Recent Trends in Polymer Electrolytes Based on Poly(Ethylene Oxide)

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RECENT TRENDS IN POLYMER ELECTROLYTES BASED ON POLY(ETHYLENE OXIDE)

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ABSTRACT

Recent work on the crystallographic and morphological structure of
semicrystalline PEO complexes with alkali metal salts is described.
The thermal properties of the materials and the influence of solvent
on complex formation is also considered. The dependence of the
ionic conductivity of the complexes on their morphology, the tem-
perature and ionic association is discussed and some current work
relating to the mechanism of conduction is considered. The various
strategies which have been adopted to suppress crystallinity and so
to optimize ionic conductivity, including networks, "comb" structures,
and linear copolymers, are reviewed. The morphological organization
and mesogenic behavior of some novel crystalline complexes of PEO
with organo-alkali salts, such as sodium phenolates and naphtholates,
are discussed. Some PEO composite materials which have mixed elec-
tronic-ionic mechanisms of conductivity are also described.

INTRODUCTION

The propensity for poly(ethylene oxide), $-(-CH_2-CH_2-O-)-$ (PEO), to
form both amorphous and crystalline complexes with a wide variety of
molecular or ionic species, in the bulk state or in solution, has been recog-
nized for a number of years. The complexes are formed by association of

the ether oxygens of the polymer chain with an electrophilic center on the smaller molecule. One of the earliest examples to arouse general interest was the crystalline complex of PEO with mercuric chloride, reported by Blumberg, Pollack, and Hoeve [1]. The possibility of preparing ionic complexes was indicated by Moacanin and Cuddihy [2] who studied the effect of lithium salts on the glass-transition temperature of poly(propylene oxide), and Lundberg, Bailey, and Callard [3] demonstrated "imposed polyelectrolyte behaviour" in methanolic solutions of PEO and various potassium and rubidium salts. The latter workers also prepared an amorphous complex of PEO with KI.

Following the preparation of the well-known crown ethers by Pedersen [4], the nature of the interaction of the ethoxy unit with inorganic salts was more readily appreciated, and several crystalline complexes of PEO with the thiocyanates of sodium, potassium, and ammonium and iodides of sodium and lithium were prepared [5], and the electrical conductivities of the sodium, potassium, and ammonium salts were measured [6] by the author. Armand [7] later suggested the use of these materials as ionic conductors for lightweight rechargeable batteries using alkali metal electrodes and also measured the conductivities of a number of PEO-alkali metal salt complexes, including those of lithium and cesium ions. Following Armand's proposal, considerable research effort has been expended by a number of groups worldwide in attempts to optimize the ionic conductivities and mechanical properties of these "polymer electrolytes" [8]. Although other polymeric ligands have been investigated, the materials currently receiving most attention for battery applications are essentially copolymers incorporating grafts or blocks of PEO. Apart from their relatively high ionic conductivity, PEO-alkali salt complexes appear to have adequate chemical stability in contact with alkali metal electrodes [9].

THE STRUCTURE OF SEMICRYSTALLINE PEO-ALKALI ION COMPLEXES

The crystalline complexes of PEO with alkali ions are formed with inorganic salts of the smaller alkali ions, Li^+, Na^+, and K^+ (and NH_4^+), which have lattice energies below an apparent upper limit of approximately 720 J/mol. The materials are readily prepared by solvent evaporation from methanol or acetonitrile solutions of PEO and the salt in appropriate stoichiometric proportion, Thus, crystalline complexes may be formed with NaI, $NaBF_4$, and NaBr, but NaCl and NaF separate from the polymer. LiI, $LiBF_4$, $LiCF_3SO_3$, and $LiClO_4$

also form stable crystalline complexes with PEO. The thiocyanates of sodium, potassium, and ammonium also form crystalline complexes but the iodides of the latter two cations, although qualifying on lattice energy grounds, form only amorphous elastomers at ambient temperature.

Lithium salts of higher lattice energy, such as LiSCN, dissolve in PEO to form amorphous complexes (perhaps indicating a more intimate ion-PEO association than in the crystalline materials). The larger alkali ions, Rb^+ and Cs^+, also form amorphous materials with PEO.

An initial assessment [5, 6] of the stoichiometry of the PEO-alkali ion complexes suggested that the crystalline phases had an EO:salt ratio of 4:1. However, later work, notably by Robitaille [10] and Hibma [11] using DSC and WAXS, confirmed that while this was true in the case of K^+ and NH_4^+ ions, the Li^+ and Na^+ ion complexes have an EO:salt ratio of 3:1. These structural differences are reflected in the maximum temperatures at which the complexes melt to an isotropic phase. For the Li^+ and Na^+ complexes, this transition is generally observed over the range 150-195°C when PEO of molecular weight $\geqslant 10\,000$ is used (see Fig. 1). Although the highest observed melting temperatures of complexes of $LiBF_4$ [12] and $LiClO_4$ [13] are approximately 160°C, the most stable samples of complexes of high molecular weight PEO with $LiCF_3SO_3$, NaI, and NaSCN melt over the range 190-195°C [12, 14]. However, the thiocyanate complexes of NH_4^+ and K^+ melt at ~78°C and ~110°C, respectively [6, 15]. (Pure, high molecular weight PEO is normally observed to melt at 68-70°C.) Thus, it seems that the Li^+ and Na^+ complexes may be isomorphous while those of the larger ions have essentially different structures.

