Index of refraction, density and viscosity measurements of poly(propylene glycol)–salt complexes

W. Wixwat, Y. Fu and J. R. Stevens*
Guelph–Waterloo Program for Graduate Work in Physics, Guelph Campus, University of Guelph, Guelph, Ontario, Canada N1G 2W1

(*Received 2 February 1990; revised 25 April 1990; accepted 17 May 1990*)

Measurements of refractive index with temperature and salt concentration have been made for poly(propylene glycol) (PPG 4000) complexed with $LiClO_4$, NaSCN, $LiCF_3SO_3$ and $NaCF_3SO_3$. For the triflate solutions, the refractive index decreases with increasing concentration; while for the NaSCN and $LiClO_4$ solutions, it increases. Measurements of viscosity and density are also reported and used to explain these results.

(Keywords: refractive index; density; poly(propylene glycol); lithium and sodium salts)

INTRODUCTION

Since the mid-1970s, there has been considerable interest[1] in complexing lithium and sodium salts with polyethers such as poly(ethylene glycol) (PEG) and poly(propylene glycol) (PPG) and their copolymers. This interest stems from a desire to synthesize polymeric electrolytes that may be used in batteries, fuel cells, smart windows, etc.

Raman and Brillouin light scattering techniques, among others, have been used to study these complexes[2–5]. Interpretation of these results and others is aided by a knowledge of the variation of refractive index, glass transition temperature, viscosity and density with salt concentration in the polyethers. While there have been some reports on glass transition temperature measurements[6–11], viscosity[9,11] and specific volume[7,8,10], there has been no discussion of the variation of refractive index with salt concentration and temperature in these complexes.

In this paper, we report on changes of refractive index with temperature and salt concentration in PPG 4000 complexed with $LiClO_4$, NaSCN, $LiCF_3SO_3$ and $NaCF_3SO_3$. Measurements of density and viscosity are also included over the same temperature and concentration range and assist in the discussion of the refractive index results.

EXPERIMENTAL

Great care was taken in the preparation of the samples of PPG (Polyscience Inc., molecular weight 4000) complexed with alkali-metal salts. The PPG 4000 as received was clear and was dried in a sealable flask on a vacuum line at 10^{-4} Torr using a freeze–thaw method with continual pumping. After about ten cycles, no bubbles evolve after thawing and the crazing that occurs on fast freezing in liquid nitrogen has been considerably reduced. It is then assumed that the PPG is sufficiently free of dissolved gases such as O_2 and low-molecular-weight solvents and oligomers including bound water. In support of this assumption, we note that our *FT*i.r. and Raman measurements of poly(propylene oxide) (PPO) capped with C_4H_9 and a short sequence of poly(dimethylsiloxane) and prepared in the same way showed, respectively, no evidence of the H_2O bending mode at $1635\ cm^{-1}$ and no evidence of the OH stretch in the $3600–3700\ cm^{-1}$ region. In fact, the Raman background (2 counts/s per cm^{-1}) was 30 times lower than the nearest PPO peaks in the $2900–3000\ cm^{-1}$ region. We also performed a thermogravimetric analysis on the dried PPG 4000 using a Perkin–Elmer TGAA-7. Raising the temperature ($20°C\ min^{-1}$) from 30 to 130°C produced a change in weight of 0.06%. This weight loss would include low-molecular-weight organic substances. The sealed flask containing the dried PPG 4000 was then transferred to a large, dry argon atmosphere glove-box.

The salts $LiCF_3SO_3$ (98% Aldrich), $NaCF_3SO_3$ (98% Alfa, Morton Thiokal Inc.), $LiClO_4$ (anhydrous, Alpha) and NaSCN (98% Aldrich) were used immediately on receipt, except for NaSCN, and opened in argon. The NaSCN was dried in a vacuum oven at 150°C for three days before use and transferred directly to the argon atmosphere. Salts are stored under vacuum.

