MECHANISM OF IONIC CONDUCTION IN POLYETHER–POLYURETHANE NETWORKS CONTAINING LITHIUM PERCHLORATE

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Summary

The swelling behaviour of polyethylene oxide–urethane networks (with and without LiClO$_4$) was studied with several organic liquids and water. All the results are consistent with a model for the network–salt interaction involving the solvation of Li$^+$ ions by oxygen atoms of the ether. More specifically, strong interactions take place between ionic quadrupoles and two polyether chains leading to reversible physicochemical (ionic) crosslinks. The number of such interactions grows with salt concentration up to a limit characterised by one ionic crosslink every twelve ethylene oxide units. An ionic transport mechanism (conduction) is proposed on the basis of this model considered in a dynamic context.

Introduction

Polymeric membranes based on high molecular-weight polyethylene oxide (PEO) or polyether–urethane networks containing various salts have proved to be useful as solid electrolytes in lithium batteries [1, 2]. Further development of such devices depends upon a clearer understanding of the mechanism of ionic conduction within the macromolecular electrolyte [2]. This paper reports a specific study on the interactions of lithium cations with PEO chains, based on the swelling behaviour of the system polyethylene oxide–urethane networks containing LiClO$_4$. Indeed, all our research has been oriented towards cross-linked materials in order to avoid crystallization and creep and to obtain a homogeneous isotropic structure.

Experimental

The preparation and conditioning of the networks have already been described [3], but in this investigation particular care was taken to keep the

polymer concentration in methylene chloride constant during each synthesis. This parameter is very important in the present context and the value adopted was 0.43 (ratio of the volume of reagents to the volume of reagents plus solvent), unless otherwise stated.

Two types of networks were prepared:

(i) saltless networks based on PEO glycols ($\bar{M}_n$ = 200, 420, 640, 1050, 1550, 2100, 3200, 3800, 6000 and 10 000) crosslinked with a triisocyanate, namely, $HC(p\text{-}C_6H_4NCO)_3$, in stoichiometric ratios (NCO/OH = 1).

(ii) networks containing $LiClO_4$ prepared as above, but only with PEO glycols 1050 and 2100. The salt concentration was varied over a wide range of values.

The swelling of these materials by CH_2Cl_2, $CHCl_3$, CCl_4, C_6H_6 and H_2O at 22 °C was characterized by the equilibrium swelling ratio, q, expressed as the equilibrium volume divided by the volume of the dry network sample.

Results and discussion

Effect of PEO chain length on q, for saltless networks

Qualitatively, q increased with decreasing crosslink density, as expected. Figure 1 shows that two distinct trends were observed with all solvents above and below a boundary value of PEO chain length between crosslinks of about 32 units. The corresponding correlations were $q \propto M_n^{0.64}$ for $M_n < 1400$ and $q \propto M_n^{0.31}$ for $M_n > 1400$.

Effect of LiClO₄ concentration on q

The results on these networks showed a marked dependence on medium polarity and are discussed according to this criterion. It must be emphasized that water could not be tested because it produced a rapid extraction of the salt from the network.

With "polar" agents (e.g., CH_2Cl_2, $CHCl_3$), a linear relationship was obtained between q and $LiClO_4$ concentration, as shown in Fig. 2. The following equations characterize this behaviour (here C is expressed in g $LiClO_4$/100 g PEO):

$q = 7.1 - 0.17\,C$ for PEO-1050/CHCl$_3$

$q = 8.8 - 0.16\,C$ for PEO-2100/CHCl$_3$

$q = 5.8 - 0.08\,C$ for PEO-1050/CH$_2$Cl$_2$

$q = 7.6 - 0.06\,C$ for PEO-2100/CH$_2$Cl$_2$

Whereas the chain length has no apparent influence on the swelling features of the salt–network composites (cf. slopes), the increase in polarity from $CHCl_3$ ($\epsilon = 4.8$) to CH_2Cl_2 ($\epsilon = 9.1$) is accompanied by a more favorable swelling.