The only complete crystallographic determination of a PEO-alkali ion complex so far is the WAXS study of the $P(EO)_3$ NaI complex by Chatani and Okamura [16]. In this structure (Fig. 2), three adjacent oxygens coordinate each cation within half a rotation of a single, low-pitched helix. Sodium and iodide ions form an extended zigzag chain along the fiber direction with two NaI pairs per fiber repeat and the PEO chain coils about the ions in a $(ttgttgt\bar{g})_2$ conformation, where the trans (t) states refer to the conformation of the C—O bonds and the C—C bonds adopt either gauche positive (g) or gauche minus ($\bar{g}$) states. The adoption of the exact rotational minima for these bond conformational states ($t = 0°$, $g = +120°$, $\bar{g} = -120°$) gives a helix with a fiber repeat of 0.72 nm [17], which is exactly that of the PEO-NaSCN complex as determined by Parker, Wright, and Lee [18] and by Hibma [11]. Slight extension of this "exact helix" would be required to accommodate the larger I^- ion, giving a fiber repeat of 0.80 nm. In view of the previous remarks regarding the essential isomorphism of the sodium and lithium complexes, it
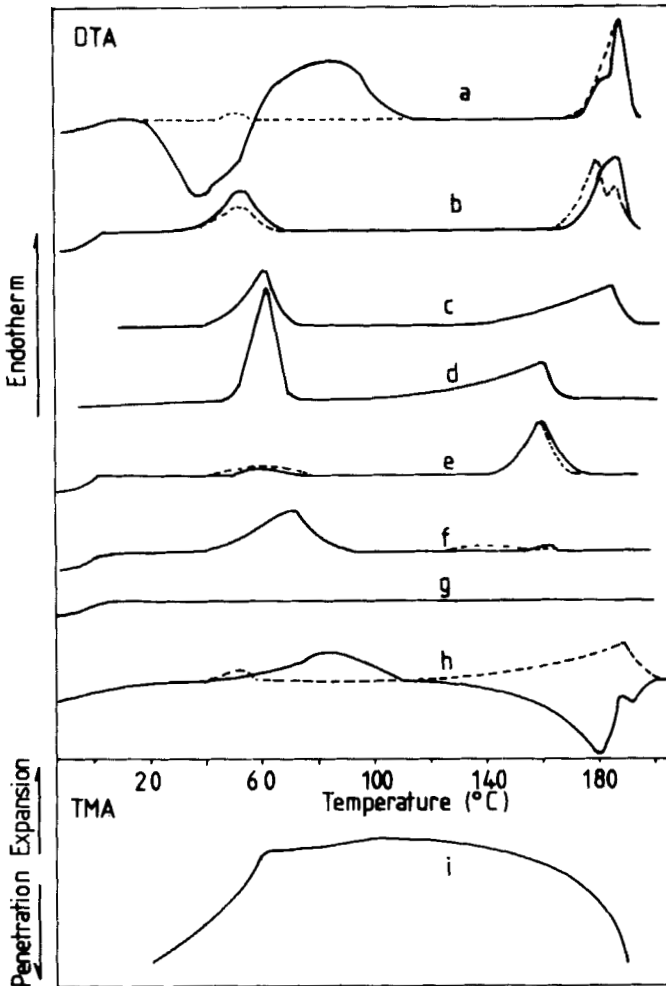
FIG. 1. Differential thermal analysis (DTA) tracings of PEO-salt complexes. Solid line is first heating cycle (solution-deposited material); dashed line is second heating cycle. Heating rates are 1-5 K/min. (a) $P(EO)_3 NaSCN$, oriented film. (b) $P(EO)_4 NaI$. (c) $P(EO)_4 LiCF_3 SO_3$. (d) $P(EO)_8 LiCF_3 SO_3$. (e) $P(EO)_4 LiBF_4$, from 2% solution in acetone-chloroform. (f) $P(EO)_4 LiBF_4$, from methanol solution. (g) $P(EO)_6 LiBF_4$, amorphous network of PEO 400 maleate. (h) $P(EO)_3 Na$ phenolate. (i) Thermomechanical analysis (TMA) of $P(EO)_4 NaI$, heating rate 5 K/min with 5-g on indenter.

FIG. 2. The crystal structure of P(EO)₃NaI. (After Y. Chatani and S. Oka-
mura, Japan-U.S. Polymer Symposium, Kyoto 1985, Preprints, Paper 4C09.
By permission of The Society of Polymer Science, Japan.)

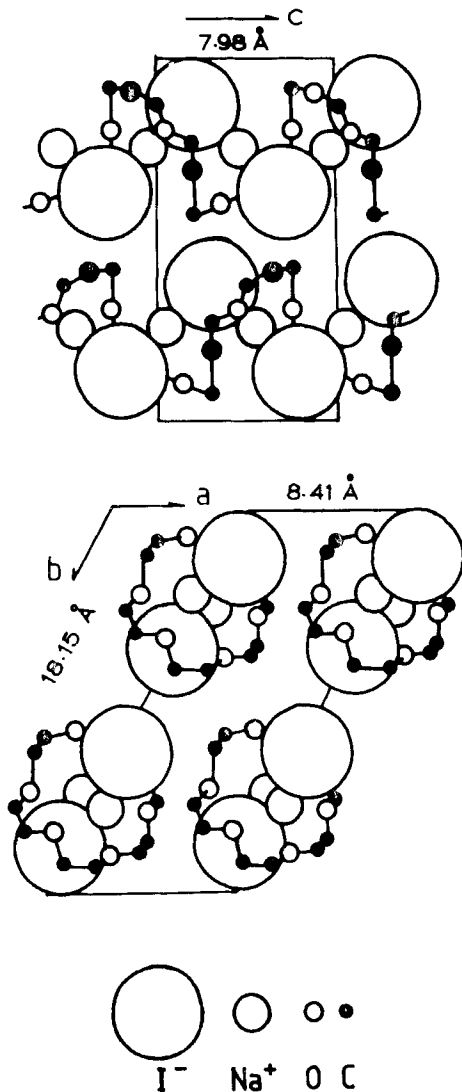seems reasonable to suppose that Chatani and Okamura's helix may be the basic structural feature for all of the sodium and lithium ion complexes, with the helix adjusting to accommodate anions of different size. Hibma also observed fiber repeats of 0.76 and 0.84 nm for PEO-NaBr and PEO-NaClO$_4$, respectively.

However, for a crystalline stoichiometry of 4:1 (EO:salt), as in the case of PEO-KSCN, the preservation of close proximity of ions in the lattice (two ion pairs per fiber repeat) requires an even higher pitched PEO helix than that given above or a double-strand arrangement in which the four oxygens are donated by two PEO chains [18]. Calculations [19] show that the double-strand helix proposed by Parker, Wright, and Lee is unable to accommodate a K$^+$ ion. However, Hibma's WAXS study [11] of PEO-KSCN indicated a unit cell in which a pair of K$^+$ ions were bounded on either side (not enclosed) by separate strands of PEO, giving a fiber repeat distance of 0.81 nm. The conformational arrangement of the PEO chains was not specified but, presumably, coordination of the cations by oxygens was intended.

