Factors Governing Solvate Stability in Polyethers Complexed with Alkali Thiocyanates

M. Dumont, D. Boils, P. E. Harvey, and J. Prud'homme*

Department of Chemistry, University of Montreal, Montreal, Quebec, Canada H3C 3V1

Received August 15, 1990; Revised Manuscript Received October 17, 1990

ABSTRACT: Solubilities of LiSCN, NaSCN, KSCN, and CsSCN in atactic poly(methyl glycidyl ether) (PMGE) have been determined by means of glass transition temperature (T_g) and calorimetric measurements. For all salts except LiSCN, step decreases in solubility were observed with increasing temperature over the range 25–200 °C. The data for NaSCN and KSCN indicate that solvates of well-defined compositions are stable over a range of temperatures on either side of the transitions. A comparison of these compositions with those reported for poly(ethylene oxide) (PEO) reveals that several factors govern solvate stability in polyethers. Among these factors are configurational entropy, cation–oxygen binding energy, ion–ion Coulombic interactions, and presumably space-filling forces related to the size of the anion. For a given O/salt (O = oxygen atom) molar ratio in the concentrated regime, the T_g elevations with respect to the salt-free polymers are substantially greater in PMGE than in PEO. This feature, which results from the complexation of the pendant groups in PMGE, indicates that the solvates formed in PMGE have lower configurational entropies than those formed in PEO. This factor, together with the decrease in binding energy with increasing cation size, is responsible for the transitions observed in PMGE. Also reported are solubility data obtained for NaSCN in a P(EO/MGE) random copolymer containing 10 mol % of MGE units. Contrary to PEO, this copolymer yielded mixtures that could be supercooled over the entire range of compositions.

Introduction

Better knowledge of ionic structure and interactions in solvent-free electrolytes consisting of alkali salts dissolved in amorphous polyethers is important for understanding the conduction mechanism of these materials.[1-4] In recent papers,[5-7] we reported an unusual and interesting feature concerning solubility of some alkali salts in poly(ethylene oxide) (PEO) that provided a route for characterizing the coordination numbers of the alkali cations in amorphous or liquid PEO. This feature is the temperature independence of the salt solubility curve in the phase diagrams of the corresponding binary systems. It suggests that salt solubility is governed by a well-defined solvation reaction according to the following equilibria:[5-7]

$$\mathrm{salt_S} \rightleftharpoons \mathrm{salt_L} \tag{1}$$

$$n\mathrm{EO_L} + \mathrm{salt_L} \rightleftharpoons (\mathrm{EO})_n\text{·}\mathrm{salt_L} \tag{2}$$

where EO denotes the repeating unit of PEO and subscripts S and L denote the solid and liquid phases, respectively. The solvation reaction (eq 2) proceeds with a substantial decrease in free enthalpy (large equilibrium constant), which favors its completion over a wide range of temperatures. Therefore, over this range, solubility corresponds to the solvate composition.

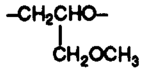
As reported in a former work[7] for LiSCN, NaSCN, KSCN, and CsSCN and as observed in a more recent work[8] for RbSCN, this solvation scheme applies to all the alkali thiocyanates. Their solvation numbers SN, as given by the variable n in eq 2, are about 3 for LiSCN, 4 for NaSCN, 5 for KSCN, 7 for RbSCN, and 9 for CsSCN. A plot of SN as a function of the cation atomic weight M_c to the power $^2/_3$, a quantity that is expected to be roughly proportional to the cation atomic spherical surface, yields a linear curve that extrapolates to SN = 2 at a zero value of M_c. From this linear correlation between SN and $(M_c)^{2/3}$, it has been deduced that the coordination numbers, CN, of the alkali cations in amorphous PEO are about 1 for Li^+, 2 for Na^+, 3 for K^+, 5 for Rb^+, and 7 for Cs^+. The fact that CN increases in the same ratio as the cation surface suggests that cation coordination is limited by spatial constraints resulting from the configuration of the polymer chains. Once a first oxygen atom is attached to a given cation, the possibility for additional links to the same cation depends upon both the size of the cation and the distribution of the oxygen atoms in the polymer matrix.

PEO amorphous electrolytes having EO/salt molar ratios in the range 8–9 could be prepared with LiSCN, KSCN, and CsSCN,[7] and also with KSO_3CF_3, $RbSO_3CF_3$, and $CsSO_3CF_3$.[8] The glass transition temperatures, T_g, of these electrolytes were in the range −36 to −26 °C. When compared at the same reduced temperatures ($T - T_g$) over the range $20 < T < 100$ °C, their conductivity magnitude (σ) increased in the same ratio as CN (or the cation surface).[7,8] It is likely that the ionic structure of such concentrated electrolytes consists of coordinated cations surrounded by an ion atmosphere of opposite sign. Under this assumption, the average distance between the ions, as well as the ion–ion interactions which depend upon this distance, would be the same in each of these series of electrolytes. Therefore, among the remaining variables, the most important one is the cation–oxygen binding energy. Since this variable is expected to increase in the same ratio as the cation surface charge density, it is probably the very factor underlying the correlation observed between σ and CN.

It was interesting to examine whether these unique features concerning solvation and conduction of alkali salts in PEO apply to other polyethers of well-defined structure. Among the homopolyethers known to dissolve alkali salts there are poly(propylene oxide) (PPO),[9-11] poly(methyl glycidyl ether) (PMGE),[12,13] and a number of other polymers that can be prepared from glycidyl ether derivatives.[13] In their atactic form, these polyethers provide interesting materials for studying the relationships between solvation and conduction in the case of alkali salts which are prone to form crystalline compounds with PEO. In the former work reported on the PEO–alkali thiocyanate systems,[7] amorphous electrolytes could not be obtained with NaSCN because such a compound, $P((EO)_3\text{·}NaSCN)$, readily crystallizes and forms a eutectic binary subsystem with PEO.[5] This feature also made it difficult to characterize solubility of NaSCN at low temperatures in amorphous PEO.[5] Similar problems were encountered with $LiSO_3CF_3$ and $NaSO_3CF_3$.[8]

In recent reports,[9-11] mixtures of atactic PPO with a variety of alkali salts, including KSCN, NaSCN, NaI, and $NaClO_4$, were shown to exhibit salt precipitation when heated above room temperature. This phenomenon, which was revealed by sharp endotherms in the DSC curves recorded on these mixtures, was reported to take place at temperatures that depended upon both the composition of the mixtures[9] and the nature of the salts.[9-11] In the case of KSCN, this temperature increased from 60 °C for O/salt = 8 (O = oxygen atom) to 120 °C for O/salt = 30. In the case of NaSCN, it increased from 160 °C for O/salt = 6 to 250 °C for O/salt = 20. These results, which indicate a substantial decrease in solubility with increasing temperature, contrast with those reported for the same salts in PEO.[5]

Contrary to PPO, PMGE has the same molecular formula as PEO. Furthermore, the oxygen atom in the pendant group of the PMGE repeating unit



$$-CH_2\underset{\displaystyle CH_2OCH_3}{\underset{|}{C}}HO-$$

is separated from the nearest oxygen atom in the chain backbone by a C–C bond. In view of these structural features, atactic PMGE appears to be a better choice than atactic PPO for undertaking a systematic investigation similar to that performed on PEO. Thermodynamically, PMGE is particularly interesting because it contains pendant groups that yield one additional ion–dipole interaction per C–C–O unit in the chain backbone.