With non-polar liquids (e.g., CCl_4, C_6H_6), a different behaviour was observed consisting of a marked decrease in q for low salt concentrations, followed by a tailing-off to an asymptotic value, common to both networks with a given solvent.
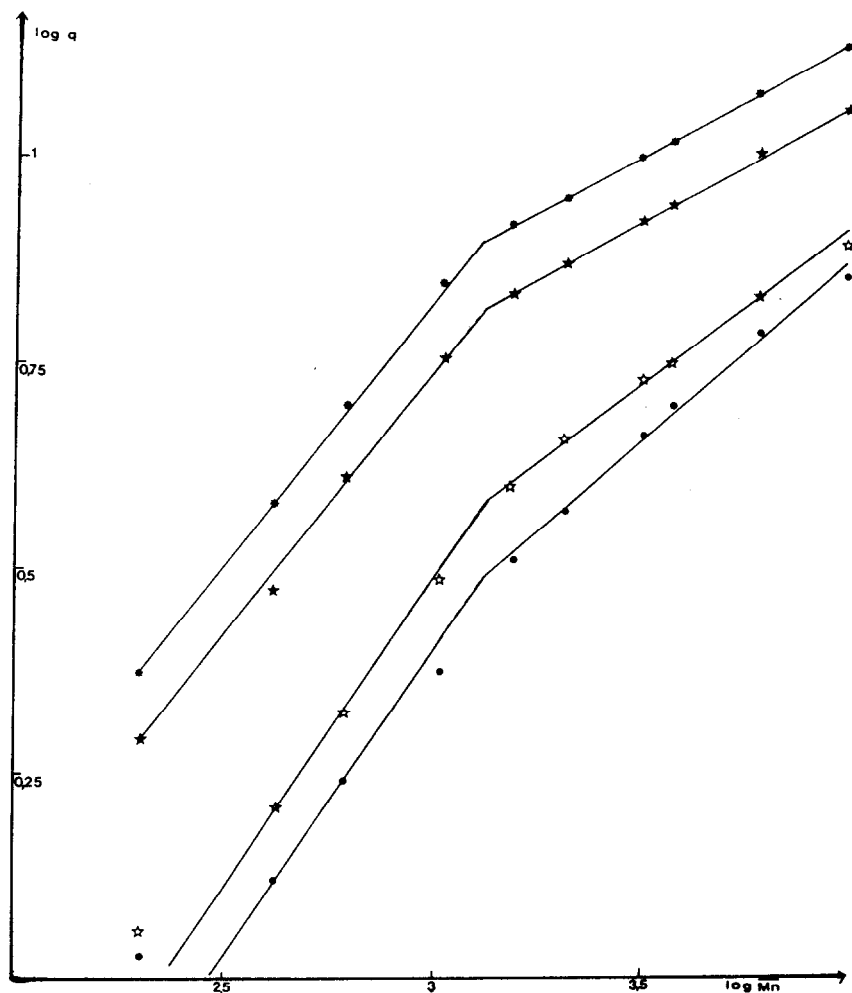
Fig. 1. Log–log plots of swelling ratio, q, as a function of PEO chain length for networks without salt. Starting concentration 0.43 except for PEO 200 (0.65). *, $CHCl_3$; ★, $CHCl_2$; ☆, H_2O; ●, C_6H_6.

If it is assumed that the lithium cations solvated by the ether oxygen atoms introduce a source of physicochemical crosslinking through polar interactions [2], the swelling behaviour, which depends upon the overall crosslink density, will show a dependence on $LiClO_4$ concentration. If n lithium cations solvated by a given PEO chain induce its partitioning into $(n + 1)$ subchains, each containing N bonds, then it follows that $N = N_o/(1 + n)$ and $n = 9.4 \times 10^{-5} \, C \, M$, where N_o is the number of bonds per PEO chain of molecular weight M. This leads to $N \simeq N_o/(1 + 0.1 \, C)$ for PEO-1050 and $N \simeq N_o/(1 + 0.2 \, C)$ for PEO-2100 networks.

