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Influence of $LiClO_4$ on the Properties of Polyether Networks: Specific Volume and Glass Transition Temperature

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ABSTRACT: A series of networks based on different polyether chains (PEO homopolymer, block and graft copolymers) joined by different urethane cross-links were prepared. Their specific volume and T_g were determined in the absence and in the presence of $LiClO_4$ as a function of various structural parameters and of salt concentration. Quantitative correlations were obtained and interpreted on the basis of specific interactions between the ether groups and the ionized salt. Chain partitioning and physical cross-linking occurred as a consequence of these associations.

Introduction

The complexation of alkali-metal salts by polyethers has been the subject of many recent publications because of the potential interest of these materials as electrolytes in solid-state batteries.[1,2] However, whereas the interactions between salts and simple ethers, e.g., THF, have been studied in detail, little was known about the behavior of systems involving polymeric media and then only on a qualitative basis.[3] This paper gives an account of a quantitative investigation which complements a previous brief report.[4]

Experimental Section

A wide range of polyether networks was synthesized in the presence or absence of $LiClO_4$. The operations leading to such materials are described below.

Purification and Characterization of Reagents. Commercial polyethers, linear homo- and copolymers, as well as branched copolymers, were purified by reprecipitation in hexane and dried by azeotropic water removal with benzene followed by vacuum treatment at 100 °C for 24 h. This drying technique left only about 100 ppm of moisture, as measured by the Karl Fisher technique. The polyether polyols thus purified and dried were characterized by (i) number-average molar masses (M_n) determined by vapor-pressure osmometry; (ii) polydispersity index, determined by size exclusion chromatography; and (iii) average hydroxyl contents measured by either esterification with acetic anhydride and back-titration of the excess acid or by reaction with *tert*-butyl isocyanate and ^1H NMR counting the relative number of appropriate protons. (iv) Whenever copolymers were used, their composition was termined by ^1H and ^{13}C NMR.

The cross-linking reagents were polyfunctional isocyanates bearing either two such moieties (hexamethylene diisocyanate, HMDI) when used with graft polyether polyols or three NCO groups with linear polyether diols [4,4′,4″-methylidynetris(phenyl isocyanate) and an aliphatic counterpart $OCN(CH_2)_6N(CONH(CH_2)_6NCO)_2$]. The only product that was distilled before use was HMDI. However, the functionality of all isocyanates was checked by the *n*-butylamine method.[5]

The catalyst for urethane formation was commercial dibutyltin dilaurate, employed as received. Finally $LiClO_4$ was vacuum dried at 130 °C for 24 h. Table I summarizes the characteristics of all reagents used.

Synthesis of Networks. The synthesis of salt-containing networks was carried out in purified CH_2Cl_2 following the procedure already described.[6] However, in this study, particular attention was paid to maintain the reagents' concentration constant in all synthesis, namely, 0.43 (total volume of reagents over volume of solution), except for the network based on PEO 200 which was prepared with a volume ratio of 0.65 in order to avoid syneresis problems. These preparations were carried out under stoichiometric conditions (OH/NCO = 1) and the extent of cross-linking was checked by submitting the products to an extraction with CH_2Cl_2. In all instances the soluble fraction did not exceed 1% by weight and was more frequently below 0.5%.

Network Densities. The specific volumes of both saltless and salt-containing networks were determined by pycnometry following two experimental procedures, both involving mercury as nonswelling liquid. One consisted of filling the pycnometer with the network sample and Hg and then vacuum degassing; the other called upon filling the pycnometer containing the sample with mercury under vacuum. All results obtained agreed within less than 1% for each network.

Glass Transition Temperatures. This property was determined by DSC on both saltless and salt-containing networks kept under nitrogen. In order to avoid complications due to the possible crystallization of poly(ethylene oxide) segments in the corresponding networks, all these determinations were conducted according to the following procedure: the samples were placed in a sealed capsule, kept at 100 °C for 1 h, then quenched into liquid nitrogen (to freeze the amorphous conformation), and thereafter analyzed from −165 to 200 °C with a heating rate of 20 °C min^{-1}.