In this paper we report DSC data (T_g and calorimetric measurements) that allow the definition of the temperature dependence of solubilities of LiSCN, NaSCN, KSCN, and CsSCN in atactic PMGE. It is shown that solubility of CsSCN is severely limited in this polymer, while solubilities of NaSCN and KSCN exhibit step decreases with increasing temperature over the range 25–200 °C. This behavior of NaSCN and KSCN provides new evidence that alkali salt solubility in polyethers is governed by well-defined solvation reactions. Furthermore, it provides a thermodynamical framework which, together with the T_g elevations measured in PMGE and PEO, allows a semiquantitative interpretation of the solvate stability in terms of binding energy and configurational entropy.

Also reported in this paper are DSC data obtained for mixtures of NaSCN with a P(EO/MGE) random copolymer containing 10 mol % of MGE units. Contrary to PEO, this copolymer yielded mixtures of low crystallinity that could be supercooled over the entire range of compositions. Since these data allow a quantitative comparison between NaSCN solubility at low temperatures in PEO and in PMGE, they are presented at the beginning of this paper. All the polymers used in this work were high molecular weight materials prepared by anionic polymerization.

Experimental Section

Materials. The PEO, P(EO/MGE), and PMGE samples were prepared by anionic polymerization by using potassium *tert*-butoxide as initiator and tetrahydrofuran (THF) as solvent. The polymerization reactions were carried out in evacuated and sealed all-glass reaction flasks (200 mL) by using the break-seal ampule technique. Monomer to initiator molar ratio was ca. 5×10^4, and monomer to solvent volume ratio was ca. 1:1. Monomers, THF, and *tert*-butyl alcohol were all contained in degassed flasks on a vacuum line. THF (distilled over sodium) and *tert*-butyl alcohol (recrystallized from the melt) were stored over sodium–potassium alloy and calcium carbonate, respectively. Potassium *tert*-butoxide was prepared by exposing a THF solution containing a weighed amount of *tert*-butyl alcohol to a potassium mirror. After filtration, the solution was subdivided into a series of break-seal ampules.

Prior to their distillation into the polymerization flask, ethylene oxide (Eastman Kodak Co.) and methyl glycidyl ether (Interchim Co.) were purified by two consecutive condensations over fresh sodium mirrors. The quantity of monomer (ca. 60 mL) was adjusted by means of a graduated cylinder attached to the vacuum line. In the case of the P(EO/MGE) copolymer, an EO to MGE volume ratio of 4 was used. Once the initiator ampule was broken and rinsed with the monomer solution, the flask was placed into a Parr bomb (2 L) under an external pressure of 2 atm and the bomb was heated to 70 °C for 72 h. At the end of this period, the viscous solution was diluted with dry dichloromethane (DCM), and a weighed amount of antioxidant (Santonox-R) dissolved in DCM was added to the mixture. The polymer was recovered by solvent evaporation in a chamber flushed with dry nitrogen. In each synthesis, the monomer to polymer conversion, as computed on the basis of the estimated weight of monomer(s), was greater than 97%. Each polymer was further dried under high vacuum at 70 °C and stored in a glovebox under a dry atmosphere. Santonox-R content in the dry polymers was ca. 0.05%. It was observed that samples not stabilized by antioxidant, including PEO samples, were undergoing chain cleavages upon their exposure to air. No special effort was made to remove the traces of initiator residues (presumably KOH) in the present polyethers. On the basis of the polymerization data, their molar ratios with respect to the monomer units were ca. 2×10^{-5}.

LiSCN, NaSCN, KSCN, and CsSCN were purified according to the methods described in the previous papers.[5,7] Polymer–salt mixtures were prepared under a dry atmosphere by mixing weighed quantities of 1–5% methanol solutions of each component. The solvent was slowly evaporated in an ampule connected to a vacuum system. The solid mixtures were subsequently dried for 1 week under high vacuum and stored in a glovebox. This drying was performed at room temperature for all mixtures except those containing LiSCN. The latter were heated to 80 °C for 24 h at the end of the drying. Methanol (reagent grade) was carefully dried before utilization.

Polymer Characterization. Molecular weight evaluations were made by means of size exclusion chromatography (GPC) by using a series arrangement of four 1.2-m Styragel columns (Waters Co.) with upper porosity limits of 10^3, 10^4, 10^5, and 10^6 Å. The solvent, reagent grade THF, was eluted at a flow rate of 1 mL/min at 35 °C, and a 2-mL portion of solution, 2.5×10^{-3} g/mL, was injected. Molecular weights corresponding to the peak maxima, M_{GPC}, and polydispersity indexes, M_w/M_n, were determined by using a calibration curve constructed with a series of polystyrene standards (Waters Co.) having molecular weights in the range 8×10^3–6×10^6. The calibration curve was tested against a few PEO standards (Waters Co.) and yielded M_{GPC} values slightly inferior (by 10–20%) to the expected values. Since molecular weight is not used as a quantitative variable in the analysis of the solvation data, no effort was made to obtain absolute molecular weights. The composition of the P(EO/MGE) copolymer (10 ± 2 mol % of MGE units) was determined by carbon-13 NMR spectroscopy.

Physical Characterization. T_g and melting endotherms were recorded at a heating rate of 40 °C/min with a Model DSC-4 Perkin-Elmer calorimeter flushed with dry helium. Sample pans were filled and sealed under a dry atmosphere in a glovebox. Temperature calibrations were made by using standard materials with melting points in the range −69 to +327 °C. Energy calibration was performed by using the melting peak of indium recorded at 10 °C/min. Glass transition temperatures, T_g, were read at the intersection of the tangent drawn through the heat capacity jump with the base line measured before the transition. Melting temperatures, T_m, were read at the peak of the melting endotherms.

X-ray diffraction patterns obtained with a Statton-Warhus camera were used to confirm the presence of the compound $P((EO)_3{\cdot}NaSCN)$ in the mixtures prepared with the P(EO/MGE) random copolymer.

Table I
Molecular Weights (M_{GPC}), Polydispersity Indexes (M_w/M_n), Glass Transition Temperatures (T_g), Melting Temperatures (T_m), and Degrees of Crystallinity (X_c), of the Polyether Samples

sample	$10^{-3}M_{GPC}$	M_w/M_n	T_g, °C	T_m, °C	X_c
PEO-1100k	1100	4.0		69	0.67
P(EO/MGE)-180k	180	2.7	−64	47 (11)[a]	0.28[b]
PMGE-45k	45	1.8	−56		

[a] Second peak recorded on specimen cooled to −100 °C at 5 °C/min in the DSC apparatus. [b] Overall crystallinity in specimen cooled to −100 °C at 5 °C/min.

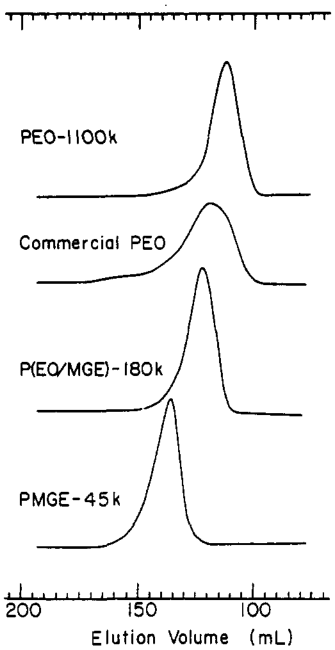


Figure 1. GPC curves of the polyether samples described in Table I compared to that of a PEO commercial sample having a nominal molecular weight of 3 × 10^5.