The PEO complexes with inorganic alkali salts are deposited from solution with spherulitic morphologies comprising crystalline lamellae approximately 20 nm in thickness [14] (see Fig. 3). Such morphologies are typical of semi-crystalline flexible polymeric materials although rather less familiar structures may be observed in annealed PEO-NaSCN complexes and alkali salts with organic anions, as described below.

THERMAL BEHAVIOR

The thermal stabilities of crystalline PEO-alkali salt complexes depend, in general, on the overall EO:salt molar ratio, the PEO molecular weight, the choice of solvent and concentration (see below), and the thermal history. The melting temperatures also, of course, depend on the nature of the complexing salt although, as mentioned above, for lithium and sodium ion complexes the dependence is not a strong one. Differential thermal analysis (DTA) traces of PEO-alkali salt complexes, in general, show two distinct endothermic regions (see Fig. 1). The lower endotherm is usually centered around 60-70°C but may extend over the range from ambient to above 100°C in some samples. The higher endotherm occurs at the transition to the isotropic melts observed by polarized light microscopy, corresponding to melting temperatures of the most stable complexed forms, as discussed previously. Both endotherms may display multiple peaks or shoulders.
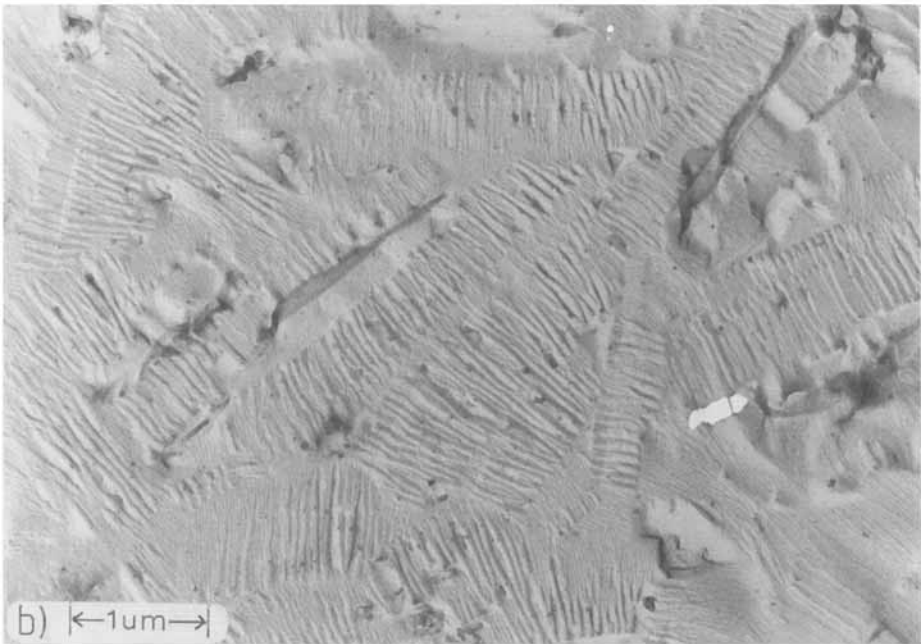
The influence of PEO molecular weight on the higher endotherms of

FIG. 3. Transmission electron micrographs (carbon replicas) of complexes of PEO 6 × 10^5 with sodium ion. a) Spherulite nucleus of P(EO)$_4$NaI, solution-deposited material annealed without melting at 165°C. b) Lamellar stacks in P(EO)$_4$NaSCN, annealed without melting at 185°C [14, 20].

NaI and NaSCN complexes has been studied in some detail by Lee [14, 20], who used slow DTA heating rates of 1 to 3°C/min. Most samples had overall EO:Na$^+$ratios of 4:1 although some samples with 3:1 and 6:1 ratios were also studied. Morphological analysis by carbon replica transmission electron microscopy showed that rapid lamellar thickening, with simultaneous increases in melting temperatures, occurred, particularly in samples with slight salt deficiencies (EO:salt = 4:1). For PEO molecular weights 1000-10 000, the corresponding first-cycle DTA endotherms ranged between 149 and 192°C and both PEO-NaI and PEO-NaSCN series were in agreement within experimental error (Fig. 4). The melting temperatures over this molecular weight range corresponded to crystalline lamellae with fully extended (unfolded) helical conformations and could be rationalized according to the
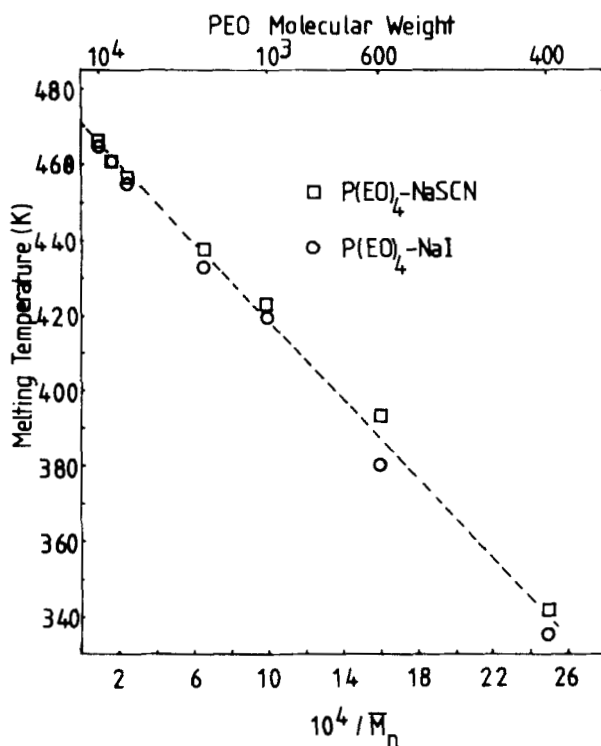

FIG. 4. Melting temperature versus reciprocal molecular weight for PEO-sodium ion complexes.