Results and Discussion

Specific Volume. Two sets of experiments were carried out, viz., those on networks without $LiClO_4$ and those on salt–networks systems. All networks were prepared with Desmodur R (see Table I).

Saltless Networks. The variable characterizing the saltless networks in the present context is the cross-link molality *m*. It was found that the specific volume $\bar{V}$ decreased linearly with the cross-link density, according to the relationship at room temperature:

$$\bar{V} = \bar{V}_0 - 0.11\ m \qquad \text{(I)}$$

as shown in Figure 1, where $\bar{V}_0$ is the extrapolated specific

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Table I
Network Precursors

polyether-ols, formula (abbreviation)	source	$\bar{M}_n$	$\bar{F}_n{}^a$	$\bar{M}_w/\bar{M}_n$
poly(ethylene oxide)-α,ω-diol (PEO), $HO-(CH_2CH_2O)_n-H$	Merck	220	2.07	1.03
		420	2.04	1.03
		620	2.03	1.03
		1050	2.03, 2.04	1.05
		1550	2.02	1.05
		2100	2.05, 2.05	1.06
		3200	2.05	1.04
		3800	2.07	
		6000	2.08	
		10000	2.06	
triblock copolymers α,ω-diol PEO-*b*-POP-*b*-PEO	BASF, Wyandotte and Ugine Kuhlmann			
$HO(C_2H_4O)_{45}(C_3H_6O)_{17}(C_2H_4O)_{45}H$ (Pluronic F 38)		4980	2.03	
$HO(C_2H_4O)_{78}(C_3H_6O)_{28}(C_2H_4O)_{78}H$ (Pluronic F 68)		8390	2.04	
graft–block copolymers poly(dimethylsiloxane)-*g*-polyether (*b*)	Rhône-Poulenc	19400	14	
PDMS-*g*-(POP-*b*-POE)OH				
$(CH_3)_3Si-(OSi(CH_3)_2)_{28}-(OSiCH_3R)_{14}-OSi(CH_3)_3$ (R = $-CH_2CH_2CH_2-(OC_3H_6)_{10}-(OC_2H_4)_{12}OH$				

multifunctional isocyanates, formula (abbreviation)	source	molar mass
hexamethylene diisocyanate, $OCN(CH_2)_6NCO$ (HMDI)	Merck	168
4,4′,4″-methylidynetris(phenyl isocyanate), $HC(C_6H_4NCO)_3$ (Desmodur R)	Bayer	367
$OCN(CH_2)_6N(CONH(CH_2)_6NCO)_2$ (Desmodur N)	Bayer	478

[a] Average functionality (OH) as determined by acetylation or ^1H NMR.

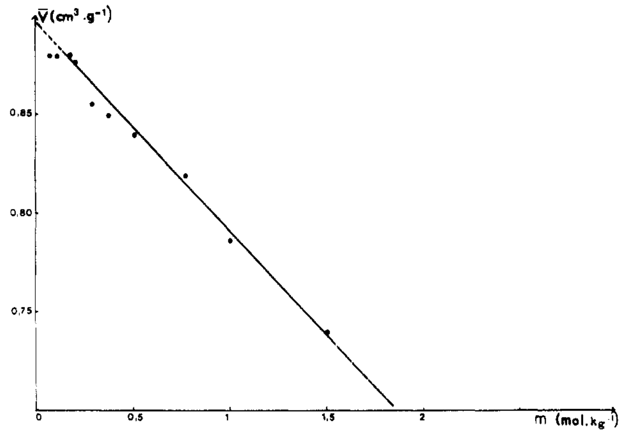

Figure 1. Dependence of the specific volume on cross-linking molality for a series of networks prepared with PEO glycols of different $\bar{M}_n$ and Desmodur R triisocyanate (see Table I).