Because of the preparation procedures for the components, we were able to dissolve the salts directly into the PPG without intermediary solvent. This was effected by stirring at temperatures in the 70–90°C range. Without the stringent drying, this dissolution is not possible in this temperature range. Generally the samples had an ether oxygen to metal cation ratio (O:M) in the range 16:1, 12:1, 10:1, 8:1 and 5:1. In addition, samples of $LiCF_3SO_3$ in PPG 4000 were prepared with ratios in the range 30:1 and 20:1.

The refractive index measurements were carried out using an Atago-1T refractometer in conjunction with an Haake temperature bath, which was outside the glove-box. The thermal fluid circulation was in a closed system. The density measurements were made pycnometrically and the viscosity measurements were made using a

---

* To whom correspondence should be addressed

0032-3861/91/071181-05

Brookfield rotating viscometer. Temperatures were controlled to ±0.2°C.

RESULTS AND DISCUSSION

Figures 1a and *1b* show plots of the density of PPG 4000–salt complexes *versus* temperature for respectively O:M ratios of 16:1 and 10:1. *Table 1* gives data on molecular weights and values of the percentage of salt in PPG 4000 by weight for various O:M ratios. As expected, all densities decrease with increasing temperature, and the higher the weight per cent salt in PPG 4000, the more dense the complex. The densities of the triflate complexes increase much less than would be expected on the basis of the molecular weights of the salts.

Figure 2a shows a plot of density *versus* M:O ratio at 52°C for ratios 0.0625 (O:M = 16:1) and 0.1 (O:M = 10:1). The relative position of the densities of these various PPG–salt complexes (*Figures 1a*, *1b* and *2a*) is a function of molecular weight and molar volume. Molar volume is in turn a function of ionic size and shape as well as salt dissociation and solvation characteristics. In *Figure 2b*, the molar volumes for PPG–salt complexes are plotted against M:O ratios at 52°C; the effect of molecular weight has been removed and we find the position of the PPG–$LiClO_4$ and PPG–NaSCN complexes inverted in comparison with *Figure 2a*. This is due to the higher compression that the PPG solvent experiences in the neighbourhood of the Li^+ cation compared to the Na^+ cation and the fact that the ClO_4^- anion is approximately spherical while the SCN^- anion is linear. Also for these concentrations there is a higher percentage of ion pairs in PPG–NaSCN[12] than in PPG–$LiClO_4$[13] where the fraction of free anions is considerably higher than the fraction of ion pairs. Lattice energies have been used to calculate anionic radii[16] (*Table 2*) involving the assumption of spherical ions.

Figures 3a, *3b* and *3c* show plots of the natural logarithm of the viscosity (ln η) *versus* reciprocal temperature for respectively PPG–$NaCF_3SO_3$, PPG–