Results and Discussion

(a) Molecular Weights and Physical Properties of the Polyether Materials. High molecular weight PEO, as well as high molecular weight P(EO/MGE) random copolymers having large contents of EO units, can be prepared easily by anionic polymerization. This is shown in Table I, where molecular weights, M_{GPC}, and polydispersity indexes, M_w/M_n, of the present materials (samples PEO-1100k, P(EO/MGE)-180k, and PMGE-45k) are listed together with their physical properties (T_g, T_m, and degree of crystallinity X_c). In Figure 1, a comparison is made of the GPC curves of the present samples with that of a PEO commercial sample having a nominal molecular weight of 3 × 10^5. This sample, which yielded a M_{GPC} value of 2.8 × 10^5, had a polydispersity index of 8.5 compared to the value of 4 obtained for homopolymer PEO-1100k prepared by anionic polymerization. Although all the samples listed in Table I were prepared with the same monomer to initiator molar ratio, their molecular weights decrease substantially in the order PEO > P(EO/MGE) > PMGE. Only homopolymer PEO-1100k has a M_{GPC} value close to the theoretical value of 2 × 10^6 computed on the basis of the polymerization data. Other copolymers were prepared under the same conditions with MGE contents in the range 3–10%. Their molecular weight decreased monotonically with increasing MGE/EO molar ratio in the polymerization mixtures. This effect is probably due to a chain-transfer reaction to the monomer MGE.

Degrees of crystallinity, X_c, quoted in Table I were computed from the melting endotherms by using a heat of fusion of 203 J/g for 100% crystalline PEO.[14] Prior to the DSC measurements, the samples were cooled from room temperature to −100 °C at 5 °C/min in the DSC apparatus. As illustrated in Figure 2, this cooling induced further crystallization in sample P(EO/MGE)-180k. This is evidenced by a broad endotherm located between the glass transition anomaly (−64 °C) and the sharper endotherm (+47 °C) which corresponds to the crystalline moiety already present in the uncooled specimen. The value of X_c of 28% quoted for this sample corresponds to its overall crystallinity at low temperatures. It is substantially smaller than that (67%) of sample PEO-1100k. As usual for such a copolymer, the presence of noncrystallizable comonomer units along the chains produces both a decrease in crystallinity and a lowering of the melting point. With respect to sample PEO-1100k, the room-temperature crystallized moiety in sample P(EO/MGE)-180k exhibits a melting point depression of 22 °C. In turn, the amorphous phase remaining in this sample, after its cooling to −100 °C, exhibits a T_g value of −64 °C compared to −56 °C for the sample PMGE-45k.

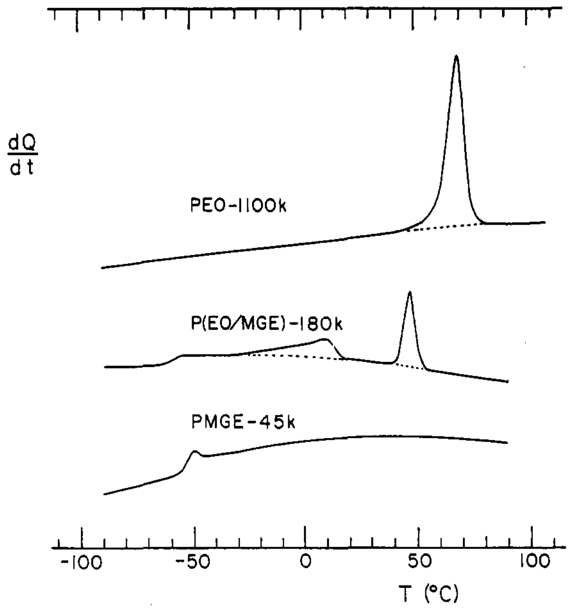


Figure 2. DSC heating curves recorded at 40 °C/min on the polyether samples described in Table I. Prior to the measurements, the samples were cooled from +25 to −100 °C at 5 °C/min in the DSC apparatus.

(b) Comonomer Effect upon Crystallinity of P((EO)$_3$·NaSCN). In Figure 3 a comparison is made between DSC heating curves recorded on O/NaSCN = 4 mixtures prepared with copolymer P(EO/MGE)-180k and homopolymer PEO-1100k, respectively. Two curves are shown for each polymer. One of these curves corresponds to the first heating of the as-cast mixtures. The other corresponds to a second heating recorded after a melt-quenching made by rapid cooling (320 °C/min) from +230 to −100 °C. The as-cast mixture prepared from homopolymer PEO-1100k exhibits a small but sharp endotherm lying at a temperature 5 °C below the melting point of the salt-free polymer. This endotherm, which corresponds to a eutectic melting,[5] is followed by a large endotherm at 190 °C, which corresponds to the dissolution of the crystalline compound P((EO)$_3$·NaSCN). The heating curve of the as-cast mixture prepared with the random copolymer is completely different. Its features are a pronounced glass transition anomaly at 2 °C, absence of eutectic melting, and a marked depression of the dissolution endotherm of the compound P((EO)$_3$·NaSCN). The latter occurs at 163 °C instead of 190 °C.

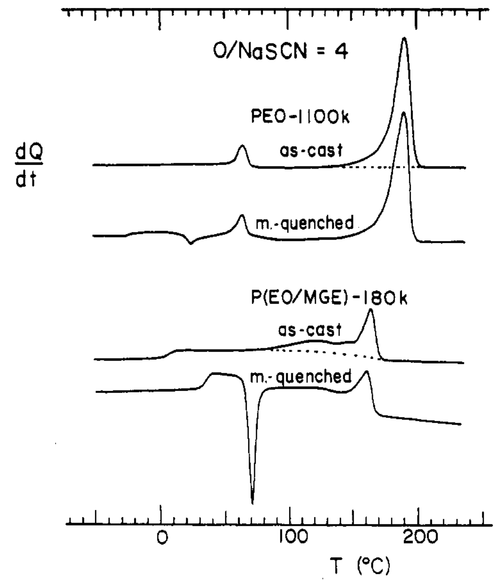


Figure 3. DSC heating curves recorded at 40 °C/min on O/NaSCN = 4 mixtures prepared with homopolymer PEO-1100k and copolymer P(EO/MGE)-180k, respectively. In each case, the upper curve was recorded on the as-cast material and the lower curve was recorded after melt-quenching performed by rapid cooling (320 °C/min) in the DSC apparatus.