volume of a linear chain of infinite DP, i.e., $m = 0$. It should be pointed out here that the value of $\bar{V}_0$ obtained, 0.896 cm^3 g^{-1} at room temperature, represents the specific volume of a high molecular weight PEO sample devoid of crystallinity and is not to be assimilated with that of the actual high molecular weight linear polymer which has a strong tendency to crystallize. Indeed, $\bar{V}$ becomes constant below a critical value of m (cf. Figure 1) because crystalline regions tend to dominate. These considerations do not take into account the presence of urethane structures. One can rewrite eq I in a form which reflects the presence of both chemical species forming the network in a additive fashion, viz.,

$$\bar{V} = \bar{V}_0 + \varphi_u(\bar{V}_u - \bar{V}_0) \qquad \text{(II)}$$

where φ_u is the weight fraction of urethane groups and $\bar{V}_u$ the specific volume of the starting isocyanate, i.e., 0.787 cm^3 g^{-1} for 4,4′,4″-methylidynetris(phenyl isocyanate), as determined by pycnometry in our laboratory on the commercial sample used. It follows from the molecular weight of 4,4′,4″-methylidynetris(phenyl isocyanate) (Table I) that $\varphi_u = 0.367\ m$ and that

$$\bar{V} = \bar{V}_0 - 0.04\ m \qquad \text{(III)}$$

if additivity principles apply. In fact, the corresponding experimental relationship is quite different (eq I), as if cross-linking produced a "shrinkage" corresponding to $\Delta\bar{V} = 0.07\ m$. This seems abnormally high and might arise either from important hydrogen bond interactions and/or from an incorrect value of the actual density of urethane links in the networks.

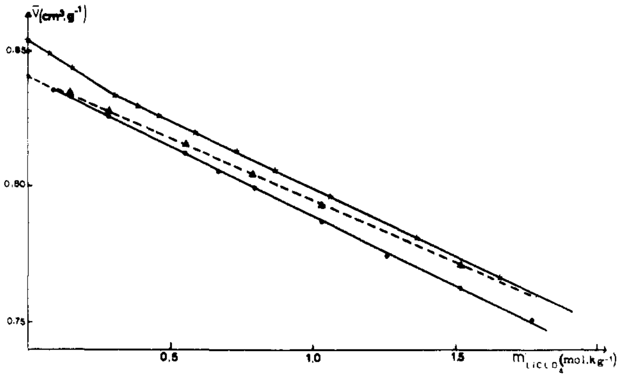

Figure 2. Dependence of the specific volume on LiClO$_4$ molality for networks based on PEO and Desmodur R triisocyanate: (●) PEO 1050; (☆) PEO 2100; (▲) calculated behavior in the case of volume additivity between salt and network.

Salt-Containing Networks. Only the networks prepared with PEO 1050 and 2100 were studied. Figure 2 shows the results as a function of the LiClO$_4$ molality m'. The linear behavior is expressed by the relationship

$$\bar{V} = \bar{V}_0' - 0.051\ m' \qquad \text{(IV)}$$

where $\bar{V}_0'$ is the specific volume of the corresponding saltless network (we have no explanation at present for the slight deviation from linearity of the $\bar{V}$ values of networks prepared with PEO 2100 at low LiClO$_4$ concentration). Once again, if one assumes volume additivity of networks and LiClO$_4$, the dottle line in Figure 2 should be expected. This corresponds to

$$\bar{V} = \bar{V}_0' - 0.046\ m' \qquad \text{(V)}$$

In fact, here too the experimental results reflect a contraction with respect to additivity; namely,

$$\Delta\bar{V} = 0.005\ m' \qquad \text{(VI)}$$

This shrinkage suggests that the introduction of lithium

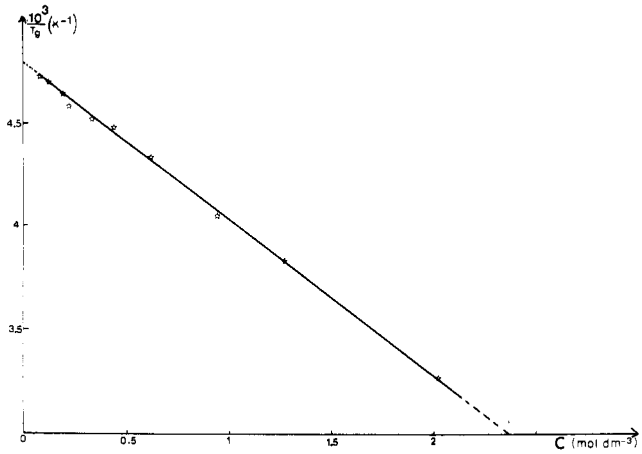

Figure 3. Dependence of the inverse of T_g on cross-linking molarity for a series of networks prepared with PEO glycols of different $\bar{M}_n$ and Desmodur R triisocyanate.