Plots of log q *versus* log$(1 + aC)$ with $a = 0.1$ or 0.2 are given in Fig. 3. Linear relationships are indeed obtained with a characteristic break in each
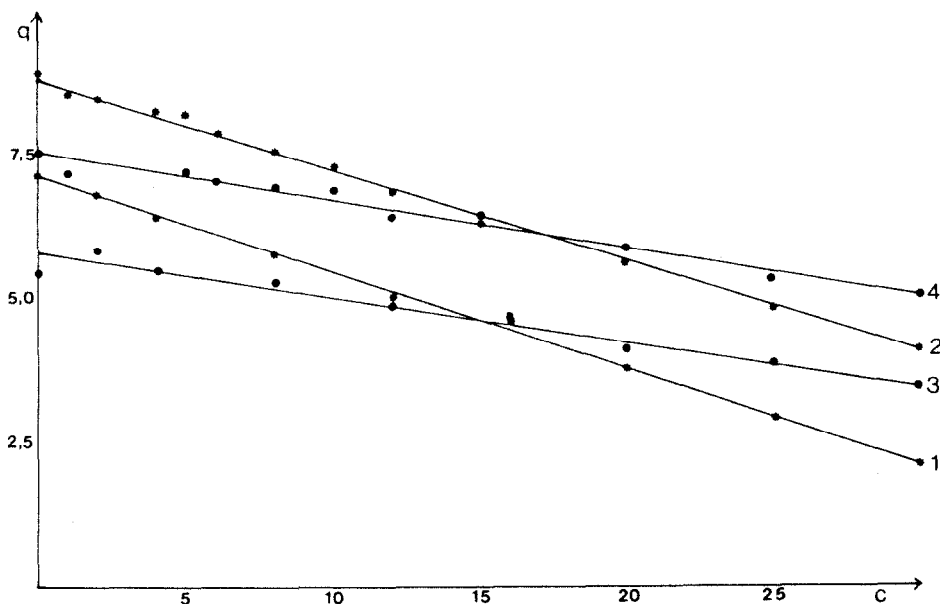
Fig. 2. Variation of swelling ratio, q, with salt concentration, C, for networks containing LiClO$_4$. C is expressed in g LiClO$_4$ per 100 g PEO. *, CHCl$_3$: 1, PEO 1050; 2, PEO 2100. ●, CH$_2$Cl$_2$: 3, PEO 1050; 4, PEO 2100.

plot defining two different slopes. Interestingly, this break occurs at *one* lithium cation per PEO-1050 chain and at *three* Li$^+$ per PEO-2100 chain. This suggests that chain partition by Li$^+$ does take place and that the resulting shortest subchains have an average length of about 12 ethylene oxide units, *i.e.*, $M \sim 500$.

The equations describing the swelling behaviour before maximum partitioning is reached (high-slope segment in Fig. 3) are:

$$q = 2.34/(1 + 0.1\ C)^{0.65} \text{ for PEO-1050/C}_6\text{H}_6$$
$$q = 4.06/(1 + 0.2\ C)^{0.70} \text{ for PEO-2100/C}_6\text{H}_6$$
$$q = 2.09/(1 + 0.1\ C)^{0.60} \text{ for PEO-1050/CCl}_4$$
$$q = 2.80/(1 + 0.2\ C)^{0.64} \text{ for PEO-2100/CCl}_4$$

which reduce to the general form:

$$q \propto (M')^{0.65}$$

where $M' = M/(1 + aC)$, *viz.*, the average molecular weight of a subchain.

The striking identity between the correlations found for the two types of networks, with and without salt, clearly indicates that the chain partitioning model proposed above is valid and, moreover, that *one* urethane irreversible crosslink is equivalent in terms of swelling to *one* reversible ionic crosslink produced by the interaction of lithium cations with PEO chains. Indeed, an inspection of Fig. 3 reveals that a saltless network from PEO-1050 has the same q value as a PEO-2100 network containing *one* Li$^+$ per PEO chain and
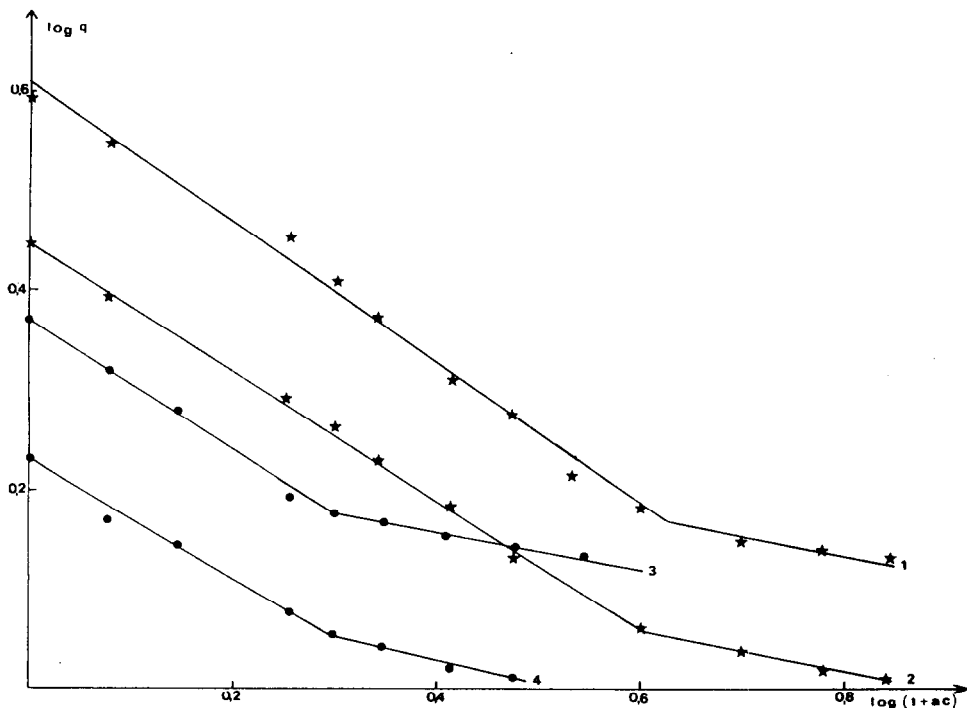
Fig. 3. Log–log plots of swelling ratio, q, as a function of $(1 + aC)$; see text. ●, PEO 1050 ($a = 0.1$): 1, C_6H_6; 2, CCl_4. ★, PEO 2100 ($a = 0.2$): 3, C_6H_6; 4, CCl_4.

