

Electrolytes for solid-state batteries: glass transition temperature of polyether networks with and without alkali metal salts

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SUMMARY

A detailed study was conducted on the dependence of the T_g of polyether networks as a function of type and size of polyether chain, nature of the crosslinking structure and alkali metal salt concentration. The nature of the branching moiety affects T_g but not the salt interactions with the network. A general law concerning the salt-containing network is obtained. It is characterized by the dominating interactions of the salt with polyethylene oxide chains.

INTRODUCTION

More than a decade has elapsed since the first studies on the use of linear polyether containing alkali metal salts as electrolytes for lithium batteries and interest in this topic has not ceased to grow since then. Papers presented at a recent symposium give the state of the art and the relevant references to previous work (1).

It was in our laboratory that the idea arose of using networks in order to improve the performance of the polyether electrolyte in terms of minimizing both creep and crystallization. The research in this field has been reviewed (2). The most important general features of systems involving a polyether network containing ionic species arising from an added salt or from ionisable functions borne by the chains are : (i) the paramount role of free volume in determining transport properties and (ii) the high contribution of anions (whenever they are free to migrate) to the overall ionic transport ($t^- > 0.7$). This "universal" behaviour was established by a wide array of measurements ranging from dynamic mechanical properties to electrical conductivity to nuclear magnetic relaxation (2).

It remained however to ascertain the role (if any) of the crosslinking moiety on the properties of these networks. The present work attempts to fill this gap through measurements of the glass transition temperature of different networks with and without added salts.

EXPERIMENTAL

Most starting materials, ie polyether glycols, polydimethylsiloxane-g-polyether-ols and di and tri-isocyanates have been described as well as the techniques of preparation of the crosslinked polyurethanes films with and without salts (2). To these materials, one must now add tris (p-isocyanato-phenyl) thiophosphate, $S=P(OC_6H_4NCO)_3$, (Desmodur RF, Bayer) used in conjunction with a variety of polyether diols, and tetramethyltetrahydrocyclotetrasiloxane $[Si(CH_3)(H)O]_4$, (D4H), as crosslinking agent for diallyl terminated polyethylene oxide (PEO). The two former compounds are

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commercially available, whereas the functionalised PEOs were prepared by the reaction of PEO glycols with excess allyl bromide in the presence of excess NaOH, following a published procedure (3). The networks resulting from D4H and diallyl PEO were prepared in toluene at room temperature (concentration during synthesis 0.43 v/v as in previous studies (4)), using H_2PtCl_6 as catalyst with $[\text{Si} - \text{H}] / [\text{C} = \text{C}] \simeq 1.1$ and $[\text{Pt}] / [\text{Si} - \text{H}] \simeq 10^{-4}$. The reaction mixture was poured into the film mould (2) and left to cure for 2 h at room temperature. At this point it was found that the polymer tended to develop surface friability if left in the mould. The crosslinked sheet was therefore demoulded and placed for 24 h under nitrogen at 60°C for final curing before being vacuum dried at 80°. These materials contained about 2 % of soluble (non-crosslinked) fraction, viz a little more than the urethane-crosslinked polyether, which only gave about 0.5 % (2).

The salts were introduced in the networks either during their synthesis or by diffusion after reticulation (2).

The measurement of T_g were carried out with a DUPONT 990 differential scanning calorimeter after quenching the sample (2).

RESULTS AND DISCUSSION

Saltless networks

a) T_g values were obtained for a set of networks in which the type and M_n of the polyether were fixed, viz PEO 1050, and the chemical nature of the crosslink moiety varied. With the tetrafunctional siloxane group resulting from D4H and diallyl PEO, the T_g was - 62°C.

With the use of trifunctional urethane group arising from triisocyanates the T_g increased to - 50, - 43 and - 33°C with $\text{OCN}(\text{CH}_2)_6\text{N} [\text{CONH}(\text{CH}_2)_6\text{NCO}]_2$ (Desmodur N, Bayer), $\text{HC}(\text{C}_6\text{H}_4\text{NCO})_3$ (Desmodur R, Bayer) and Desmodur RF respectively. The trend is quite reasonable in view of the increasing stiffness of the branching structure, at least with the first three networks. The rather large difference between the T_g s of the two materials involving aromatic triurethanes can be rationalised in terms of the establishment of polar or hydrogen-bond interactions between N-H and P=S groups in the case of Desmodur RF crosslinks, which would reduce segmental motions through further "physicochemical crosslinking". A similar finding was reported earlier (5) for ionomers based on phosphate and thiophosphate polyethers crosslinked by urethane linkages.

b) Given the above qualitative trend, a more quantitative study was carried out by varying the PEO chain length. Fig 1 shows the results with the four branching structures. The straight lines obtained extrapolate to the same value corresponding to the hypothetical T_g of amorphous PEO chains of infinite length and are described by the general equation

$$1/T_g - 1/T_{g_0} = -k c$$

Where c is the crosslink density. The slopes k obviously follow the trend observed above (point a.) and are respectively 0.10, 0.53, 0.76 and 1.05 $\text{cm}^3\text{mol}^{-1}\text{K}^{-1}$.

