

MECHANISM OF HIGH IONIC CONDUCTIVITY IN ELASTOMERIC NETWORKS

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(Received June 23, 1982; in revised form October 28, 1982)

Summary

The viscoelastic properties and the ionic conductivity of polyether-polyurethane networks containing alkali metal salts have been studied at various temperatures, salt concentrations and network structures. The reduced temperature, $T-T_g$, is the predominant parameter which governs the viscoelastic behaviour and the ionic conductivity of these networks. Using the free volume concept an expression is derived for the ionic conductivity, irrespective of the macrostructure involved. The logarithm of the reduced conductivity, σ_T/σ_{T_R} (which is the ratio of the conductivity at a given temperature to that at the reference temperature), is a linear function of the shift factor, $\log a_T$, given by the dynamic mechanical properties. A comparison is made between the WLF parameters C_1 and C_2 , obtained from conductivity and viscoelastic measurements.

Introduction

A new class of ion-containing elastomer has recently been developed in our laboratory consisting of polyether-polyurethane networks obtained by the reaction of a polyether glycol with a triisocyanate in the presence of alkali metal salts; these materials exhibit high ionic conductivities [1, 2]. Up to now, we have focussed our attention on materials containing sodium salts, e.g., sodium tetraphenylborate (NaBPh_4) [3]. Materials made of linear polyethers (polyethylene or polypropylene oxides) mixed with alkali metal salts generally exhibit lower ionic conductivities at room temperature [4 - 6]. In the latter compositions, the mechanism of ionic conductivity is still a matter of discussion, since the respective roles of crystallised and amorphous regions are not fully understood as yet. The fact that our membranes are entirely amorphous allowed us to demonstrate unequivocally that their ionic conductivity is the consequence of the elastomeric behaviour they possess [2]. We have established an expression for the reduced conductivity σ_T/σ_{T_g} as a function of temperature which proves the existence of a correlation between the conductivity and the dynamic mechanical behaviour [3, 8, 9].

Very recently we began to examine the ionic conductivity of membranes containing lithium salts. With lithium perchlorate both the conductivity and the spin-spin relaxation time of the ^7Li nucleus follow a WLF [10] behaviour, showing that these transport properties are the consequence of segmental motions allowed by the free volume in our membranes [7].

In the present study we deal with the WLF parameters C_1 and C_2 calculated from the ionic conductivity or the dynamic mechanical properties of membranes containing sodium or lithium ions.

Experimental

The detailed preparation and conditioning of the samples have been described elsewhere [8, 9]. The membranes were synthesized using dry salts and dried polyethers, as previously described, in the form of uniform disks less than 1 mm thick and were pressed between two stainless steel electrodes in a cell which could be heated under vacuum. After outgassing, conductivities were measured, using the complex impedance plot treatment, in the temperature range 20 - 120 °C [1, 3]. The glass transition temperatures were determined with a Dupont 990 thermo-analyser. The alkali metal salts, all commercially available, were dried under vacuum before use.

Volume expansion coefficients were determined using a pycnometer. In some cases glass transition temperatures were obtained from the loss tangent peaks at 11 Hz [8, 9].

Results and discussion

According to the free volume theory for transport in liquids developed by Cohen and Turnbull [11], the dependence of the diffusion coefficient upon the free volume fraction is obtained through the intermediate of the viscosity:

$$D = BRT/\eta \quad (1)$$

$$\eta = A \exp(\gamma f^*/f) \quad (2)$$

$$D = D_0 T \exp(-\gamma f^*/f) \quad (3)$$

where f^* is the free volume fraction necessary for the diffusional particle jump to occur, f is the free volume fraction at temperature T , γ the overlap factor (usually 0.5 - 1.0 [11]); A and B are constants which are determined by the nature of the system and D_0 is the diffusion coefficient pre-exponential term, essentially independent of temperature.

We assume that the free volume fraction varies linearly with temperature according to the expression:

$$f = f_g + \alpha(T - T_g) \quad (4)$$

where f_g is the free volume fraction at the glass transition temperature and α the thermal free volume expansion coefficient. Substituting (4) into (3) gives

$$D = D_0 T \exp\{-\gamma f^* / [f_g + \alpha(T - T_g)]\}. \quad (5)$$

Equation (5) can be expressed in a reduced form as

$$\log \frac{D_T T_g}{D_{T_g} T} = \frac{\gamma f^*}{2.3 f_g} \frac{T - T_g}{(f_g/\alpha) + T - T_g} = -\log a_T \quad (6)$$

where $\log a_T$ is the usual WLF shift factor defined as

$$\log a_T = \frac{-C_1(T - T_g)}{C_2 + T - T_g} \quad [10] \quad (7)$$

with $C_1 = \gamma f^* / 2.3 f_g$ and $C_2 = f_g / \alpha$.

Then:

$$C_1 C_2 = \gamma f^* / (2.3 \alpha),$$

where f^* can be interpreted as the free volume necessary for the movement of a particle to occur in the specific transport phenomenon considered (conductivity or viscoelasticity), and α as the thermal expansion coefficient.