that a PEO-1050 network containing *one* Li^+ per chain has the same q value as a PEO-2100 network containing *three* Li^+ per chain.

Below the critical $LiClO_4$ concentration giving complete chain partitioning, it is envisaged that the dominant ionic species are quadrupoles (made up of two opposed ion-pairs) which play the role of physical crosslink agents. This assertion stems from the fact that, in our conditions, ion pairs (tight or chain separated) are unlikely to be present because the dielectric constant of the dry medium is too low. We measured this parameter (from complex impedance diagrams) on a series of networks containing variable amounts of $LiClO_4$ and consistently obtained values lower than 8: these results seem to us sufficiently clear to indicate the formation of ionic aggregates larger than ion pairs.

Above the critical $LiClO_4$ concentration, it is supposed that ionic aggregation growing onto existing quadrupoles is the dominant phenomenon. This implies that the actual concentration of ionic crosslinks does not increase further as, indeed, suggested by the fact that q does not vary appreciably above the critical salt concentration.

As for the role of the swelling agents, the different behaviour shown in Figs. 2 and 3 is rationalized by considering the fact that non-polar liquids do

not affect the concentration of quadrupoles (ionic crosslinks), whereas more polar ones tend to split these ionic aggregates into ion pairs.

If attention is now directed to the actual transport properties of these electrolytes, *i.e.*, to a dynamic model of their structure, it must be first emphasized that a number of complementary studies based on electrical conductivity, ionic transport number, and nuclear magnetic relaxation [2, 4] show, irrefutably, the existence of the same critical salt concentration as observed here.

A thorough inspection of all these results, some of which will be submitted in detail shortly, leads to the formulation of a mechanism of ionic conduction in two stages:

(i) Segmental motions periodically place in contact ionic species fixed on different chains. It can be visualised that such encounters readily produce dipole transfers, shown schematically as:
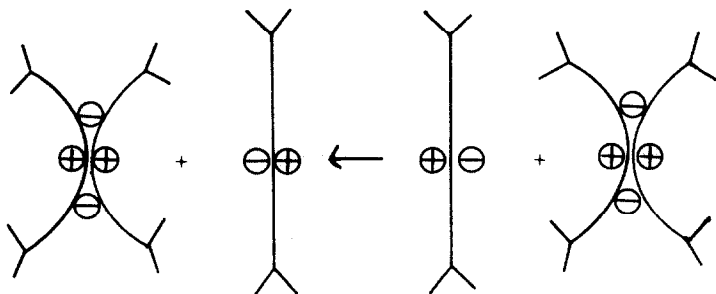
Since this movement is random, it does not provide directional charge transport and takes place irrespective of the presence of an electric field.

(ii) For ionic transport to occur, it is necessary that a defect exists at a given ionic site, *viz.*, the lack of an anion or of a cation. This will ensure charge migration under an electric field.

Thus, both phenomena are required for ions to move towards the respective electrodes, although the latter provides the actual transport. The role of the former is related to the free volume available and, indeed, dominates the overall energetics as shown by the WLF behaviour of these systems [2 - 4].

References

1 M. Armand, *Solid State Ionics, 9 & 10* (1983) 745.
2 A. Gandini, J. F. Le Nest, M. Lévêque and H. Cheradame, in L. A. Kleintjens and P. J. Lemstra (eds.), *Integration of Fundamental Polymer Science and Technology*, Elsevier Applied Science, London, 1986, p. 250.
3 A. Killis, J. F. Le Nest, A. Gandini and H. Cheradame, *J. Polym. Sci., Polym. Phys. Ed., 19* (1982) 1073.
4 J. F. Le Nest, *Doctorat d'Etat Thesis*, Grenoble, 1985.