As expected, the influence of siloxane branching points concentration on T_g is very small. The urethane crosslinks produce a pronounced rigidification which increases in the expected way, viz aliphatic < aromatic < aromatic plus thio groups.

c) The influence of the nature of the polyether chain was also studied for a given chain length and crosslinking agent. With polypropylene oxide (PPO) $M_n = 1030$, the

network gave a Tg of - 33°C, i.e 10 degrees higher than that of the corresponding PEO networks. Here again the results is as expected, given the higher chain stiffness of PPO.

Networks with added salts

The general trend observed follows the equation

$$1/T_g - 1/T_{g_0} = -k' c'$$

Where c' is the salt concentration. No deviation from this behaviour was encountered in the present study, i.e all plots of $1/T_g$ vs c' were linear.

a) The effect of the nature of the crosslinks was studied with a series of networks prepared with the same PEO glycol ($M_n = 1050$) and filled with the same salt, namely $LiClO_4$. The value of k' was found to be $0.27 \pm 0.01 \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$, independent of the branching structure, notably those arising from Desmodur N, Desmodur R and D4H, as shown in Fig. 2.

This finding is very important because it shows clearly that the ions from the salt do not interact in an appreciable way with the urethane or the siloxane moieties. The increase in Tg with increasing $LiClO_4$ concentration is therefore only due to ether-salt interactions (2,4). Similar results have been obtained and a similar conclusion reached from conductivity measurements (6).

b) For a given crosslink (from Desmodur R) the PEO chain length was varied and the Tg measured on each of these networks as a function of $LiClO_4$ concentration. Again, k' was found to be 0.27 ± 0.01 , independent of the M_n of the PEO glycol used, namely 420, 1050, 2100, 3800.

These results corroborate the conclusion regarding the negligible (if any) contribution of urethane groups in terms of their possible interactions with $LiClO_4$. The networks with PEO chains of only 9-10 units ($M_n = 420$) would have shown such interactions, if they were at all important, by an increase in the k' value.

c) The influence of the nature of the added salt was also studied with a given network, viz PEO 1050 + Desmodur R with $LiClO_4$, $KClO_4$, $NaBPh_4$ and NH_4ClO_4 . The same straight line was obtained with $k' = 0.27 \pm 0.01$.

The lack of any trend as a function of salt structure indicates that monovalent cations establish the same extent of complexation with EO units independent of their nature and of the type of anion associated with them, provided the degree of ionisation is high.

d) Finally, the effect of the nature of the polyether was studied with a given crosslinking agent (Desmodur R) and $LiClO_4$.

First networks based on homopolymers, PEO ($M_n = 420$) and PPO ($M_n = 430$), were compared : k' increased from 0.27 to 0.65. Then two PEO - b - PPO - b - PEO copolymers were used to build the networks. The first had M_n of 2000 - b - 1000 - b - 2000, the second 3400 - b - 1500 - b - 3400. The k' values were 0.39 and 0.33 respectively.

Previous work has shown that $LiClO_4$ is more solvated in PEO-based than in PPO-based networks and that this leads to more important inter-chain associations with the salt (2,4). The present results seem to confirm this conclusion. In fact, the high k' value with PPO-based networks can be rationalised by the tendency of the salt to form aggregates (lack of solvation) which play the role of charge, thus producing a more important increase in Tg with increasing salt concentration.

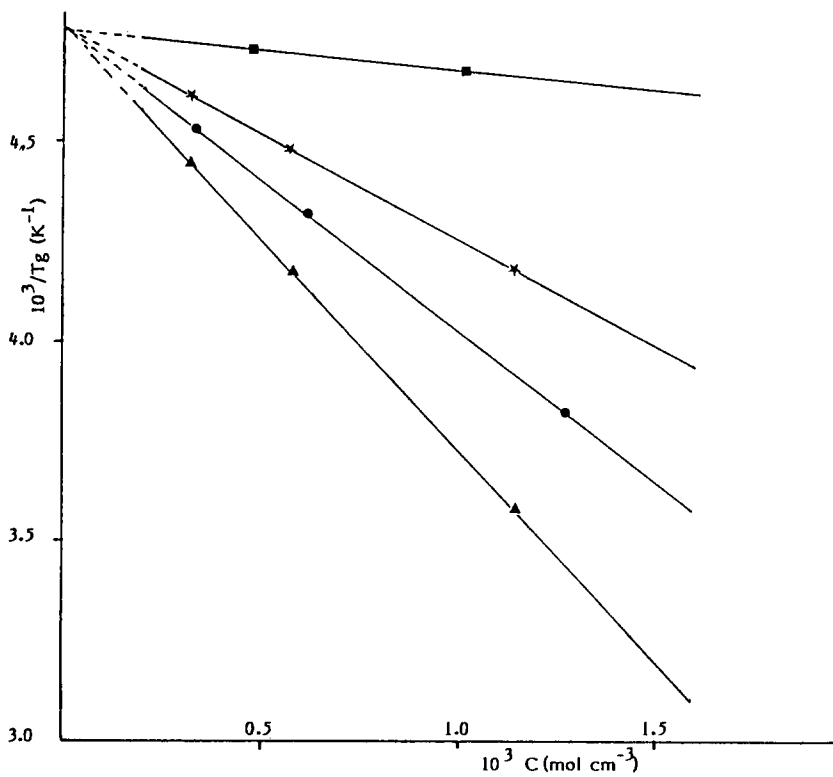


Figure 1 : Dependence of the inverse of T_g on the crosslink density c , for a series of networks based on PEO of different chain length and on different crosslink agents : (▲) Desmodur RF ; (●) Desmodur R ; (✱) Desmodur N ; (■) D4H (See text).