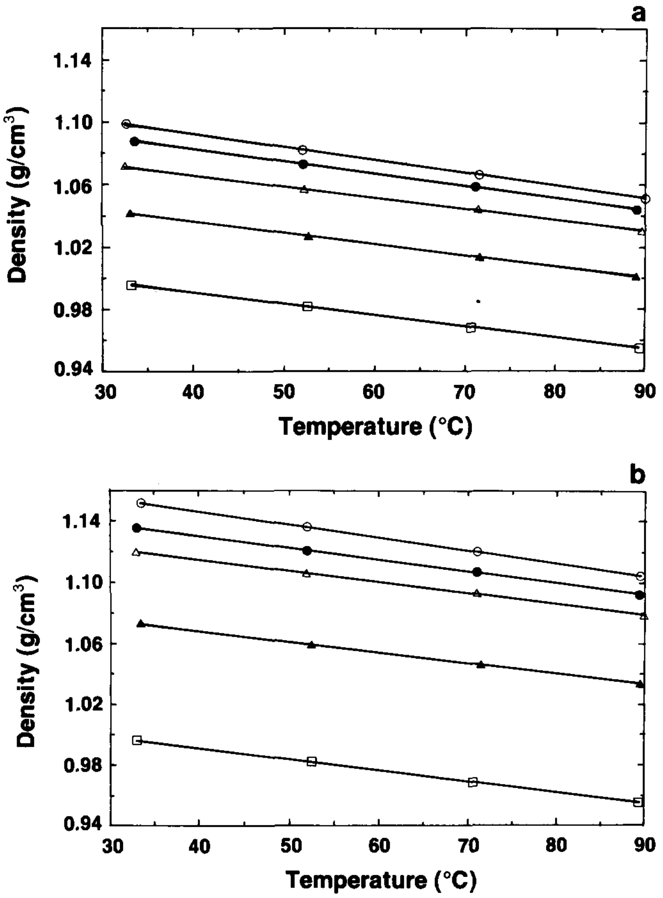

Figure 1 Density *versus* temperature for M:O ratios of (a) 1:16 and (b) 1:10 for the various PPG–salt complexes: (○) $NaCF_3SO_3$, (●) $LiCF_3SO_3$, (△) $LiClO_4$, (▲) NaSCN and (□) pure PPG

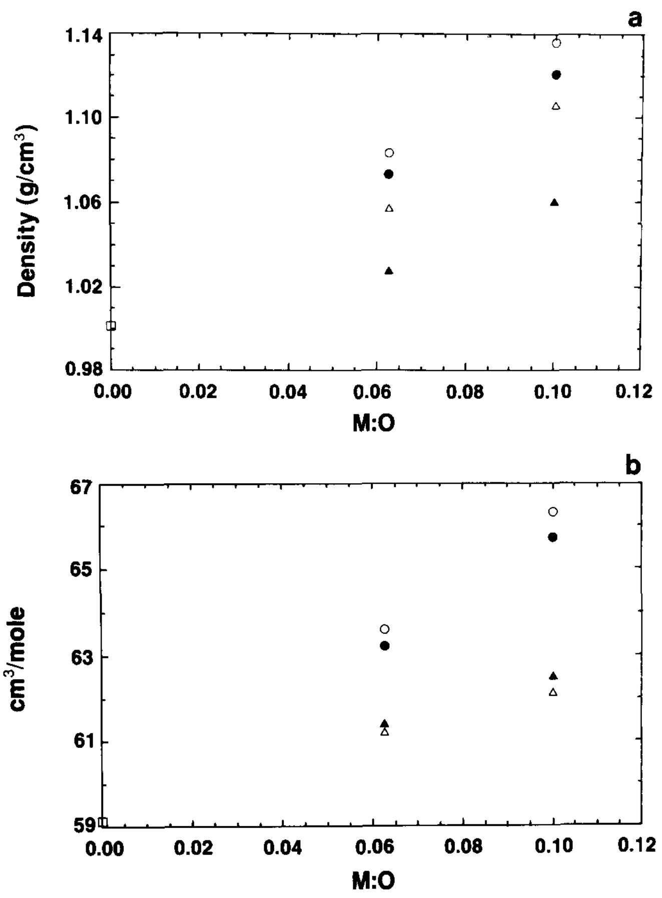

Figure 2 (a) Density and (b) molar volume *versus* salt concentration for the various PPG–salt complexes at 52°C: (○) $NaCF_3SO_3$, (●) $LiCF_3SO_3$, (△) $LiClO_4$, (▲) NaSCN and (□) pure PPG

Table 1 Amounts of salt in complexes

		Salt (%) dissolved in PPG 4000 for various O:M ratios				
	Mol. wt. (g mol^{-1})	16:1	12:1	10:1	8:1	5:1
$NaCF_3SO_3$	172.01	15.6	19.8	22.9	27.0	37.2
$LiCF_3SO_3$	155.96	14.4	18.3	21.2	25.2	35.0
$LiClO_4$	106.39	10.3	13.3	15.4	18.7	26.8
NaSCN	81.06	8.0	10.4	12.3	14.9	21.8

Table 2 Cationic and anionic radii

	Ionic radius (nm)	Ref.
Li^+	0.068	14
Na^+	0.097	14
$CF_3SO_3^-$	0.289	15
ClO_4^-	0.240	16
SCN^-	0.213	16