Flory theory of melting as applied by Booth and coworkers [21] for pure PEO fractions:

$$T_m = T_m{}^\circ \left[1 - \frac{2\sigma_e}{(\Delta h)\zeta} \right] \Big/ \left[1 + \frac{RT_m{}^\circ}{\Delta h} \left(\frac{1}{\bar{X}_n} - \ln I\zeta \right) \right].$$

In a scheme detailed elsewhere [20], which is at least internally consistent, $T_m{}^\circ$, the melting temperature of crystals of infinite length is 473 K; σ_e, the end interfacial free energy ranges between 8.4 and 16.8 kJ/mol of emerging chains over a molecular weight range following similar trends to those found for pure PEO by Booth and coworkers; $\bar{X}_n$ is the number-average degree of polymerization; and I is the probability of choosing a sequence ζ units in length which does not contain a chain end. The heat of fusion, Δh, was taken to be 11.8 kJ/mol of EO unit as estimated from calibrated DTA melting peak areas of annealed PEO 10 000-NaI complexes. Thus, these polymeric complexes behaved similarly to conventional linear polymers in their melting behavior.

However, the entropies of fusion calculated from the thermal analyses, ~25 J·(mol of EO)$^{-1}$·K^{-1}, are no greater than that for pure PEO crystals, as estimated by similar procedures, despite the additional ionic components in the complex crystals. This implies that the complex melts are organized to some degree and/or the crystals are disorganized at their melting temperatures and exist as a mesophase. Evidence for the latter was obtained by Lee, who studied broad-line ^{1}H NMR of PEO-NaI and PEO-NaSCN complexes. He observed that narrowing of the broad-line component began at temperatures in the range 60-90°C and continued to the isotropic melting temperatures (see Fig. 5a). This increase in molecular motion of the PEO chains in the complexes below their melting points is reflected in the deterioration of the mechanical properties of the complexes on heating. This is demonstrated by thermomechanical analysis (see Fig. 1i) which shows a progressive compensation of thermal expansion by penetration of the indenter at temperatures above ~90°C. However, there is no deterioration of birefrigence in these 4:1 stoichiometric materials at temperatures below the melting region. Furthermore, substantial morphological changes occur in PEO-NaSCN complexes annealed at 10-20 K below their isotropic melting temperatures. Annealed complexes of PEO 6×10^5 and NaSCN have morphologies shown in Fig. 3(b), which consist of stacks of fragments of thickened lamellae. The observation that such stacking occurs only in high molecular weight PEO-NaSCN complexes [14] indicates a requirement for molecular connectivity between lamellae in these structures.
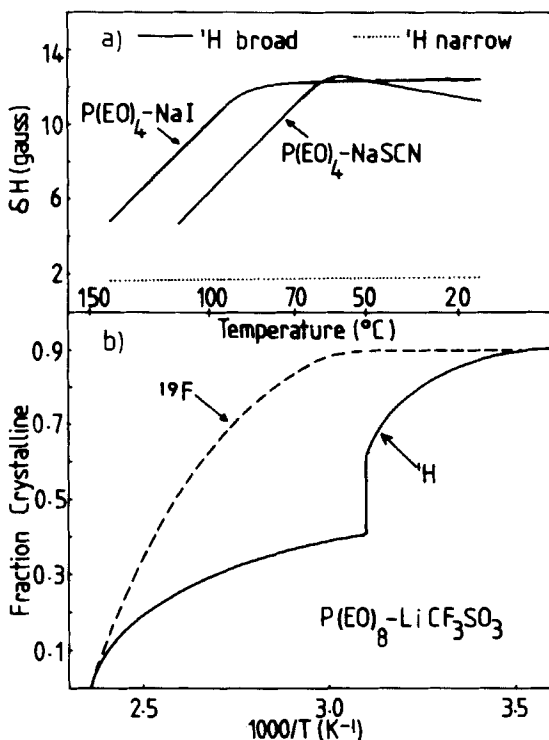
FIG. 5. Nuclear magnetic resonance investigations of PEO complexes.
a) Line width versus temperature measurements in broad-line NMR spectra
of $P(EO)_4 NaSCN$ and $P(EO)_4 NaI$ [14]. b) Measurements of the fractions of
hydrogen and fluorine atoms in crystalline phases in $P(EO)_8 LiCF_3SO_3$. After
Berthier et al. [22].

This mesogenic behavior was attributed to an increased local mobility of
the anions between the PEO-Na$^+$ adduct, so allowing the latter to slip in an
axial direction but without disintegration into an isotropic melt.

Berthier and coworkers [22] have used NMR to study the relative propor-
tions of crystalline and elastomeric phases over a range of temperature in
salt-deficient complexes $P(EO)_8 LiCF_3SO_3$ and $P(EO)_{10} NaI$ (Fig. 5b). They
also estimated the salt concentration in the respective phases. In
$P(EO)_8 LiCF_3SO_3$ the fraction of protons (i.e., PEO) belonging to crystalline
phases is $\simeq 0.9$; on heating to 55°C, this fraction sharply drops to 0.4 as pure

PEO crystals melt and slowly declines to zero at 160°C. The fraction of fluorine (i.e., anions) in the crystalline phase shows no sharp decline at 55°C but, above 90°C, begins a progressive decline to zero at 160°C. (The observed increase in anion mobility and decrease in the fully organized crystalline complexed phase above 90°C in this sample is consistent with Lee's observations but was interpreted as "progressive dissolution" of the complexes phase by these authors.) Below 90°C the absence of motional narrowing in ^{19}F or ^{7}Li resonance lines indicated that ion mobility was present only in the amorphous phase at these temperatures. The EO:salt ratio in the amorphous phase was estimated to be $\simeq 30$ at approximately 55°C, becoming more salt-rich (EO:salt $\simeq 8$) at 160°C. Similar conclusions were reached for the $P(EO)_{10}NaI$ sample, and in both cases an EO:salt ratio in the crystalline phase $\simeq 3.5$ was deduced.

Phase diagrams for the important cases of PEO-LiClO$_4$, determined by Robitaille and Fauteux [13], and for PEO-LiCF$_3$SO$_3$, studied by several groups [13, 22, 23], are sketched in Figs. 6(a) and 6(b). WAXS, DSC, polarized light microscopy and NMR were used in these determinations. In addition to the high melting complex, the PEO-LiClO$_4$ system features a crystalline complex of composition $P(EO)_6LiClO_4$, which was identified by WAXS and melts at ~65°C. This complex also forms a lower-melting eutectic with PEO. A similar phase diagram was observed [13] for the PEO-LiAsF$_6$ system, but in this case the 6:1 stoichiometric complex melts at 136°C, and complexes richer in salt than $P(EO)_5LiAsF_6$ are thermally unstable. The PEO-LiCF$_3$SO$_3$ system apparently comprises only the high-melting complex, $P(EO)_3LiCF_3SO_3$, the pure PEO crystalline phase, and the liquid, complexed elastomeric phase.

