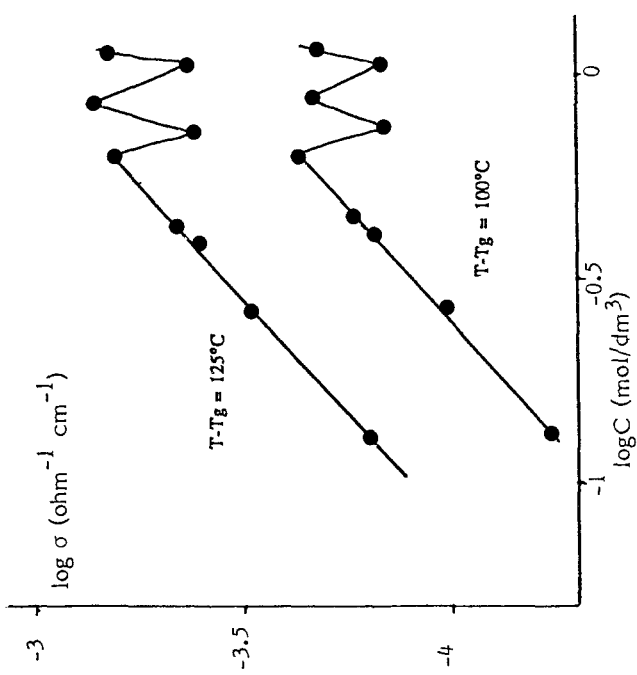
Fig.5. Effect of LiClO$_4$ concentration on ionic conductivity at two constant reduced temperatures with network (I + II).
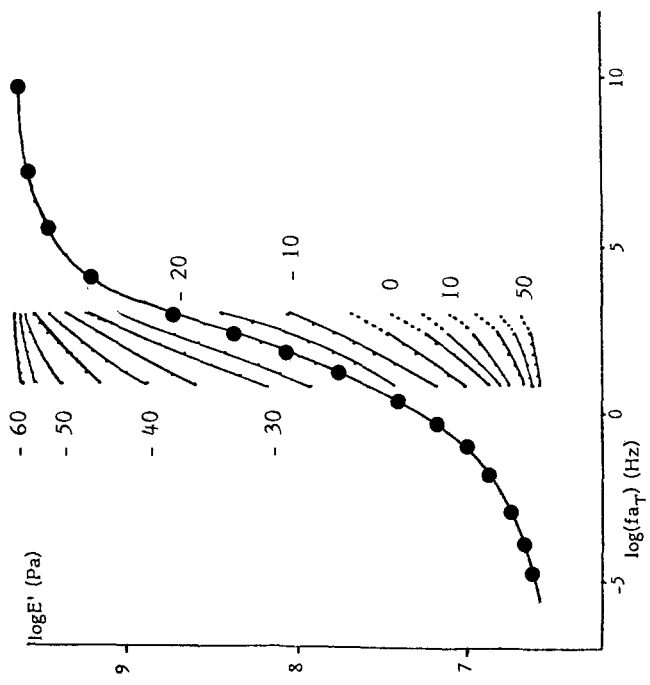
Fig.3. Master curve constructed from data referring to network (I + II) containing 2.2 mol dm^{-3} of LiClO$_4$ (reference temperature - 20°C).
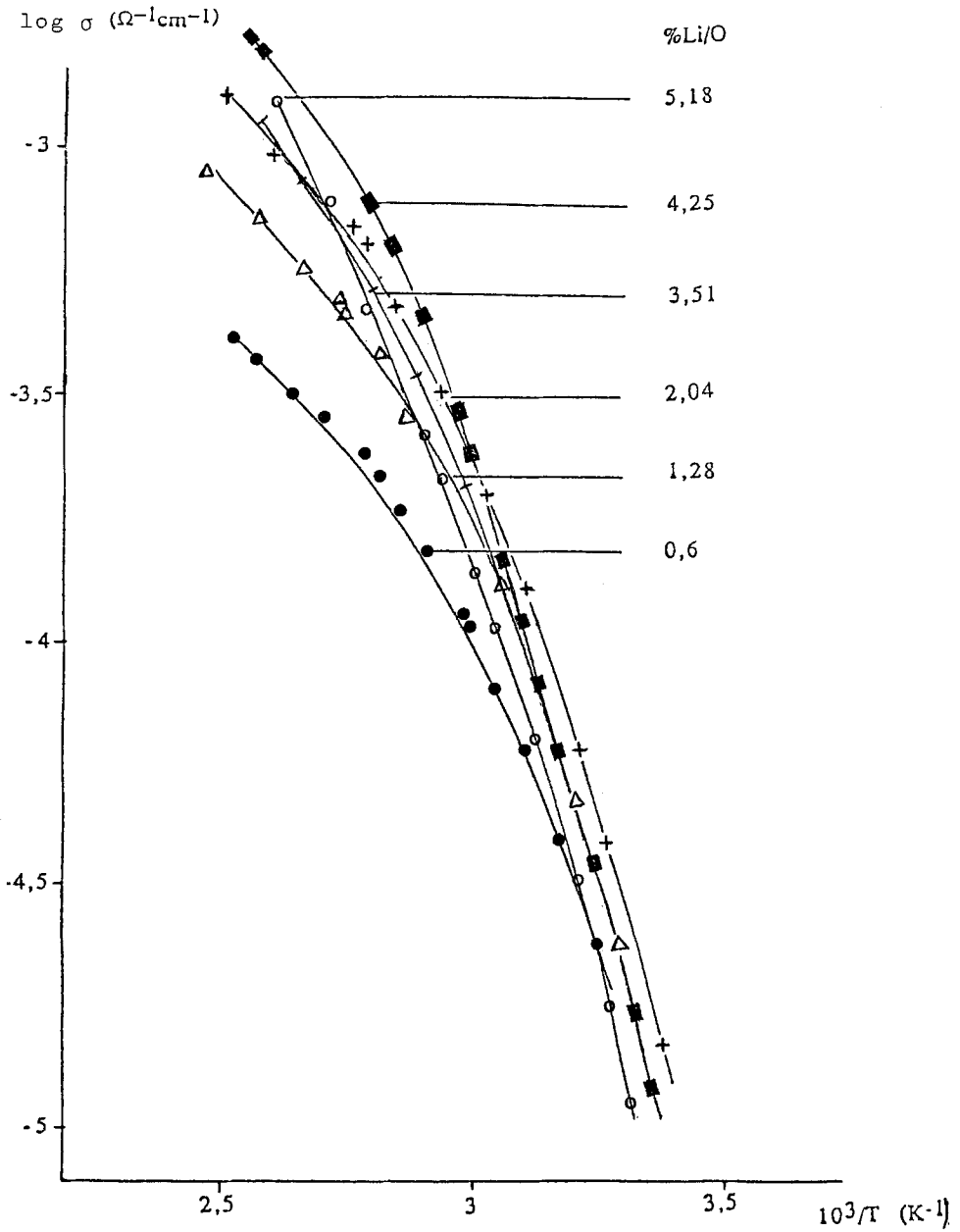
Fig. 4. Dependence of ionic conductivity on reciprocal temperature for network
(I + II) containing different amounts of LiClO$_4$.