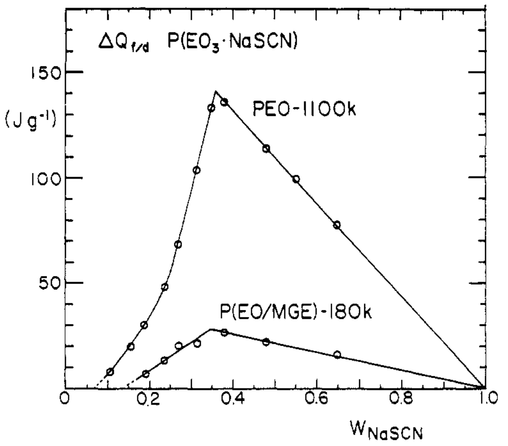


Figure 4. Calorimetric diagram showing the variation with NaSCN weight fraction, W_{NaSCN}, of the latent heat per gram of sample, $\Delta Q_{f/d}$, corresponding to the fusion (or dissolution) endotherms of $P((EO)_3{\cdot}NaSCN)$ recorded on mixtures prepared with homopolymer PEO-1100k and copolymer P(EO/MGE)-180k, respectively.

These features are reminiscent of those observed in the DSC curve of the salt-free material (Figure 2). Crystallization of $P((EO)_3{\cdot}NaSCN)$ is severely perturbed by the presence of the MGE comonomer units along the polymer chains. This perturbation is such that NaSCN-rich mixtures can be completely supercooled by melt-quenching. This is revealed by a large crystallization exotherm near 70 °C in the heating curve of the quenched specimen related to sample P(EO/MGE)-180k. In comparison, only the eutectic moiety had been supercooled in the case of the mixture prepared with sample PEO-1100k. This may be inferred from the presence of a single but small exotherm near 23 °C in the heating curve of the corresponding material.

Figure 4 shows plots, as a function of NaSCN weight fraction, W_{NaSCN}, of the latent heat of fusion (or dissolution) per gram of sample, $\Delta Q_{f/d}$, corresponding to the $P((EO)_3{\cdot}NaSCN)$ melting (or dissolution) endotherms recorded on series of as-cast mixtures prepared with samples PEO-1100k and P(EO/MGE)-180k, respectively.

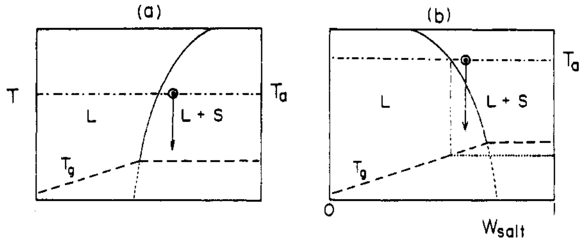


Figure 5. Schematic illustration of polymer–salt systems exhibiting either a decrease (diagram a) or an increase (diagram b) of salt solubility with decreasing temperature. The point of interest is the T_g measured on a saturated mixture (circle) after its cooling from an annealing temperature T_a. When cooling is performed under equilibrium conditions, either system should exhibit a ceiling value of T_g (dashed horizontal segment) for any composition greater than the intersection point of the solubility curve (full curve) with the T_g curve (dashed ascendant curve). Upon fast cooling, due to the fact that dissolution is a slow process, a departure from these conditions occurs for the mixture in diagram b. In that case, the system exhibits a ceiling value of T_g (dotted horizontal curve) for any composition greater than solubility at T_a.

These plots exhibit a maximum at a composition slightly inferior to the stoichiometry (W_{NaSCN} = 0.38) of the crystalline compound. According to the value of 172 J/g previously reported[5] for the magnitude of the maximum in a similar calorimetric diagram constructed with a low molecular weight PEO sample ($M_n = 4 \times 10^3, X_c = 96\%$),[15] crystallinity of $P((EO)_3{\cdot}NaSCN)$ in sample PEO-1100k is depressed to 82% due to chain entanglements. On the same basis, it appears that crystallinity of this compound in sample P(EO/MGE)-180k is 16% only.

(c) Solubility of NaSCN in the P(EO/MGE) Copolymer. Measurements of T_g as a function of salt content can provide a quantitative approach to determine salt solubility at low temperatures in noncrystallizable polyethers. The principle of this approach, as well as its limitations, is described in Figure 5. Phase diagrams are depicted for two hypothetical systems that exhibit either an increase (diagram a) or a decrease (digram b) of salt solubility with increasing temperature. In either case, the assumption is made that T_g (dashed curves) increases with increasing salt content in the liquid or amorphous phase. This situation corresponds to the general behavior of polyether–alkali salt systems. The other variables are the annealing temperature, T_a, and the cooling rate prior to the T_g measurements. Since the P(EO/MGE)–NaSCN mixtures could be supercooled by melt-quenching, the present discussion will be limited to rapid cooling only. Slow cooling or equilibrium conditions only apply to noncrystallizable polymers such as PMGE.

In the case where salt solubility decreases with decreasing temperature (diagram a), it is likely that even with rapid cooling, salt concentration in the saturated phase will readily adjust to the composition of the liquidus curve down to its point of intersection with the glass transition curve. At this particular point, the liquid phase will be frozen by vitrification, and salt rejection will no longer occur upon further cooling. Therefore, as indicated by the dashed horizontal segment in diagram a, a ceiling value of T_g is expected to appear at the composition corresponding to this particular point (or temperature) on the solubility curve. Note that this approach yields salt solubility at a single temperature only. Since this temperature depends upon both the T_g elevation with composition and the liquidus curve of the salt, it thus depends upon the nature of the system.

The case where salt solubility increases with decreasing temperature (diagram b) is completely different. In this

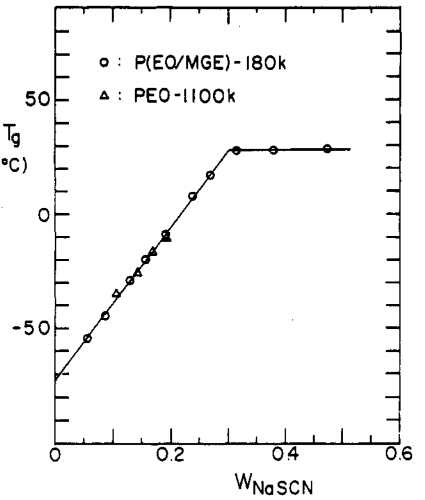


Figure 6. Variation of T_g with NaSCN weight fraction, W_{NaSCN}, for supercooled mixtures obtained with copolymer P(EO/MGE)-180k and homopolymer PEO-1100k, respectively. Prior to the T_g measurements, the mixtures were melt-quenched by rapid cooling (320 °C/min) in the DSC apparatus.

case, it is likely that salt dissolution will be hindered upon rapid cooling. Therefore, in this situation, as indicated by the dotted horizontal segment in diagram b, a ceiling value of T_g is expected to appear at the composition corresponding to the solubility at the annealing temperature T_a. Since this ceiling value depends upon the magnitude of T_a, this situation can be easily identified by making a series of measurements with different values for this variable. As will be shown in part d of this paper, such a situation is encountered for the PMGE–NaSCN and the PMGE–KSCN systems.