THE INFLUENCE OF SOLVENT ON COMPLEX FORMATION

Although the phase diagrams apparently represent equilibrium compositions, the possibility of forming metastable, salt-rich complexed phases was demonstrated by Payne and Wright [12] who investigated the effect of solvent polarity on the structure of $P(EO)_4$-Li$^+$ complexes. These workers observed that $P(EO)_4LiBF_4$ was deposited from dilute (2%) solutions in chloroform-acetone as almost entirely the high-melting form (Fig. 1e), whereas methanol-deposited materials of the same composition were almost entirely low-melting (Fig. 1f). Both materials gave the same WAXS patterns and suffered only minor redistributions in proportions of the phases on thermal cycling. However, LiBF$_4$ complexes prepared from short PEO chains (e.g., PEO 4000) are invariably of the high melting form, irrespective of the solvent.
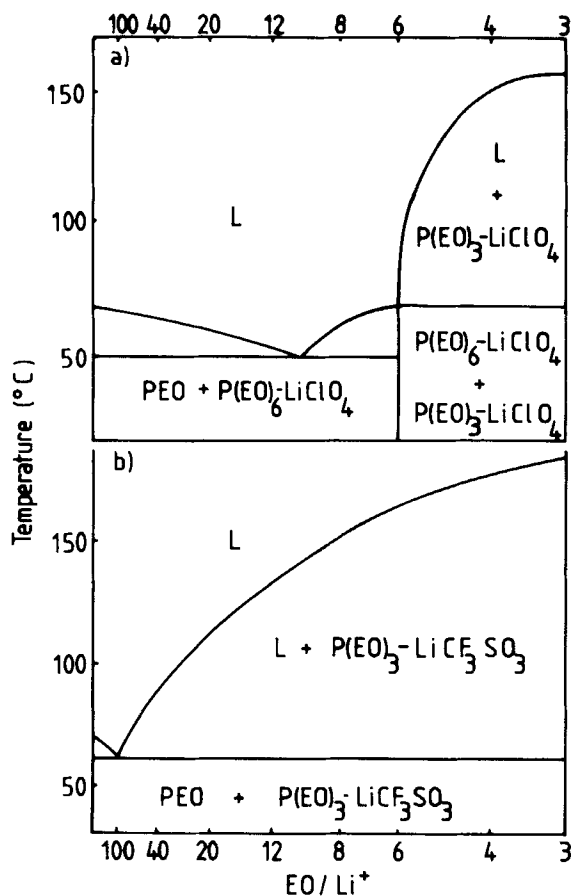
FIG. 6. Phase diagrams for a) PEO-LiClO$_4$ after C. D. Robitaille and D. Fauteux [13] and b) PEO-LiCF$_3$SO$_3$ after Robitaille and Fauteux [13], Berthier et al. [22], and Sørensen and Jacobsen [23].

These observations suggest that the formation of crystalline PEO–alkali salt complexes generally involves the formation of "precursor ion–polymer complexes" in solution to a greater or lesser degree. The degree of association of the polymer and salt will depend on the nature of the cation and anion and their degree of solvation by the solvent. Thus, poor ion solvation should promote the formation of precursor complexes in dilute solutions,

and the conformational freedom available to the polymer chains under such conditions should beget well-organized crystalline phases. (Furthermore, the organization of the polymer-salt adduct may also be retained to some degree in the melt, as noted by Lee [14] for PEO-NaSCN complexes.) On the other hand, good ion solvation, particularly of lithium salts, should tend to retard polymer-ion association until the solvent is removed so that entanglement constraints on polymer mobility at the higher concentrations may give rise to crystal phases which, although having the same basic lattice arrangement, incorporate defects, particularly in the organization of the polymer chains (which are readily removed thermally if short-chain PEO is used). The morphologies of films of PEO complexes with organic salts, discussed later, apparently provide strong evidence for the formation of precursor complexes.

Such strong influence by the conditions of preparation on the thermal stability of flexible-chain, semicrystalline polymers is unusual and reflects considerable organizational constraints on the formation of the polymer-salt adduct. Parker and coworkers [18] cited this circumstance as evidence for possible double-strand coordination of the alkali ions by PEO. However, this behavior is perhaps equally well accounted for by Chatani and Okamura's low-pitch helix. In this structure, 18 skeletal bonds of length $\simeq 23$ Å when fully extended, propagate a mere 7-8 Å along the fiber direction. The "reeling-in" of high molecular weight chains from an entangled phase to form such a structure is likely to proceed much more slowly than the organization of the more mobile ionic components and unstable defects such as reversals in helical sense should be readily incorporated.

Nevertheless, in some stoichiometric (3:1) samples of Na^+ and Li^+ complexes, low-temperature endotherms and exotherms on DTA traces are readily removed by thermal cycling. Thus, the stability of lower-melting structures may depend on stoichiometry and anion association.

In general, therefore, the "lower" endotherms on DTA traces of most samples with large salt deficiencies will correspond to the melting of pure PEO crystals, but the lower-melting complexed structures, either metastable salt-rich forms or other equilibrium structures, such as those described by Robitaille and Fauteux, will contribute to DTA tracings.