We measured the conductivity of membranes consisting of polyethylene oxide glycols (PEO) or polypropylene oxide glycols (PPO) cross-linked with p'', p', p -triphenylmethanetriisocyanate in the presence of variable amounts of NaBPh_4 or LiClO_4 . The main characteristics of the materials are given in Table 1 together with the values of the $C_1 C_2$ products obtained for them.

The C_1 and C_2 constants were calculated from conductivity measurements [3] using the expression:

$$\log (\sigma_T / \sigma_{T_g}) = \frac{C_1(T - T_g)}{C_2 + T - T_g},$$

TABLE 1

Comparison between conductivity and viscoelastic properties of different networks

Polyether (M wt.) + salt	Salt		T_g at 11 Hz (°C)	Thermal exp. coeff. (cc/g K $\times 10^4$)	$C_1 C_2$ conductiv.	$C_1 C_2$ viscoel.
	(Polymer)	wt/wt (%) M—O— (%)				
PEO (400) + NaBPh_4	8	1.03	26	4.0	820	850
	13	1.71	31	3.3	510	420
	26	3.44	40	3.9	590	550
	40	5.01	45	3.2	710	620
PPO(425) + NaPBh_4	6	1.03	46	7.7	320	500
	10	1.70	57	6.3	480	620
	20	3.39	65	7.5	550	1240
	30	5.14	69	4.5	540	1030
PEO (1000) + LiClO_4	8	3.3	-11	4.3	470	390

TABLE 2

Glass transition temperature and conductivity of some lithium salt-containing polyether networks

Salt	Polyether used	T_g , °C (D.S.C.)	σ , 40 °C, (Ω cm) ⁻¹	C_1C_2
LiClO ₄	POE 1 000	-38	1.5×10^{-5}	570
LiBF ₄	POE 1 000	-35	6.9×10^{-6}	430
LiCF ₃ SO ₃	POE 1 000	-40	4.8×10^{-6}	310
LiSCN	POE 1 000	-22	8.1×10^{-7}	370
LiCF ₃ CO ₂	POE 1 000	-41	4.1×10^{-7}	600
LiCH ₃ CO ₂	POE 1 000	-46	5.9×10^{-8}	—

where σ_T is the measured conductivity at the temperature T and σ_{T_g} was calculated from the linear correlation of conductivity with dynamic mechanical data [3, 12]. In Table 1 we also report the values of C_1C_2 obtained from dynamic mechanical measurements. In the case of networks based on PEO the C_1C_2 products are quite similar for both types of determination. The individual values of C_1 and C_2 will be discussed in more detail elsewhere [12]. The above conclusion seems to apply both to sodium and lithium ions. On the other hand, the values of C_1C_2 derived from the conductivities of networks based on PPO are somewhat lower than those determined from dynamic mechanical properties, the gap widening as the salt concentration is increased.

If one also assumes that α is constant over the concentration range used in this work for the added salt, it can be concluded that the minimum free volume needed for the movement of a sodium or lithium ion in PEO-based networks is essentially the same as that required for a segmental polymer motion. This is not quite so with PPO-based networks where the former is lower than the latter, the discrepancy being more pronounced at high salt concentrations.

Polyether networks containing different lithium salts, all having the ratio of lithium atoms to ethereal oxygen atoms equal to 4.1% were also prepared. The glass transition temperature and the conductivity of the samples are reported in Table 2. A plot of the reciprocal logarithm of the reduced conductivity $1/\log(\sigma_T/\sigma_{T_r})$ against $1/(T - T_r)$, T_r being a reference temperature, Fig. 1, showed that the conductivity follows a WLF type law with all other salts used, as already found with polyether networks containing sodium tetraphenylborate [2-4, 7-9]. A mathematical analysis of the latter plot gives an estimate of the C_1 and C_2 constants of the WLF shift factor at T_g for each membrane. The results indicate that the C_1 constant has practically the same value for all membranes exhibiting a WLF behaviour. This observation may be rationalised assuming that the free volume fraction at the glass transition temperature is essentially constant in these membranes.

By contrast, the calculated C_1C_2 product varies appreciably from one salt to another.