The limit case common to both diagrams a and b in Figure 5 corresponds to the situation where salt solubility is temperature independent. To discriminate this situation from that described in diagram a, independent data concerning salt solubility at temperatures higher than the ceiling value of T_g are required. In the case of the PEO–alkali thiocyanate systems, such independent data were provided by phase diagram construction.[5,7] Nevertheless, in the case of the PEO–NaSCN system, an important condition for applying the present method based upon T_g measurements was not fulfilled. For mixtures having O/salt molar ratios inferior to 6, the compound P((EO)$_3$·NaSCN) crystallized even upon melt-quenching.[5]

Figure 6 shows a plot as a function of W_{NaSCN} of T_g measured on P(EO/MGE)–NaSCN mixtures that were supercooled by melt-quenching in the DSC apparatus. Included in this plot are data points corresponding to four mixtures prepared with sample PEO-1100k (O/salt = 8, 9, 11, and 15) that could be supercooled by the same method. These data points are nearly superimposable on the curve drawn through the data points of the copolymer. Also superimposable on this curve are the data (not shown) previously reported for two mixtures (O/salt = 8 and 16) prepared with a low molecular weight ($M_n = 4 \times 10^3$) PEO sample.[5] With increasing NaSCN content, the T_g data of the copolymer exhibit a ceiling value of 28 °C for values of W_{NaSCN} superior to 0.302 (O/salt = 4.25). Interestingly, this ratio almost coincides with the ratio O/salt = 4.1 reported for NaSCN solubility at considerably higher temperatures in liquid PEO.[5]

Indeed, in the phase diagram reported for the PEO–NaSCN system,[5] the compound P((EO)$_3$·NaSCN) formed with a low molecular weight PEO sample ($M_n = 4 \times 10^3$) exhibited an incongruent melting at 182 °C. Upon melting, this compound disproportionated into the solid salt and a peritectic liquid of composition O/salt = 4.1. Sample PEO-1100k yielded a very similar phase diagram (not shown) in which the tie line was located at 190 °C instead of 182 °C. This change was presumably due to the formation of thicker crystallites in the case of the high molecular weight PEO sample. A similar tie line was located at 163 °C in a partial phase diagram constructed for the P(EO/MGE)–NaSCN system. As observed under the microscope for mixtures with O/salt ratios in the range 3–4, the salt crystals formed at either 182 or 190 °C in the case of the low- or high molecular weight PEO sample and at 163 °C in the case of the random copolymer remained unaltered with further heating up to about 240 °C. Above this temperature, they slowly dissolved into the liquid phase. From this behavior, together with the T_g data in Figure 6, it may be deduced that the solubility of NaSCN in liquid or amorphous PEO remains almost unchanged over a range of 200 °C above room temperature.

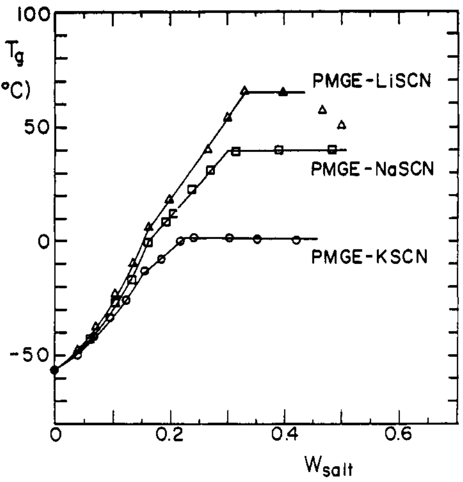


Figure 7. Plots showing the variation of T_g with salt weight fraction, W_{salt}, for mixtures of the PMGE–LiSCN, PMGE–NaSCN, and PMGE–KSCN systems, respectively. Measurements were carried out upon the first heating of the mixtures. Prior to the measurements, the mixtures were cooled from +25 to −100 °C at 5 °C/min in the DSC apparatus.

(d) Cation Size Effect upon Solubility in PMGE. PMGE–LiSCN, PMGE–NaSCN, and PMGE–KSCN mixtures containing various amounts of salt within the range $0.04 < W_{\mathrm{salt}} < 0.5$ were examined by DSC. They all exhibited single, sharp glass transitions. Plots of the T_g data as a function of W_{salt} are shown in Figure 7. Each plot presents a plateau above a critical value of W_{salt}, though in the case of LiSCN a T_g depression is observed at the upper range of the compositions ($W_{\mathrm{salt}} > 0.4$) at the right of the plateau. For this salt, the ceiling value of T_g defined by the plateau occurs at the same composition as that ($W_{\mathrm{salt}} = 0.33$, O/salt = 3.0) reported for the PEO–LiSCN system.[7] In the case of NaSCN, it occurs at the same composition as that ($W_{\mathrm{salt}} = 0.30$, O/salt = 4.3) obtained in the preceding section for the EO-rich P(EO/MGE)–NaSCN system. For KSCN, however, it occurs at a composition ($W_{\mathrm{salt}} = 0.22_5$, O/salt = 7.6) that departs substantially from that ($W_{\mathrm{salt}} = 0.31$, O/salt = 4.9) reported for the PEO–KSCN system.[5,7] It thus appears that, contrary to LiSCN and NaSCN, KSCN is less soluble in PMGE than in PEO. This difference between the two polymers increases dramatically with further increase of the cation size. Indeed, on the basis of a few T_g data (not shown) obtained for mixtures of PMGE with CsSCN, solubility of this salt in PMGE ($W_{\mathrm{salt}} = 0.04$, O/salt = 54) is reduced by a factor of 8 with respect to that ($W_{\mathrm{salt}} = 0.32$, O/salt = 9.2) reported for the PEO–CsSCN system.[7]

Another difference between PMGE and PEO concerns the composition dependence of T_g over the range below saturation. Contrary to those reported for PEO,[5,7] the relationships depicted in Figure 7 are not linear over the entire range of compositions. With increasing salt content, T_g first exhibits an accelerated rise within the range $0 < W_{salt} < 0.15$–0.16 and then adopts a linear relationship up to saturation. The O/salt molar ratios corresponding to the onset of the linear variation are 7.7 for LiSCN, 9.7 for NaSCN, and 12.8 for KSCN. There is a similarity between these ratios and those reported for saturation in PEO. Both correspond to W_{salt} values that are almost cation size independent. Since this feature of the PEO–alkali thiocyanate systems has been rationalized in terms of a linear relationship between the solvation number (SN) and the cation surface, it is tempting to give a similar interpretation to the present ratios. On this ground, the change of regime observed in the T_g–W_{salt} relationships would correspond to the completion of a solvation reaction. Depending upon the salt, this reaction would yield solvates with solvation numbers greater than those formed in PEO by a factor of 2.3–2.6. It is also tempting to interpret the linear relationships observed in the range above $W_{salt} = 0.15$–0.16 as the result of a gradual rearrangement of these solvates into solvates with lower solvation numbers similar to those formed in PEO. Though this interpretation is entirely speculative, further evidence for such a rearrangement, as will be shown shortly, appears in the temperature dependence of the solubilities of NaSCN and KSCN in PMGE.

The T_g data depicted in Figure 7 were obtained upon the first heating of specimens that were cooled from +25 to −100 °C at 5 °C/min in the DSC apparatus. Among these specimens, only those that were saturated by LiSCN (O/salt < 3) exhibited a second thermal anomaly upon further heating in the range between T_g and the melting point of the salt (284 °C for LiSCN, 309 °C for NaSCN, and 176 °C for KSCN). This anomaly was a small, broad endotherm near 120 °C. Though the physical process associated with this anomaly could not be identified, it did not correspond to salt precipitation since the T_g of the specimens remained almost unchanged after quenching from temperatures above 120 °C. Moreover, when the same mixtures were heated under the microscope at 20 °C/min, a progressive and complete dissolution of LiSCN was observed within the range 210–250 °C. This latter process, which was apparently much too progressive to be detected by DSC, suggests that at elevated temperatures LiSCN is soluble in all proportions in PMGE.