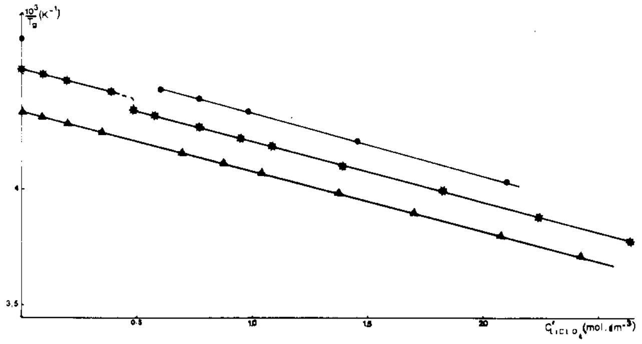

Figure 4. Dependence of the inverse of T_g on LiClO$_4$ molarity for networks based on PEO and Desmodur R triisocyanate: (▲) PEO 1050; (★) PEO 2100; (●) PEO 3800.

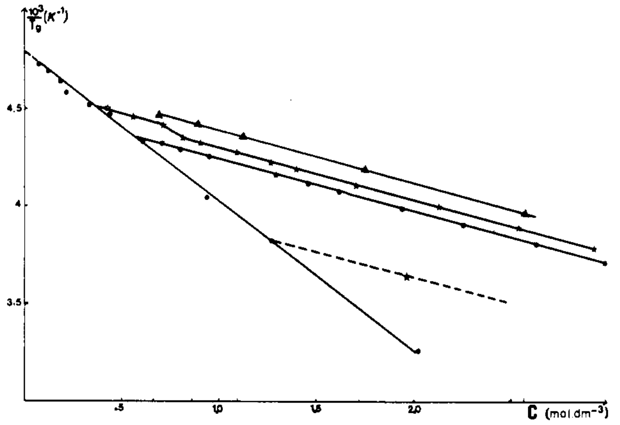

Figure 5. Dependence of T_g^{-1} on the combined influence of chemical (urethane) and physical cross-links (LiClO$_4$) for a series of networks prepared with PEO glycols of different $\bar{M}_n$ and Desmodur R triisocyanate: (●) without salt; (★) PEO 420 + LiClO$_4$; (*) PEO 1050 + LiClO$_4$; (☆) PEO 2100 + LiClO$_4$; (▲) PEO 3800 + LiClO$_4$.

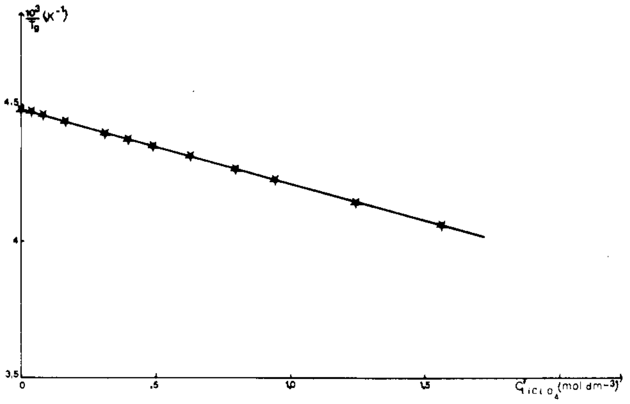

Figure 6. Dependence of T_g^{-1} on LiClO$_4$ molarity for networks based on PEO 1050 and Desmodur N triisocyanate (see Table I).

cations in the matrix induces a complexation with the ether functions, i.e., physicochemical cross-linking.

Glass Transition Temperature. As in the preceding section, T_g was determined on both saltless and salt-containing networks. In all instances, only one transition was recorded, indicating that these systems are thermodynamically homogeneous irrespective of the compositions tested.