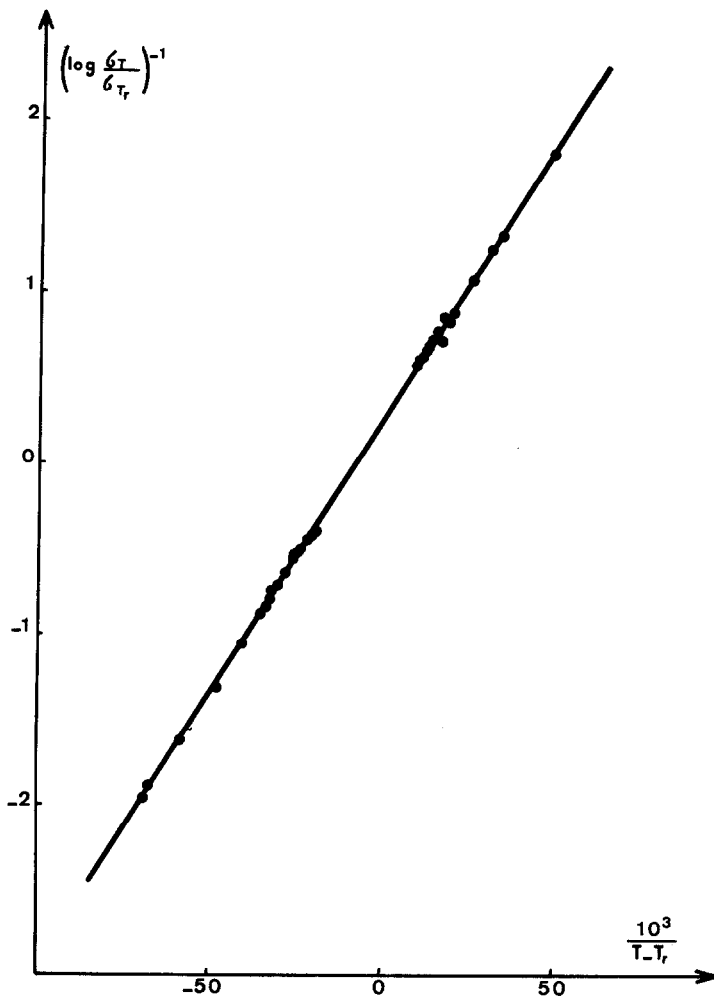


Fig. 1. "Free volume" plot of the ionic conductivity at the reference temperature $T_r = 52^\circ\text{C}$ for a polyether-polyurethane network based on polyoxyethylene, $\bar{M}_w = 1000$, containing lithium perchlorate ($\text{Li}/\text{—O—} = 3.4\%$).

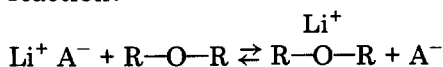
The results of the detailed calculations of the C_1 and C_2 constants are not in contradiction with previously published discussions about the membranes containing NaBPh_4 [3], since at that time we were only interested in qualitative arguments about the WLF behaviour of the mechanical properties of these ionically conducting cross-linked materials. The published values, $C_1 = 10.5$ and $C_2 = 100$, must be considered only as means, since we now know that these constants may vary with the nature of the salt and its concentration, although to a limited extent.

The C_1 and C_2 constants given by the study of their conductivity seem to be less sensitive to change of anion and concentration. This is understandable, assuming that the minimum free volume fraction allowing the jump of

a given cation remains unchanged. Our present analysis shows that the ratio of the C_1 constants given either by conductivity experiments or by mechanical measurements is varying [9], and this must be attributed to variations of the C_1 mechanical constant. One can rationalise this finding assuming that the mean local conformation of the macromolecular chains changes with salt concentration, which influences the minimum size of the free volume hole for the displacement of the monomer units but not necessarily the size of the hole for a cation jump, contrary to our previous belief [3]. The fact that the constant is approximately the same in the case of the lithium cation as in the case of the sodium cation in PEO membranes can be ascribed to the fact that the same free volume size is needed. Consequently, the better conductivity generally observed in the lithium-containing networks at a given temperature must be attributed to a lower glass transition temperature (for instance, PEO 400 NaBPh₄ 3.44% T_g D.S.C. = 14 °C, PEO 400 LiCF₃SO₃ 3.44% T_g D.S.C. = 12 °C).

Some conclusions about the conduction mechanism can be drawn from the results. The variation of T_g with salt concentration indicates that the ions are probably not responsible for ionic crosslinking but rather that the chains can be considered as a random copolymer between free monomer units and salt complexed units. This conclusion is consistent with the structural analysis of polyether salt complexes published by Shriver [13] and explains why the C_1 constant is rather insensitive to the nature of the cation.

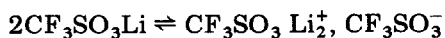
Since the ether linkage can be considered as a strong base, it must interact strongly with the lithium ion which is a strong acid. The extent of the reaction:



will depend essentially on the dissociation energy of the salt $\text{Li}^+ \text{A}^-$. We can expect therefore that the lower this dissociation energy, the higher the conductivity. However, the conductivity values exhibited by our materials did not follow the order of strength of the parent acids of the salts, *viz.*:



In fact, we observed that LiClO₄ always gives the highest conductivity in the temperature range explored in this study, while an inversion took place between the conductivities of LiCF₃SO₃ and LiBF₄ below 30 °C. Also, the conductivities given by CF₃COOLi were lower than those measured with LiSCN. It does not seem therefore possible to rationalise this overall behaviour with the exclusive help of the principles of the HSAB theory. A knowledge of the structure of the aggregates present in our materials and of the possible formation of salt homoconjugates, *i.e.*:



is obviously needed to reach a better understanding of our results.

Acknowledgements

We thank the Direction des Recherches Etudes et Techniques and the Société Elf Aquitaine for financial help.

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