Contrary to the mixtures rich in LiSCN, those rich in NaSCN and KSCN exhibited sharp endotherms at the melting point of the salt (as well as the crystalline transition of KSCN[5] at 140 °C). Figures 8 and 9 show plots, as a function of W_{salt}, of the latent heat per gram of sample, $\Delta Q_{f,309}$ and $\Delta Q_{f,176}$, corresponding to the melting endotherms recorded at 309 and 176 °C, respectively. As shown in the former works on PEO,[5,7] under the assumption that the mixtures remain chemically stable up to the melting point of the salt, solubility at this temperature may be deduced from the composition-axis intercept of such calorimetric plots. In the case of NaSCN (Figure 8), the intercept is $W_{salt} = 0.263$ (O/salt = 5.2), indicating that solubility of this salt at 309 °C is inferior to that ($W_{salt} = 0.30$, O/salt = 4.3) deduced from the T_g data (Figure 7). Note that this feature of the PMGE–NaSCN system is just the opposite to that reported for the PEO–NaSCN system.[5] A more substantial difference is observed for KSCN. Indeed, as deduced from the composition-axis intercept ($W_{salt} = 0.08$, O/salt = 25) of the corresponding plot (Figure 9), solubility of KSCN at 176 °C is inferior by a factor of 3 to that ($W_{salt} = 0.22_5$, O/salt = 7.6) deduced from the T_g data.

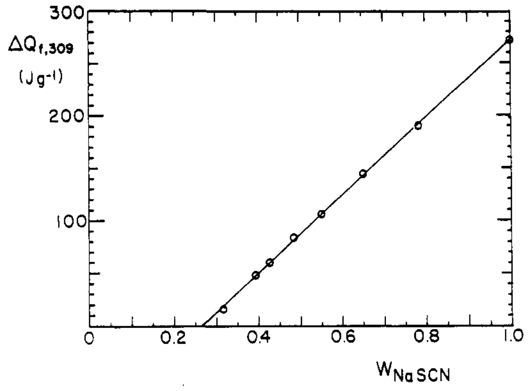


Figure 8. Plot as a function of NaSCN weight fraction, W_{NaSCN}, of the latent heat per gram of sample, $\Delta Q_{f,309}$, corresponding to the endotherms of fusion recorded at the melting point (309 °C) of NaSCN on mixtures prepared with sample PMGE-45k.

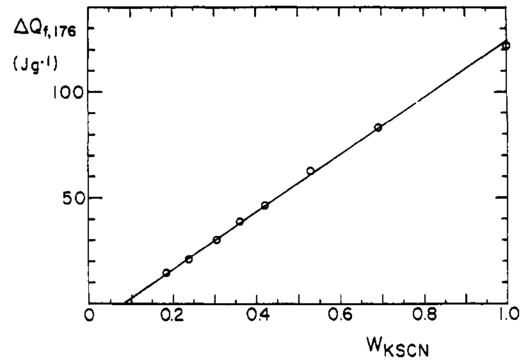


Figure 9. Plot as a function of KSCN weight fraction, W_{KSCN}, of the latent heat per gram of sample, $\Delta Q_{f,176}$, corresponding to the endotherms of fusion recorded at the melting point (176 °C) of KSCN on mixtures prepared with sample PMGE-45k.

As mentioned in part c of this work (Figure 5), the solubility limits deduced from the T_g data may correspond to different temperatures depending upon the sign of the temperature coefficient of solubility. For systems like PMGE–NaSCN and PMGE–KSCN, which both exhibit an increase of solubility with decreasing temperature, T_g measurements made on quenched mixtures can provide a route to characterize the solubility curve over a wide range of temperatures. The principle behind this approach is that salt dissolution should be hindered under rapid cooling conditions. Therefore, T_g of saturated mixtures quenched from an annealing temperature T_a should reflect the solubility at this temperature. To apply this approach under optimal conditions, a procedure was defined in which consecutive T_g measurements were made on the same specimen by increasing T_a by steps of 20 °C within the range 25–230 °C. The annealing time was 30 min and the specimens were quenched by rapid cooling (320 °C/min) to −100 °C.

When this procedure was applied to mixtures of the PMGE–LiSCN system, no significant changes of T_g were measured except for the mixtures with O/salt < 3, that is, those mixtures that contained an excess of salt prior to their study. As may be seen in Figure 10, where T_g is plotted as a function of T_a for selected compositions of the three systems, such a mixture (O/LiSCN = 2.2) exhibited a slight decrease of T_g (from 65 to 58 °C) for T_a values inferior to 120 °C. This change is difficult to interpret. It is correlated with the (already quoted) small endotherms

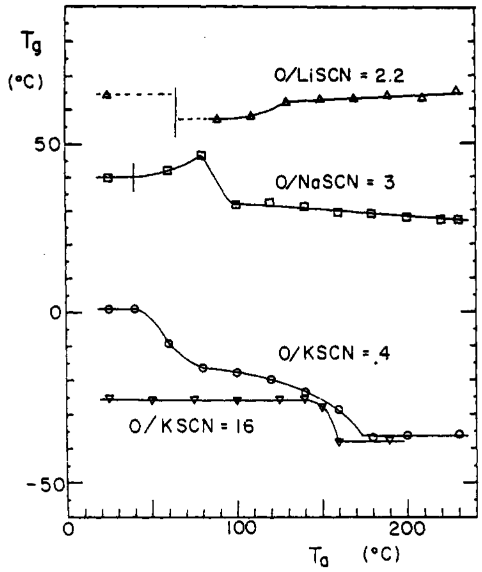


Figure 10. Plots showing the variation of T_g as a function of annealing temperature T_a for selected mixtures of the PMGE–LiSCN, PMGE–NaSCN, and PMGE–KSCN systems, respectively. Prior to the T_g measurements, the mixtures were quenched from T_a to −100 °C at 320 °C/min in the DSC apparatus. The vertical bars on the curves of the PMGE–LiSCN and PMGE–NaSCN mixtures indicate the limits above which T_a was greater than the T_g of the as-cast mixtures.

recorded near 120 °C upon the first heating of the same mixtures. Both these features result from an unknown perturbation associated with the presence of the solid salt dispersed in the glassy matrix.

Also depicted in Figure 10 are plots of T_g as a function of T_a obtained for mixtures that contained, prior to their study, either an excess of NaSCN (O/NaSCN = 3) or an excess of KSCN (O/KSCN = 4). Each of these plots exhibits a step decrease of T_g at moderate values of T_a, that is, over the range 80–100 °C for NaSCN and over the range 50–80 °C for KSCN. Furthermore, as may be seen for the O/KSCN = 4 mixture, as well as for a second mixture with O/KSCN = 16, another step decrease of T_g is observed with increasing T_a over the range of temperatures at the proximity of the melting point of KSCN (176 °C).

Similar changes were observed over the same ranges of temperatures for other mixtures of these salts. In each case, the T_g data were coherent with the transitions depicted in Figure 10. Concerning the PMGE–NaSCN mixtures, a small T_g elevation was observed for T_a values within the range 60–80 °C. This effect, which could not be explained, was more pronounced for the mixtures rich in salt, such as the O/NaSCN = 3 mixture depicted in Figure 10. Finally, similar measurements (not shown in FIgure 10) were made on a mixture containing CsSCN in a ratio O/salt = 16. With increasing T_a within the range 25–120 °C, the T_g of this mixture decreased progressively from −50 °C to the value of −56 °C recorded for the salt-free polymer.