Saltless Networks. These networks were prepared with Desmodur R (see Table I). Figure 3 shows the dependence of T_g on the molarity C of urethane bonds, which takes the linear form

$$T_g^{-1} = T_{g_0}^{-1} - 7.6 \times 10^{-4}\ C \qquad \text{(VII)}$$

where T_{g_0} is the extrapolated glass transition temperature of an infinitely loose network (Figure 3, T_{g_0} = 209 K). This extrapolated value reflects a fictional entity and is not to be assimilated to the T_g of a high-molecular weight linear amorphous PEO. Equation VII can be rearranged to give

$$\frac{T_g - T_{g_0}}{T_{g_0}} = \frac{0.16C}{1 - 0.16C} \qquad \text{(VIII)}$$

which shows the same form as Di Marzio's relationship[7]

$$\frac{T_g - T'_{g_0}}{T'_{g_0}} = \frac{aC}{1 - aC} \qquad \text{(IX)}$$

where, however, T'_{g_0} refers to a linear copolymer possessing the same composition as the network.

Salt-Containing Networks. The networks studied included those prepared with PEO 1050, 2100, 3800. Figure 4 shows that for a given PEO cross-linked with Desmodur R triisocyanate, a linear relationship is obtained between T_g^{-1} and the LiClO$_4$ molar concentration C'; viz.,

$$T_g^{-1} = T_{g_0}^{-1} - 2.7 \times 10^{-4}\ C' \qquad \text{(X)}$$

where T_{g_0} is the glass transition temperature of the corresponding salt-free network. As in the context of the specific volume results, one can compare here the effect of covalent cross-link density with salt concentration, i.e., eq VII and X. In both situations it is clear that T_g increases with the relevant parameter but again, as with $\bar{V}$, the stiffening effect of urethane cross-links is more important than that of ionic interactions with PEO segments by a factor of about 3. Figure 5 shows the combined influence of chemical and physical cross-links in an abacus form which allows the reckoning of T_g for all network situations within the specific context (here PEO–Desmodur R–LiClO$_4$). This leads to a master curve obtained by redefining for each network an apparent cross-link density calculated by considering that three ionic junctions are needed to produce the same effect as one urethane branching point. Thus, the knowledge of the $\bar{M}n$ of the PEO glycol and of the LiClO$_4$ concentration allows the straightforward reading of the T_g of the resulting network prepared with Desmodur R triisocyanate.

Similar networks were prepared with another trifunctional isocyanate, viz., Desmodur N (see Table I). The behavior was close to that encountered above (see Figure 6) and described by the empirical relationship (X). Thus, the only variations that the change of cross-link agent introduced was a slight decrease in T_g for the same overall

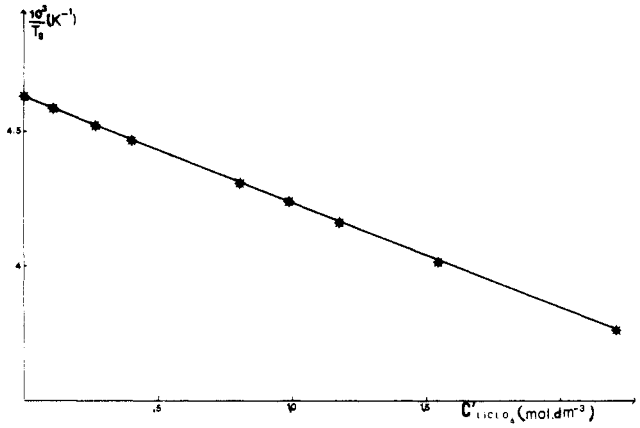

Figure 7. Dependence of T_g^{-1} on $LiClO_4$ molarity for networks based on a triblock copolymer, PEO-*block*-PPO-*block*-PEO glycol ($\bar{M}_n$ = 4980) and Desmodur R triisocyanate (see Table I).

cross-link density, due to the increased flexibility of the urethane moieties when going from an aromatic to an aliphatic triisocyanate.