IONIC CONDUCTIVITY IN PEO-ALKALI SALT COMPLEXES

The ionic conductivities of PEO complexes with sodium, potassium, and ammonium salts are presented as Arrhenius plots in Fig. 7 and conductivities of complexes with lithium salts are shown in Fig. 8. The latter are the most
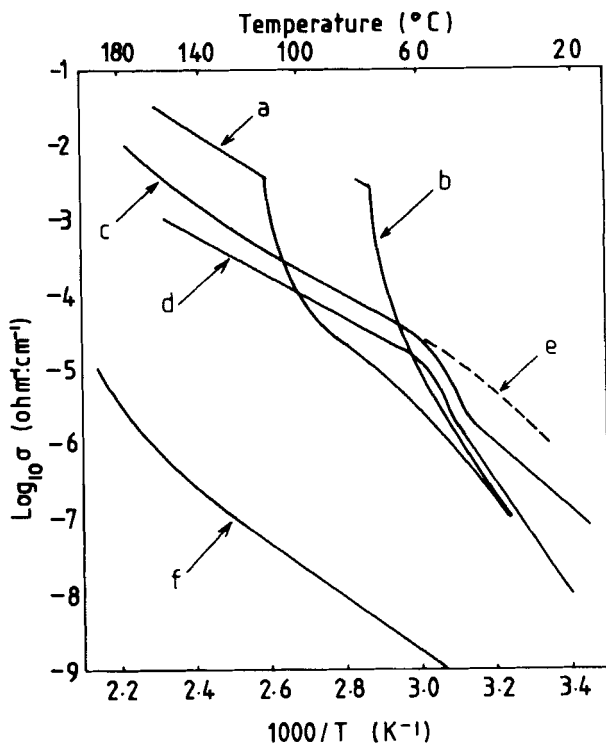
FIG. 7. Electrical conductivity of PEO-salt complexes [6, 14]. (a)
P(EO)$_4$KSCN; (b) P(EO)$_4$NH$_4$SCN; (c) P(EO)$_4$NaSCN; (d) P(EO)$_4$NaI;
(e) P(EO)$_6$NaI, PEO 600 maleate network; (f) P(EO)$_3$NaI.

widely studied in recent years in view of their potential importance for light-
weight rechargeable batteries.

A prominent feature of many of the plots for crystalline complexes is a
"knee" marking a transition to a lower activation energy for conduction at
higher temperatures with the two regions of the plots apparently separated
by a discontinuity in many samples. Such behavior contrasts with that to
be expected for diffusion of a low molecular weight species in an amorphous
polymer system when the temperature passes through a glass transition. In
the latter case the larger-scale motion of polymer segments in the elastomer
is accompanied by a greater activation energy than is the local segmental
motion in the glass. The glass-transition temperatures observed in the PEO-
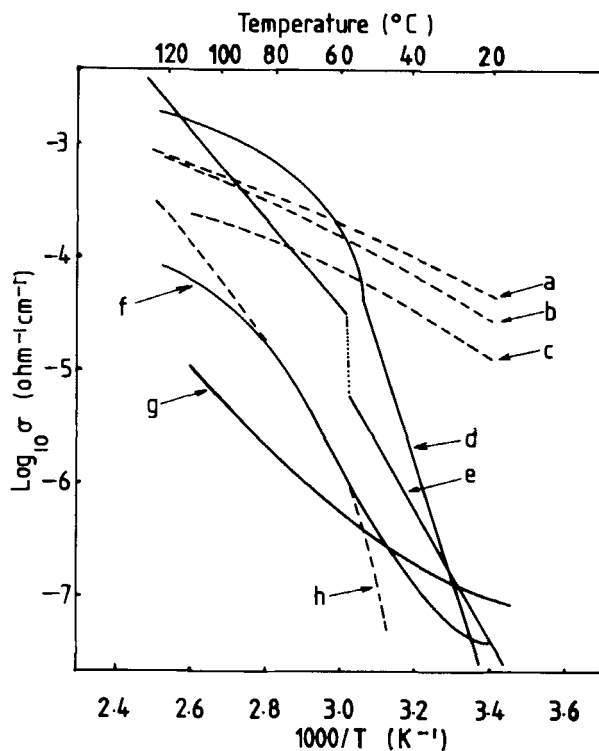
FIG. 8. Electrical conductivity of PEO–lithium salt complexes. Solid lines denote complexes that are semicrystalline at temperatures below ~65°C. Dashed lines denote complexes that are fully amorphous throughout the temperature range. (a) P(EO)$_{25}$LiCF$_3$, oxymethylene-lined PEO 400("amorphous PEO") [38]; (b) PEM22-LiCF$_3$SO$_3$, polymethacrylate "comb" polymer with (EO):salt = 18:1 [31]; (c) P(EO)$_{60}$LiBF$_4$, PEO 400 maleate network [12]; (d) P(EO)$_{20}$LiClO$_4$ [13]; (e) P(EO)$_{20}$LiCF$_3$SO$_3$ [13]; (f) P(EO)$_4$LiBF$_4$, from methanol solution [12]; (g) P(EO)$_4$LiBF$_4$, from 2% solution in acetone-chloroform [12]; (h) P(EO)$_5$LiSCN [7].

alkali complexes are typically significantly below the temperatures of the transitions in conductivity and may be observed by thermal analysis in the region of 0°C in, for example, P(EO)$_4$LiBF$_4$ (see Fig. 1).

The transitions in the conductivity behavior of the PEO complexes clearly coincide with the first-order thermal transitions on the DTA traces. In the

cases of the KSCN and NH_4SCN complexes, these correspond to the forma-
tion of fully isotropic melts at $\sim$110 and 79°C, respectively. This suggested
that conduction occurs most readily, with lower activation energy, in the
amorphous phase in these materials [6]. (Analogous behavior is to be found
in the transition to a lower activation energy conduction process following
the melting of crystallites in plasticized poly(vinyl chloride) [24, 25].)

In the cases of the sodium and lithium ion complexes, however, the transi-
tion occurs at the temperature of the lower DTA endotherm, 50-65°C, with
the lamellar structure of the higher-melting phase remaining intact. As dis-
cussed above, the lower endotherm corresponds to the melting of crystals of
pure PEO in samples with sufficient deficiencies of salt or to the melting of
low-stability complexed forms. The principal conducting pathway in these
cases was therefore identified as the interlamellar amorphous elastomer phase
which is created when the various lower melting structures disintegrate [6].
This is confirmed by the NMR studies of Berthier and coworkers [22], dis-
cussed above, which suggested that ion mobility in $P(EO)_8LiCF_3SO_3$ is re-
stricted to the amorphous phase at temperatures below 90°C. The creation
of new conducting pathways in the materials is consistent with the observa-
tion of discontinuities at the transition regions of the conductivity plots
[6, 13].

The complexes of PEO 5×10^6 and $LiBF_4$ (4:1), described earlier, display
different conductivity behavior according to their method of preparation [12].
The low-melting form prepared from methanol shows a transition to a more
conducting phase on melting, whereas the high-melting sample prepared from
acetone-chloroform shows no such transition at this temperature and is a poor
ion conductor. This behavior, which is consistent with the absence of a lower
DTA endotherm and the improved structural order, is also shown by the stoi-
chiometric $P(EO)_3$-NaI sample.