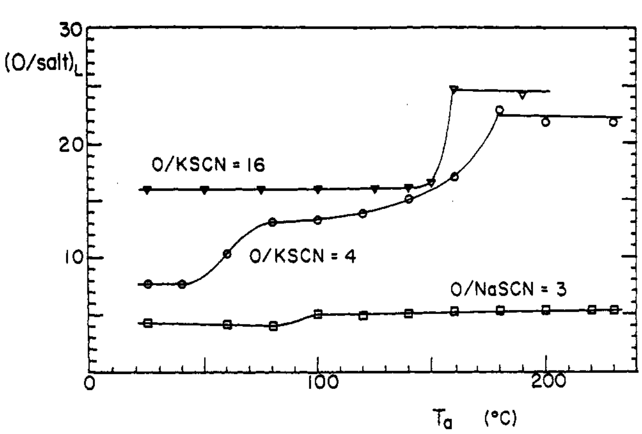


Figure 11. Plots showing the variation as a function of the annealing temperature T_a of the composition $(\mathrm{O/salt})_L$ of the liquid (or amorphous) phase in selected mixtures of the PMGE–NaSCN and PMGE–KSCN systems. Values of $(\mathrm{O/salt})_L$ were deduced from the T_g data in Figure 10 by means of the T_g–composition relationships depicted in Figure 7.

A quantitative analysis of the T_g data in Figure 10 can be made on the basis of the T_g-W_{salt} relationships depicted in Figure 7. The results of such an analysis are presented in Figure 11 under the form of plots of $(\mathrm{O/salt})_L$, the composition of the liquid phase, as a function of T_a. For NaSCN, it may be seen that the value of this ratio increases from 4 to 5 upon the transition observed in the range 80–100 °C. At 230 °C, its value (O/NaSCN = 5.2) is the same as that deduced from the calorimetric diagram in Figure 8. Therefore, solubility of NaSCN in PMGE remains almost unchanged over a range of 200 °C above the transition. This feature is remarkable. Also remarkable are the $(\mathrm{O/salt})_L$ vs T_a curves obtained for the PMGE–KSCN mixtures. Upon the first transition, which takes place over the range 50–80 °C, the value of $(\mathrm{O/salt})_L$ increases from 7.6 to 13. Upon the second transition near the melting point of KSCN, depending on the composition of the mixtures, $(\mathrm{O/salt})_L$ increases to values in the range 22–25. This latter result is in agreement with the ratio O/KSCN = 25 deduced from the calorimetric diagram in Figure 9. Also note that the first transition yields a saturated phase that has about the same composition as the one (O/KSCN = 12.8) where a change of regime is observed in the T_g-W_{salt} relationship depicted in Figure 7.

(e) Factors Governing Solvate Stability in Polyethers. On the basis of the foregoing data, it is clear that NaSCN and KSCN exhibit solubilities in PMGE that are governed by the formation of solvates of well-defined stoichiometries. Straightforward evidence for this feature is provided by the compositional stability of the saturated phases over wide ranges of temperatures as in the case of PEO. In the previous papers on PEO,[6,7] the solvation numbers SN derived from such solubility data were interpreted as the sums of two independent variables: the coordination number CN of the cation and a second number that was assumed to correspond to the minimum number of uncoordinated polymer units required to stabilize the whole solvate structure. This second number was shown to increase with increasing anion size.[6,7] Its value was about 2 for the alkali thiocyanates, 4 for NaI, and 6 for $NaBPh_4$. From this feature, it may be deduced that several factors are involved in the stabilization of a given solvate. Among these factors, there are entropic factors (to be discussed shortly) and energetic factors such as ion–ion Coulombic interactions, ion–dipole interactions (cation coordination), dipole–dipole interactions (anion solvation), and presumably space-filling forces related to the size of the anion.

The sharp transitions observed at moderate and elevated temperatures in PMGE, as well as the substantial decreases in solubility in this polymer with increasing cation size, are features that may help to clarify the role of each of these factors. When written on an ether group molar basis, –O–, the transitions observed for the PMGE–NaSCN and PMGE–KSCN systems correspond to equilibria of the

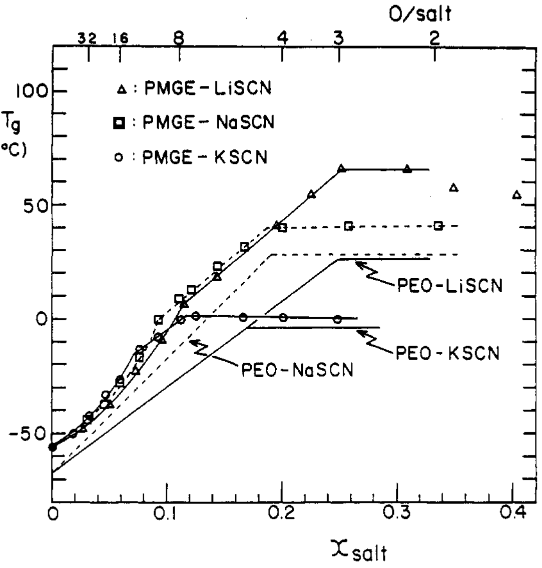


Figure 12. Plots of the T_g data of the PMGE-LiSCN, PMGE-NaSCN, and PMGE-KSCN systems (Figure 7) as a function of salt molar fraction, x_{salt}, computed according to eq 4 on the basis of the total amount of ether groups in PMGE. A comparison is made of these plots with the relationships obtained for supercooled mixtures of the same salts with PEO (and copolymer P(EO/MGE)-180k in the case of NaSCN).

form

$$[\text{-O-}]_n\cdot\text{salt}_L \rightleftharpoons (n/m)[\text{-O-}]_m\cdot\text{salt}_L + [1-(n/m)]\text{salt}_S \qquad (3)$$

where n and m denote the solvation numbers in the initial and final states, respectively, and subscripts L and S denote the liquid and solid phases, respectively. Since these processes are spontaneous, they involve a negative change in free enthalpy ($\Delta G = \Delta H - T\Delta S < 0$). Under the assumption that these processes are endothermic like those reported for the same salts in PPO,[9-11] it may be deduced that the driving force for the transitions is an entropic factor. This factor might be the gain in configurational entropy resulting from the change in the number of uncoordinated units in the liquid phase. The main feature of the transition described by eq 3 is the stabilization of a new solvate instead of a complete phase separation of the components. This feature indicates that the interactions in the new solvate remain high enough to compensate for the further gain in entropy expected for a total demixing.