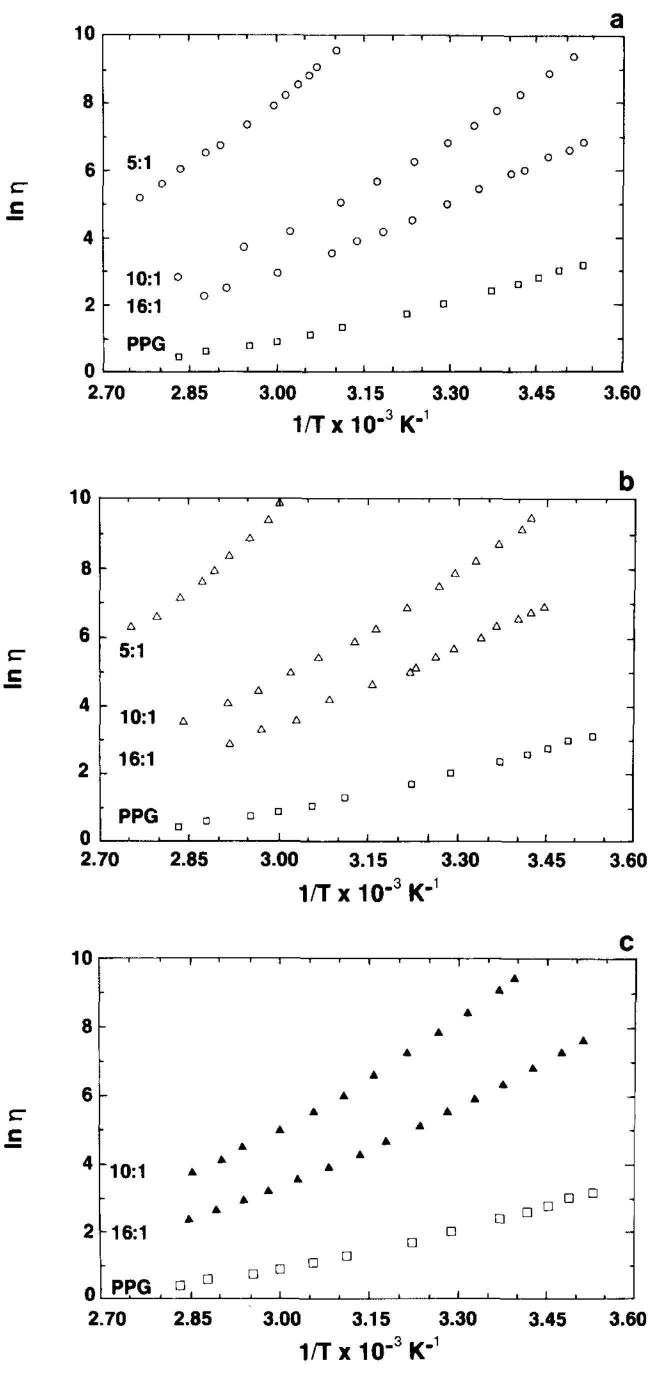

Figure 3 Viscosity *versus* temperature for various salt concentrations in PPG: (a) $NaCF_3SO_3$; (b) $LiClO_4$; (c) NaSCN

$LiClO_4$ and PPG–NaSCN for various O:M ratios. Viscosity was measured in poise. Viscosity data for pure PPG 4000 are included in each figure and are in approximate agreement with Eisenberg *et al.*[11] and Wang *et al.*[17] except at low temperatures where their viscosities are higher. For the 10:1 samples, $\eta(\text{PPG–NaCF}_3\text{SO}_3) < \eta(\text{PPG–LiClO}_4) < \eta(\text{PPG–NaSCN})$. For the 16:1 samples, $\eta(\text{PPG–NaCF}_3\text{SO}_3) < \eta(\text{PPG–LiClO}_4) \approx \eta(\text{PPG–NaSCN})$. The viscosity data for the PPG–$NaCF_3SO_3$ complex for an O:M ratio of 16:1 are in agreement with McLin and Angell[9]. However, the viscosity data for the PPG–$LiClO_4$ complex are lower than that obtained by Eisenberg *et al.*[11]. These authors dissolved their salts directly into the PPG 4000, which they obtained from Polysciences. Sources of discrepancy would be the fact that they used capillary viscometers and that PPG was not as stringently dried as in our experiment. Noteworthy are the values of the glass transition temperature obtained by Eisenberg *et al.*[11], which were higher than those obtained by us[6], especially for pure PPG, indicating a tendency towards higher viscosities. The agreement with McLin and Angell[9] is interesting since they used methanol to get the salt into the PPG 4000, which was not as stringently vacuum-treated as ours.