Also shown in Fig. 8 is Armand's plot of the conductivity of the
$P(EO)_5LiSCN$ complex [7]. This complex is fully amorphous and apparently
is disqualified from forming a crystalline complex phase by virtue of the high
lattice energy of the salt. $P(EO)_8CsSCN$ is also amorphous [7], presumably
on account of the larger cation size. Thus, in neither of these cases is a transi-
tion between two linear, or approximately linear, regions observed on the
Arrhenius plot. However, Armand [7] observed that linearization of these
data is obtained from free-volume theory by plotting $\ln(\sigma T^{0.5}/A)$ versus
$(T - T_0)^{-1}$ according to the Vogel-Tamman-Fulcher (VTF) equation

$$\sigma = AT^{-0.5} \exp\left[-E_a/(T - T_0)\right],$$

where, for $P(EO)_5 SCN$, $A = 2.57$; the reference (glass transition) temperature $T_0 = -15°C$; the apparent activation energy, $E_a = 7.57 \times 10^{-2}$ eV.

Nevertheless, regardless of the fully amorphous nature of the complexed phase, the $P(EO)_5 LiSCN$ material has a lower conductivity at ambient temperatures than the semicrystalline complexes formed with a lower lattice energy salt. Thus, together with the morphology of the polymeric medium, apparently ionic association is also a major influence on the conduction behavior of PEO-salt complexes. The dissociation of ions of alkali salts in media of relatively low dielectric constant will be sensitive to the charge density of the ions as reflected, for example, in the lattice energy of the salt. Thus, the larger, "soft" ions, such as ClO_4^-, exert weaker electrostatic interactions on cations than do Cl^- or Br^-, while their relatively high polarizability induces favorable stabilizing interactions with the polyether.

In their exhaustive study of PEO-lithium salt complexes, Robitaille and Fauteux [13] observed that the conductivities of complexes with $LiCF_3SO_3$, $LiClO_4$, and $LiAsF_6$ varied with overall composition in a complex way. Conductivity isotherms at temperatures above PEO melting for complexes with $LiCF_3SO_3$, $LiClO_4$, and $LiAsF_6$ show conductivity maxima for EO:salt compositions over the range 12-20, and a maximum is also present at lower salt compositions (50-100). These variations presumably reflect not only morphological changes but also changes in ion aggregation with salt concentration.

The activation energies for conduction in the higher-temperature regime of the Na^+ and K^+ complexes ranged between 0.54 and 0.6 eV [6], which is close to the value of 0.61 eV found by Binks and Sharples [26] for pure molten PEO, suggesting that similar motions of the PEO chains may control the conduction process in each case. However, a wider range of corresponding activation energies in PEO-$LiClO_4$ is reported by Robitaille and Fauteux [13]. The activation energies are $\simeq 0.7$ eV for higher proportions of salt and $\simeq 0.3$ eV for samples with lower proportions (20:1). However, the high-temperature regime of the latter is perhaps better described by free volume (VTF) expressions than by the Arrhenius law (Fig. 8). On the other hand, the PEO-$LiCF_3SO_3$ system exhibits Arrhenius behavior at all compositions. Such contrasts in behavior may perhaps reflect differences in the structure of ion aggregates and their local effect on transient crosslinking of the PEO chains.

Thus, the ionic conductivities of simple PEO-salt mixtures are dependent on several structural factors. As the examples in Figs. 7 and 8 indicate, the highest conductivities are observed with low lattice energy salts in overall salt concentrations which may be much lower than the stoichiometric proportions of the most stable crystalline complexed phases (particularly for lithium salts) and at temperatures above the melting temperature of pure PEO. These trends

reflect the requirement for 1) maximization of the proportion of amorphous phase, 2) minimization of restrictions on segmental mobility brought about by polymer-salt association (Watanabe [27] has pointed out that the lower lattice energy salts which maximize conductivity are also most effective in increasing the glass-transition temperature), and 3) maximization of the concentration of current carriers by reduced ion-ion associations at low salt concentrations.

TOWARD IMPROVED AMBIENT CONDUCTIVITY

The observation of enhanced conductivity in amorphous PEO has prompted the synthesis of a variety of polymeric systems which incorporate PEO segments in such a way as to inhibit or eliminate the crystallization both of PEO and of the PEO-salt complex. In such materials the higher temperature, lower activation energy regime of the Arrhenius plots for the semicrystalline PEO complexes with low lattice energy salts may be effectively extrapolated back to ambient temperatures without suffering the sharp decline in conductivity at temperatures below 60°C which normally accompanies the loss of the amorphous pathways. Arrhenius plots for these amorphous materials generally show a slight curvature, as in the examples in Figs. 7 and 8. In many cases, ambient conductivities over the range 10^{-5}-10^{-4} S/cm are observed. As in the simple PEO complexes, salt concentrations are usually low in the most conductive systems consistent with high segmental mobility (low T_g) and higher concentrations of charge-carrying species.

Many different chemical structures have been synthesized. Some of the various strategies which have been adopted, together with some examples, are summarized below.

(1) Networks

Payne and Wright [12] reacted short-chain poly(ethylene glycols) PEO 400 or PEO 600 with maleic anhydride to give high molecular weight linear products which were then crosslinked with peroxides to form clear gels. Salts were then diffused into the networks from solvents. An ambient conductivity $\simeq 3 \times 10^{-5}$ S/cm was observed for a gel with EO:LiBF$_4$ $\simeq 60$ (Fig. 8).

A variety of polyurethane networks were synthesized by Gandini and co-workers [28] by reacting isocyanates with polyether diols and triols having molecular weights of several thousand. Both ethylene oxide and propylene oxide polymer and copolymer networks have been prepared and $\sigma \simeq 10^{-4}$

S/cm is reported [29] for a PEO-PPO-PEO block copolymer crosslinked by triisocyanates and complexed with $LiClO_4$. Watanabe et al. [30] prepared similar polyether triol-diisocyanate networks with EO:salt = 50. Higher lattice energy salts (e.g., LiBr) allowed PEO crystallites to separate, whereas lower lattice energy salts such as $LiClO_4$ were fully amorphous, giving $\sigma \simeq 10^{-5}$ S/cm at ambient.
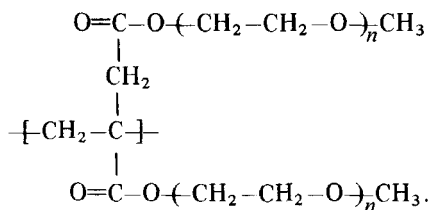
(2) Branched "Comb" Polymers

In these systems, short oligomeric side-chains of PEO represent the "teeth" of the comb which are appended to a high molecular weight polymeric backbone. The PEO is attached at a density of one or two side-chains per pair of skeletal bonds. Side-chains may incorporate up to 40 EO units, but the longer PEO sequences may tend to crystallize. Comb polymers may be conveniently cast into films from solutions, but dimensional stability may be a problem with these materials.