The absence of such transitions in PEO might be interpreted in terms of a greater binding energy in this polymer than in PMGE. However, it is important to note that for a given O/salt molar ratio in the liquid phase, there is twice as much ion-dipole interactions per monomer unit in PMGE than in PEO. This difference, which results from the complexation of the pendant groups in PMGE, is expected to yield solvates having lower configurational entropies than those of the same compositions formed in PEO. Indirect evidence for this feature may be found in Figure 12, where a comparison is made of the T_g data obtained for these two polymers. The T_g data are plotted as a function of the salt molar fraction, x_{salt}, with respect to the total amount of ether groups in the mixtures.

$$x_{salt} = [(\text{O/salt}) + 1]^{-1} \qquad (4)$$

In the composition ranges inferior to saturation, the T_g data corresponding to PMGE exhibit about the same relationship, while those corresponding to PEO exhibit two distinct relationships depending upon the nature of the salts. As reported in a former work,[7] the T_g elevation produced by NaSCN in PEO is substantially greater than that produced by the other alkali thiocyanates. This feature of the PEO-NaSCN system was tentatively interpreted as an indication that a specific conformation of the PEO chain might yield a coordinated species with NaSCN having greater binding energy than those with the other alkali cations. The fact that this feature is not observed for PMGE seems to confirm this interpretation. On this basis, the T_g data of the PEO-NaSCN system should not be included in the present comparison.

For x_{salt} values inferior to 0.05 (O/salt > 19), the T_g elevations produced by the three salts in PMGE are about the same as those produced by LiSCN and KSCN in PEO. For values of x_{salt} above this range, the T_g elevations in PMGE are greater than those in PEO. At the composition x_{salt} = 0.116 (O/salt = 7.6), which corresponds to the greatest solubility of KSCN in PMGE, T_g of the PMGE-KSCN mixture is 2 °C compared to -26 °C for the PEO-KSCN mixture. This difference of 28 °C is about 3 times greater than the difference of 11 °C between the T_g's of the salt-free polymers. At the composition x_{salt} = 0.19 (O/salt = 4.3), which corresponds to the greatest solubility of NaSCN in PMGE, the difference is further increased to 36 °C. Therefore, due to the complexation of the pendant groups in PMGE, the salt-rich solvates formed in this polymer exhibit a substantial decrease in chain mobility with respect to comparable solvates formed in PEO. This effect on the dynamics of these solvates is necessarily accompanied by a similar effect upon their configurational entropy.

Changes in configurational entropy with respect to PEO are apparently not the sole factor that accounts for the thermal instabilities observed in PMGE. Ion-dipole binding energies and probably ion-ion Coulombic interactions also contribute to these processes. The contribution of binding energies is clearly evidenced by the effect of cation size on solubility in PMGE. In the former work on PEO,[7] the same T_g elevation observed for LiSCN, KSCN, and CsSCN was interpreted as an indication that cation-oxygen binding energy was proportional to the cation surface charge density. The same feature may be deduced from the plots depicted in Figure 12 for the PMGE-thiocyanate systems. Such a decrease in binding energy with increasing cation size can also be predicted on the basis of a simple physical argument. Indeed, the interaction potential between a dipole and a point charge should decrease in the same ratio as the square of the distance between the dipole and the charge.[16] On this basis, it is expected that the contribution of the binding energy to the stabilization of the solvates decreases with increasing cation size. This expectation is in accord with the experimental data. At low temperatures, solubilities of LiSCN and NaSCN in PMGE are unchanged with respect to those in PEO. Under the same conditions, solubility of KSCN in PMGE is reduced by a factor of 1.4 with respect to that in PEO, while this factor reaches the value of 8 for CsSCN. At higher temperatures, no transition is observed for the PMGE-LiSCN system. A single but small transition is observed near 90 °C for the PMGE-NaSCN system, while two substantial transitions occur near 60 and 160 °C, respectively, for the PMGE-KSCN system.

Ion-ion Coulombic interactions, like cation-oxygen interactions, should provide a stabilization effect on the solvate structure. Indeed, the solvation process yielding to saturated mixtures may be considered as an ion condensation process similar to salt crystallization. Therefore, the Coulombic energy liberated by this process should compensate in part for the energy cost related to the lattice energy of the salt. The magnitude of this effect, however, should decrease with increasing distance between the ions, that is, with decreasing salt content in the solvates. It should also decrease with increasing temperature due to the thermal expansion of the system.

A last remark concerns the change of regime observed in the T_g–W_{salt} relationships depicted in Figure 7. In view of the same solubility data obtained at low temperatures for either LiSCN or NaSCN in both PMGE and PEO, it may be deduced that, under favorable conditions (small cation, low temperature, and large salt content in the liquid phase), solvation is provided equally by either type of ether groups in PMGE. However, the change of regime observed near $W_{salt} = 0.15$–0.16 in the case of PMGE suggests that at low salt contents a preferential solvation takes place with either the pendant groups or the chain backbone or with specific conformations involving a partial amount of each type of ether groups. Also possible is that the step decreases in solubility of NaSCN and KSCN with increasing temperature might correspond to the stabilization of new solvate structures involving such a preferential solvation. This is apparently the case for KSCN. The composition of its second solvate (O/salt = 13, W_{salt} = 0.145) is about the same as the composition where a change of regime is observed in the T_g–W_{salt} relationship.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Research Council of Canada and by the Research Institute of Hydro-Quebec.

References and Notes

(1) Gauthier, M.; Armand, M.; Muller, D. In *Electroresponsive Molecular and Polymeric Systems*; Skotheim, T. A., Ed.; Marcel Dekker Inc.: New York, 1988; Vol. 1, p 41.
(2) Ratner, M. A.; Shriver, D. F. *Chem. Rev.* **1988**, *88*, 109.
(3) Cameron, G. G.; Ingram, M. D. In *Polymer Electrolyte Reviews—2*; MacCallum, J. R., Vincent, C. A., Eds.; Elsevier Applied Science: New York, 1989; p 157.
(4) Vincent, C. A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1989**, *30* (1), 422.
(5) Robitaille, C.; Marques, S.; Boils, D.; Prud'homme, J. *Macromolecules* **1987**, *20*, 3023.
(6) Besner, S.; Vallée, A.; Prud'homme, J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1989**, *30* (1), 406.
(7) Besner, S.; Prud'homme, J. *Macromolecules* **1989**, *22*, 3029.
(8) Besner, S.; Prud'homme, J., unpublished results.
(9) Teeters, D.; Stewart, S. L.; Svoboda, L. *Solid State Ionics* **1988**, *28–30*, 1054.
(10) Wintersgill, M. C.; Fontanella, J. J.; Greenbaum, S. G.; Adamic, K. J. *Br. Polym. J.* **1988**, *20*, 195.
(11) Greenbaum, S. G.; Pak, Y. S.; Wintersgill, M. C.; Fontanella, J. J. *Solid State Ionics* **1988**, *31*, 241.
(12) Chabagno, J. M. Thesis, Institut National Polytechnique, Grenoble, France, 1980.
(13) Ballard, D. G. H.; Cheshire, P.; Mann, T. S.; Przeworski, J. E. *Macromolecules* **1990**, *23*, 1256.
(14) Wunderlich, B. *Macromolecular Physics*; Academic Press: New York, 1980; Vol. 3, p 67.
(15) Robitaille, C.; Prud'homme, J. *Macromolecules* **1983**, *16*, 665.
(16) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*; Butterworths Scientific Publications: London, 1955; p 52.

Registry No. PMGE (SRU), 132491-85-1; MGE (homopolymer), 28325-89-5; LiSCN, 556-65-0; NaSCN, 540-72-7; KSCN, 333-20-0; CsSCN, 3879-01-4; (EO)(MGE) (copolymer), 64786-16-9.