Figure 4a shows the temperature variation of refractive index (n) for pure PPG 4000 and complexes PPG–$LiCF_3SO_3$, PPG–$NaCF_3SO_3$ and PPG–$LiClO_4$ for O:M = 12:1. The temperature coefficients are listed in *Table 3*; these become less negative with increase in salt concentration.

Figure 4b shows a plot of n *versus* M:O for the same five systems. It can be seen that n decreases with increasing temperature over the temperature range studied. Also n increases with concentration for PPG–

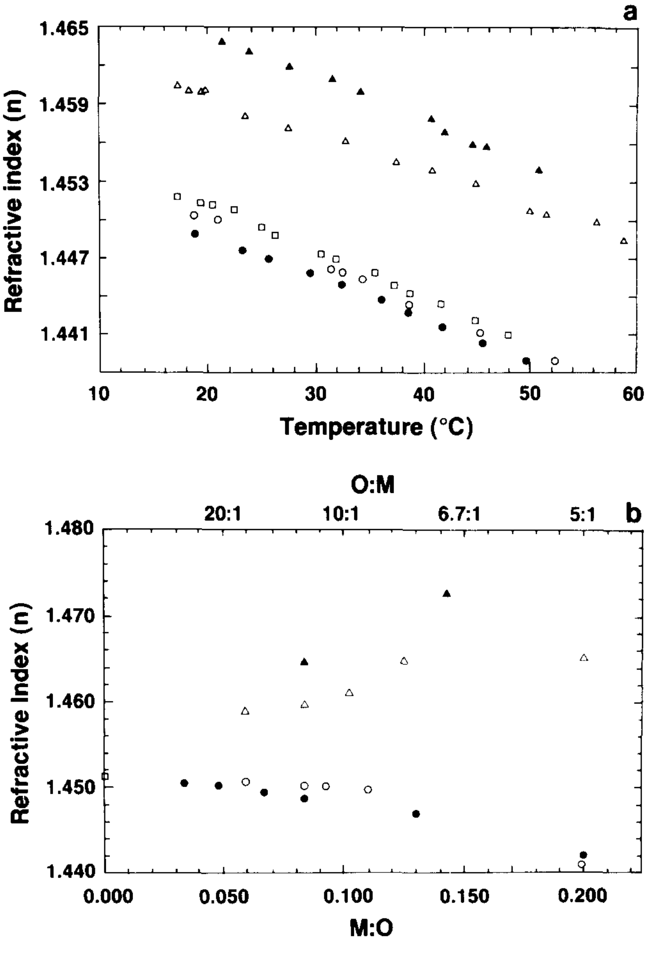

Figure 4 Refractive index n *versus* (a) temperature for M:O = 1:12 and (b) salt content at 20°C for various salts in PPG: (○) $NaCF_3SO_3$, (●) $LiCF_3SO_3$, (△) $LiClO_4$, (▲) NaSCN and (□) pure PPG

Table 3 Temperature coefficients of refractive index

Solution	O:M	d*n*/d*T* (10^{-4} K^{-1})
PPG 4000	–	−3.64
PPG–$NaCF_3SO_3$	17:1	−3.45
	12:1	−3.44
	11:1	−3.42
	8:1	−3.41
	5:1	−3.03
PPG–$LiCF_3SO_3$	30:1	−3.56
	21:1	−3.48
	15:1	−3.47
	12:1	−3.26
	8:1	−3.11
	5:1	−3.04
PPG–$LiClO_4$	17:1	−3.35
	12:1	−3.27
	10:1	−3.21
	8:1	−3.10
	5:1	−3.01
PPG–NaSCN	12:1	−3.50
	7:1	−3.40