If one replaces the PEO glycol with a triblock copolymer, viz., PEO-*block*-PPO-*block*-PEO glycol (see Table I), cross-linking with either Desmodur R or Desmodur N (see Table I) leads to networks whose T_g variations are typified in Figure 7. It was found again that T_g decreased with increasing sequential size, increased with increasing $LiClO_4$ concentration, and decreased slightly when Desmodur R was replaced by Desmodur N. However, the slope of the T_g^{-1} versus C' plots (Figure 7) were somewhat higher with block copolymers than with PEO (3.9×10^{-4} K^{-1} mol^{-1} dm^3). This general trend is readily explained qualitatively by the fact that the lithium ions are solvated more strongly by the PEO than by the PPO units. Confirmation of this preferential solvation was obtained by looking at the ^7Li NMR[8] of PEO-*block*-PPO-*block*-PEO based networks containing $LiClO_4$. Up to a critical concentration (corresponding to a partitioning by $LiClO_4$ of PEO blocks into subchains of 12 EO units), only one line was observed whose frequency was the same as that corresponding to $^7Li^+$ in PEO-based networks.[9] Above this critical concentration, a second line appeared as a shoulder on the first one.[9] This behavior suggests that before any complexation with PO units can occur, the PEO chains must first be "saturated" with $LiClO_4$, i.e., that PEO is a better solvating agent than PPO.

Networks prepared with HMDI and PDMS-*graft*-(PPO-*block*-PEO) (see Table I) were also studied. The siloxane units were found not to solvate $LiClO_4$. This was confirmed by experiments with linear PDMS since $LiClO_4$ could not be dissolved in these silicone oils. Thus, the only sites for physical cross-linking were again the PPO-*block*-PEO branches (and preferably the PEO blocks). However, the PDMS trunk contributed to a considerable lowering of T_g, as expected. Figure 8 shows the dependence of T_g^{-1} upon C' and again a linear correlation was obtained. The slope is here the highest encountered among all types of networks studied (5.6×10^{-4} K^{-1} mol^{-1} dm^3), a fact which is readily explained by the incompatibility of $LiClO_4$ with PDMS chains. Note that this does not imply any phase segregation, since these networks exhibited a single T_g.

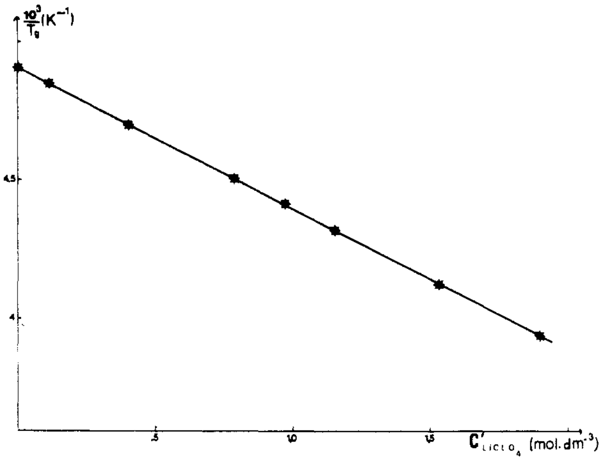

Figure 8. Dependence of T_g^{-1} on $LiClO_4$ molarity for networks based on a graft copolymer PDMS-*graft*-(PEO-*block*-PPO) polyol and HMDI (see Table I).

Conclusion

It seems well established that the ions arising from the dissociation of $LiClO_4$ can bind strongly with oxygen atoms belonging to ether groups of different chains. These interactions are equivalent to (reversible) cross-links and manifest themselves through a characteristic shrinkage of the network and an increase of its glass transition temperature. Both phenomenon have been quantified and suggest regular PEO chain partitioning by the salt.

Registry No. (PEO)(4,4′,4″-methylidynetris(phenyl isocyanate)) (copolymer), 75587-26-7; (PEO)(1,3,5-tris(6-isocyanotohexyl)biuret) (copolymer), 67554-44-3; (PEO)(Desmodur R) (copolymer), 75587-27-8; (PPO)(Desmodur R) (copolymer), 75587-62-1; (PEO)(Desmodur N) (copolymer), 67544-33-0; $LiClO_4$, 7791-03-9; (4,4′,4″-methylidynetris(phenyl isocyanate))(pluronic) (copolymer), 87091-98-3.

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