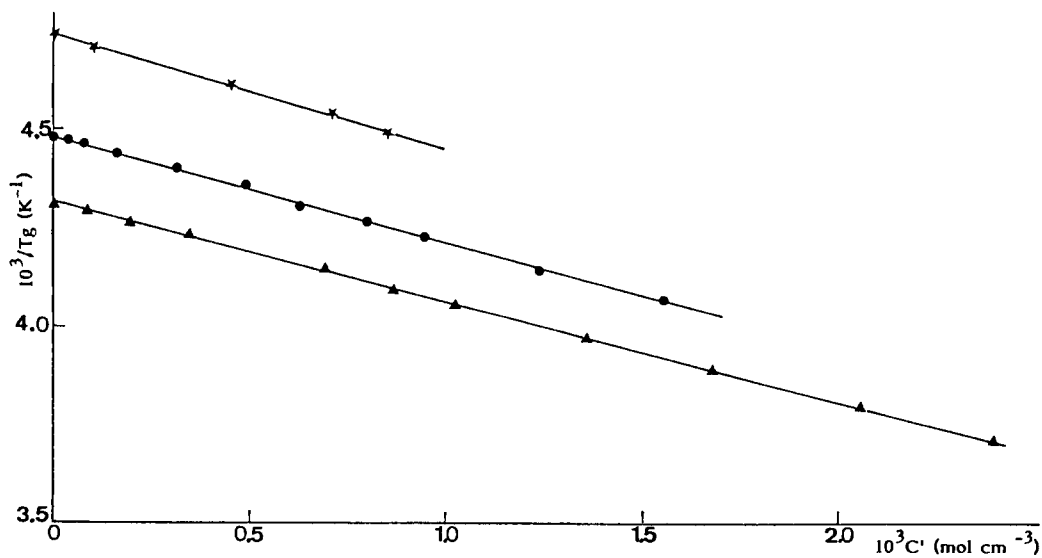


Figure 2 : Variations of T_g as a function of $LiClO_4$ concentration for networks prepared with PEO glycol, $M_n = 1050$ and different crosslinking agents : (▲) Desmodur R ; (●) Desmodur N ; (✱) D4H (See text).

When block copolymers are used it appears that the LiClO_4 tends to associate preferentially with the PEO sequences because of stronger interactions, as already noticed by ^7Li magnetic relaxation studies (4). If the assumption is made that this selectivity is high, one can recalculate k' on the basis of a corrected c' and the new values of 0.30 (cf 0.39) and 0.26 (cf 0.33) respectively are obtained, viz once again the characteristic general value of about 0.27. Instead if the calculations are carried out considering the ponderal contribution to k' of each block based on the k' values for the homopolymers, one obtains 0.35 (cf 0.39) for the short blocks and 0.37 (cf 0.33) for the longer ones. These new values follow a trend opposite to the actual results.

It follows that the interpretation suggesting a large difference in affinity toward LiClO_4 (and similar salts) between PEO and PPO is correct. Thus in the first approximation when one dissolves LiClO_4 in a network based on a PEO-PPO block copolymer, the salt will migrate selectively to the PEO chains up to a critical concentration which was however never attained in our experiments.

One last set of experiments concerned networks formed by a polydimethylsiloxane (PDMS) grafted with PPO-PEO-OH block copolymers (2) and hexamethylene-diisocyanate and filled with increasing amounts of LiClO_4 . The value of k' was 0.56. One can certainly rule out any interaction between LiClO_4 and the siloxane units (suffice it to note that LiClO_4 is insoluble in PDMS). If one also excludes again any important solvation of the salt by the PPO blocks, k' can be recalculated on the basis of "real" LiClO_4 concentrations referred exclusively to the PEO segments of the network as done above for the PEO-PPO-PEO block copolymers. The new k' value of 0.25 ± 0.02 is in excellent tune with all other figures referring to the interaction of LiClO_4 (and other salts) with PEO chains. It therefore confirms the lack of solvation effects by siloxane and PPO chains when PEO chains are present in the networks.

CONCLUSION

The structure of the crosslink can influence the T_g of polyether-based networks, mostly by the degree of stiffening, but also by more specific interactions. On the other hand, these factors do not affect the role or the extent of complexation between an alkali metal salt introduced into the network and the polyether chains. Finally the latter interactions are much stronger with PEO segments than with PPO segments, and practically inexistent with PDMS chains.

This work has thus allowed the establishment of further general features characterizing the behaviour of polyether networks containing ionic species.

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