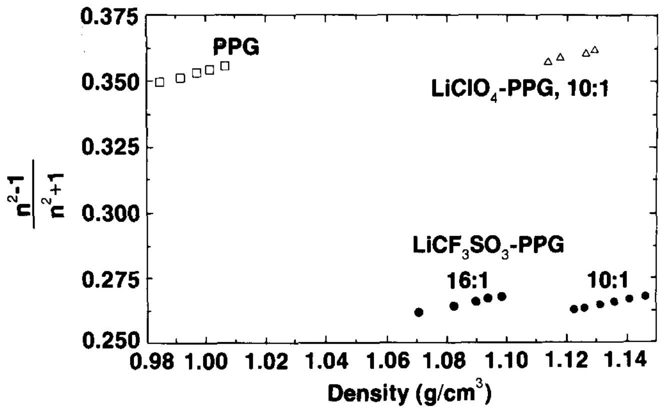

Figure 5 Plot of $(n^2-1)/(n^2+1)$ *versus* density for (△) PPG–$LiClO_4$, (●) PPG–$LiCF_3SO_3$ and (□) pure PPG

$LiClO_4$ and PPG–NaSCN (greatest increase) and decreases with concentration for PPG–$LiCF_3SO_3$ and PPG–$NaCF_3SO_3$.

One of the empirical relationships for refractive index is the Lorentz–Lorenz relationship (cgs units):

$$\frac{n^2-1}{n^2+2}=\frac{4\pi}{3}\rho'\alpha \tag{1}$$

where ρ' is the number density and α is the polarizability. The Clausius–Mossotti equation for high-frequency alternating fields is:

$$\frac{\varepsilon_\infty-1}{\varepsilon_\infty+2}=\frac{4\pi}{3}\rho'\alpha \tag{2}$$

in which ε_∞ is the dielectric constant at a probe frequency for which the permanent dipoles (i.e. the orientational polarization) can no longer follow the changes of field but where the atomic and electronic polarizations are still the same as in static fields. Thus, induced polarization is characterized by ε_∞. At still higher frequencies such as those in the visible region, only the electronic polarization responds and $n^2=\varepsilon_\infty$. Thus, α in equation (1) is a measure of that polarizability related to the electronic polarization and is applicable here since the viscous liquids being studied are colourless. Critically speaking, $n^2(\omega)=\varepsilon'(\omega)$ where $\varepsilon'(\omega)$ is the real part of the dielectric constant and α should be obtained by extrapolating to zero frequency without taking into account any contribution from the atomic or orientational polarization. Since the change in n with frequency is small, we will consider $\alpha=\alpha^e$, the electronic polarizability.

In *Figure 5*, we plot $(n^2-1)/(n^2+2)$ *versus* density for $LiClO_4$–PPG 4000 (O:M = 10:1), $LiCF_3SO_3$–PPG 4000 (O:M = 16:1 and 10:1) and PPG 4000. Although it would be better to have measured n and ρ over a wider temperature range, the indication is that the Lorentz–Lorenz relationship holds. For pure PPG 4000, the polarizability can be calculated to be 8.1×10^{-24} cm^3. The effective polarizabilities for PPG–$LiCF_3SO_3$ (10:1 and 16:1) are 6.2×10^{-24} cm^3. The effective polarizability for PPG–$LiClO_4$ (10:1) is not significantly different from pure PPG 4000, slightly lower if anything.

When the salt is introduced into the PPG 4000 solvent, it first dissociates. The polyether chain is a Lewis base; the ether oxygens are donors and the salt cations acceptors; the cations are solvated. The anion is probably only weakly solvated (if at all) and locates among the polymer chains. Studies on the triflate anion show it to be a very poor ligand[18].