This result was surprising because it was felt that the highest conductivities reached previously represented an upper limit for PEO-based networks containing LiClO$_4$ (3). It has been shown previously (3) that neither crown ethers nor linear methoxylated PEO chains added to urethane-type networks containing LiClO$_4$ induce any increase in ionic conductivity and indeed any change in Tg. The increase in conductivity obtained here can therefore only be related to the network structure and/or topology. One possible explanation is that each PEO sequence between crosslinks is "interrupted" by two urethane spacers which might influence negatively its conformational regularity and thus induce a higher degree of disorder. If one considers moreover that those sequences are not uniform in length because of the bimodal character of the diisocyanate, the likelyhood of high local disorder is enhanced, and with it a optimal medium for ionic transport (shortest mean pathway). Another reason for the increase in conductivity could be the role of the urethane groups in the middle of the PEO chains as polar moieties capable of inducing a substantial increase in the dielectric properties of the network. These groups are spaced rather evenly throughout the structure, whereas they were concentrated near the crosslinks in the former approach (2). The difference might be significant in terms of the solvating power of the medium.

It cannot be said without further work whether the first explanation is correct or the second, or indeed a combination of both, but it seems certain that the novel network structure provides a notable improvement in the ionic mobility and/or dissociation.

The wavy shape of the non-linear portions of the conductivity vs concentration plots shown in Fig.5 again simulates qualitatively the features already encountered with the other networks (2,3). However, once more the *actual values* of the critical salt concentrations corresponding to the conductivity maxima and minima differ and are considerably lower with the present systems if one compares them with those of a network with urethane crosslinks and PEO chain lengths equivalent to the present *total* length of the chain between two branching points (i.e. 2 x 800 for the segments arising from the triol plus 900 for the PEO diisocyanate). The reasons for this early saturation are not clear at present but must be looked for in the difference of topology between the two types of network.

The ensemble of the results related to the ionic conductivity strongly suggest that the interruption of uniform sequences of ethylene oxide units along the PEO chains by urethane groups perturbs even locally the conformational regularity thus favouring ionic mobility, but also inducing the occurrence of subchains with a certain individuality in terms of the interactions with the ionic species arising from the added salt.

The Role of a Plasticizing Salt

The membranes were also charged with the lithium salt of bis(trifluoromethanesulfone)imide, LiN(CF$_3$SO$_2$)$_2$, recently synthesized and characterized (8). The anion of this salt can be considered as a "plasticizing" entity (when compared for exemple with the perchlorate anion) because of the low rotational barrier around the S-N bonds. Other considerations based on negative charge delocalization and leaving properties (9) make this salt particularly suited as a source of ions in polymer electrolytes.

The influence of this salt on the Tg was studied: when the concentration of LiN(CF$_3$SO$_2$)$_2$ in the networks was varied from zero to 0.8 mol dm^{-3} the Tg only increased by a few degrees. This modest sensitivity compared with the important

effect of similar amounts of $LiClO_4$ is probably due to the plasticizing properties of the imide anion underlined above.

The ionic conductivity of these systems again followed a typical free-volume behaviour with the characteristic WLF constants already found with $LiClO_4$. The actual values were however systematically higher by a factor of two to three with the new salt compared with those obtained in the same conditions with $LiClO_4$. The same plasticizingng role of the anion can be tentatively invoked to explain this improvement.

CONCLUSION

The change in network topology described in this communication has turned out to be significant in terms of its repercussion on certain physical properties of the resulting electrolyte systems. Thus, whereas qualitatively their behaviour is still dominated by free-volume factors, there is a quantitative gain in electrical conductivity which stems from a higher degree of local disorder caused by the presence of urethane moieties *along* the PEO chains. A new salt was also tested: the improvement in conductivity it produced with respect to $LiClO_4$ can be attributed to the plasticizing effect of its anion. However, with both salts the basic feature remains the establishment of physical crosslinks induced by the charge-dipole interactions between the ions and the ether groups of two PEO chains. These quadrupole-chains electrostatic links are dominant below room temperature but tend to vanish above about 35°C to be replaced by salt ion pairs which do not form such crosslinks.

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