From the results of *Figures 1* to *4*, it can be seen that the main influence on the refractive index is density. The $CF_3SO_3^-$ anions open up the PPG 4000 at the molecular level and offset the effect of the compression due to the Li^+ and Na^+ cations. Coupled with the 2–3% lowering of the effective polarizability, the refractive index decreases with increasing concentration, the $LiCF_3SO_3$ solution being the lowest except at the highest concentration where the higher compression around the smaller Li^+ ion causes less reduction in n for the 5:1 concentration. On the other hand, the smaller ClO_4^- and SCN^- anions are not able to overcome the compressional effects of the cations and, since the effective polarizability does not make a significant contribution, the refractive index increases with increasing concentration, the NaSCN solution having the largest increase in n since the SCN^- anion requires less volume than the ClO_4^- anion and where solvation takes place is more strongly solvated[19]. A mixture (O:M = 10:1) of PPG–$LiCF_3SO_3$ (87 wt%)–$LiClO_4$ (13 wt%) gives a refractive index equal to that for PPG 4000.

Structural relaxation in these systems is responsible for the movement of the ions[5,20,21].

CONCLUSIONS

The variation of refractive index with temperature and salt concentration has been measured for the complexes formed between poly(propylene glycol) and some lithium and sodium salts. Generally, refractive index decreases with temperature, with the rate of change increasing as the concentration increases. For the larger anion triflate systems, the refractive index decreases with concentration, but for the smaller anions of SCN^- and ClO_4^-, the 'structure-making' properties of the Li^+ and Na^+ cations more than offset the 'structure-breaking' properties of the anions. The Lorentz–Lorenz relation holds.

ACKNOWLEDGEMENT

Acknowledgement is given for financial support from the

Natural Sciences and Engineering Research Council of Canada.

REFERENCES

1 MacCallum, J. R. and Vincent, C. A. (Eds) 'Polymer Electrolyte Reviews 1 and 2', Elsevier Applied Science, London, 1987, 1989
2 Schantz, S., Torell, L. M. and Stevens, J. R. *J. Appl. Phys.* 1988, **64**, 2038
3 Schantz, S., Sandahl, J., Borjesson, L., Torell, L. M. and Stevens, J. R. *Solid State Ionics* 1988, **28–30**, 1047
4 Sandahl, J., Schantz, S., Borjesson, L., Torell, L. M. and Stevens, J. R. *J. Chem. Phys.* 1989, **91**, 655
5 Sandahl, J., Borjesson, L., Stevens, J. R. and Torell, L. M. *Macromolecules* 1990, **23**, 163
6 Stevens, J. R. and Schantz, S. *Polym. Commun.* 1988, **29**, 328
7 LeNest, J.-F., Gandani, A., Cheradame, H. and Cohen-Addad, J.-P. *Macromolecules* 1988, **21**, 1117
8 LeNest, J.-F., Gandani, A. and Cheradame, H. *Br. Polym. J.* 1988, **20**, 253
9 McLin, M. and Angell, C. A. *J. Phys. Chem.* 1988, **92**, 2083
10 Moacanin, J. and Cuddihy, E. F. *J. Polym. Sci.* (*C*) 1966, **14**, 313
11 Eisenberg, A., Ovans, K. and Yoon, H. N. 'Ions in Polymers' (Ed. A. Eisenberg), Adv. Chem. Ser. No. 187, American Chemical Society, Washington, DC, 1980, p. 267
12 Teeters, D. and Frech, R. *Solid State Ionics* 1986, **18/19**, 271
13 Schantz, S., Torell, L. M. and Stevens, J. R. *J. Appl. Phys.* 1988, **64**, 2038
14 'Handbook of Chemistry and Physics', 68 Edn (Ed. R. C. Weast), CRC Press, Boca Raton, FL, 1987–1988, p. F-159
15 Munshi, M. Z. A. and Owens, B. B. *Polym. J.* 1988, **20**, 577
16 Jenkins, H. D. B. and Thakur, K. P. *J. Chem. Educ.* 1979, **56**, 576
17 Wang, C. H., Fytas, G., Lilge, D. and Dorfmuller, Th. *Macromolecules* 1981, **14**, 1363
18 Scott, A. and Taube, H. *Inorg. Chem.* 1971, **10**, 62
19 Parker, A. J. *Quarterly Rev.* 1962, **16**, 163
20 Albinsson, I., Mellander, B.-E. and Stevens, J. R. *Polymer* in press
21 Sandahl, J., Schantz, S., Börjesson, L., Torell, L. M. and Stevens, J. R. *J. Chem. Phys.* 1989, **91**, 655