Bannister et al. [31] and Fish et al. [32] studied poly(methoxy poly(ethylene glycol) methacrylates).

$$
\begin{array}{c}
CH_3 \\
| \\
-[-CH_2-C-]- \\
| \\
C \\
/\!\!/ \quad \backslash \\
O \qquad O-(-CH_2-CH_2-O-)_n CH_3
\end{array}
$$
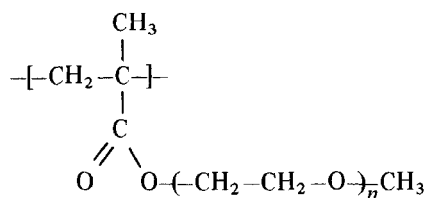
Fully amorphous systems were observed for $n = 9$, but for $n = 22$ the tendency to crystallize depended on the nature of the complexing salt. However, with $EO:LiCF_3SO_3 = 18:1$, conductivities in the range 10^{-5}-10^{-4} S/cm were observed with the higher value being observed for $n = 22$ (Fig. 8).

Cowie and Martin [33] prepared some related materials based on itaconic acid,

$$
\begin{array}{l}
O=C-O-(-CH_2-CH_2-O-)_n CH_3 \\
\quad | \\
\quad CH_2 \\
\quad | \\
-[-CH_2-C-]- \\
\quad | \\
\quad O=C-O-(-CH_2-CH_2-O-)_n CH_3.
\end{array}
$$

Blonsky and coworkers [34] developed some comb polymers with a flexible polyphosphazene backbone. Greater skeletal flexibility may off-set to some degree the undesirable increases in glass-transition temperature brought about by the interactions of the salt with the PEO component. The polyphosphazene structures,
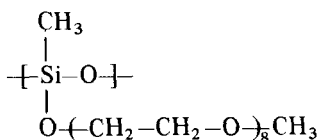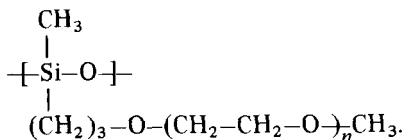
$$
\begin{array}{c}
(O-CH_2-CH_2\rightarrow_n O-CH_3 \\
| \\
+N=P+ \\
| \\
(O-CH_2-CH_2\rightarrow_n O-CH_3,
\end{array}
$$
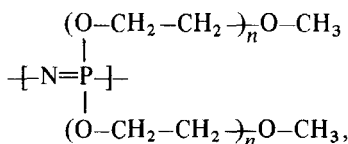
having a range of values of n have been synthesized, and the system $n = 2$, which has been coded MEEP, has received much attention. When com-plexed with lithium salts, MEEP gives conductivities which are similar to those of the polymethacrylate ($n = 22$) systems, but a high ambient con-ductivity of $\simeq 2 \times 10^{-4}$ S/cm is reported for an $AgCF_3SO_3$ complex.

Employing a similar strategy which emphasizes the flexibility of the polymer backbone, Smid and coworkers prepared comb polymers with polysiloxane backbones:

$$
\begin{array}{cc}
CH_3 & CH_3 \\
| & | \\
+Si-O+ & +Si-O+ \\
| & | \\
O+CH_2-CH_2-O\rightarrow_8 CH_3 & (CH_2)_3-O-(CH_2-CH_2-O\rightarrow_n CH_3.
\end{array}
$$

$$
\begin{array}{cc}
I & II\ (n = 8\ or\ 12)
\end{array}
$$

The ambient conductivities of both I and II ($n = 12$) with $EO:LiClO_4 = 25$ is 7×10^{-5} S/cm but the chemical stability of the Si–C linkage in II is greater than the Si–O bond in I. However, in common with other comb-polymer systems, these polysiloxanes are viscous oils at ambient tempera-tures. Light crosslinking or blending with PEO is reported to improve dimensional stability of the films while giving ambient conductivities which are still in excess of 10^{-5} S/cm.

Kihara and Yasukawa [36] reported the polymerization of a series of tris[methoxy(polyoxyethylene)ethoxy] siloxy alkyl acrylates. A material of structure

$$
\begin{array}{c}
+CH_2-CH+ \\
| \\
CO-O-CH_2CH_2-O-Si\equiv[-O+CH_2CH_2O\rightarrow_{12}CH_3]_3
\end{array}
$$
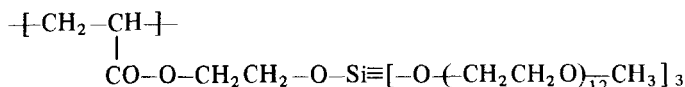
has a conductivity at 25°C of 10^{-4} S/cm. The high transparency to visible light rendered this material of interest for electrochromic display devices.

(3) Regular and Random Copolymers

The tendency for PEO and its complexes to crystallize may be suppressed by interrupting the regular EO sequence in a long chain at appropriate intervals with a different unit. Watanabe's group [37] linked PEO oligomers with dimethylsiloxane units:

$$-[-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{Si}}}}-O-(-CH_2CH_2O-)_n]-,$$
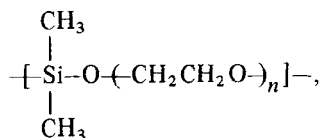
where $n = 1, 2, 4,$ and 9. For $n = 4$ with EO:LiClO$_4$ = 33, a conductivity of 1.5×10^{-4} S/cm is reported. Craven and coworkers [38] linked poly(ethylene glycol) of number-average molecular weight 400 with methoxy units to give so-called "amorphous PEO:"

$$...CH_2CH_2O)-CH_2O-(CH_2CH_2O....$$
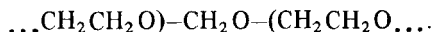
Lithium ion conductivities approximating that of the corresponding MEEP system are observed.

(4) Interpenetrating Networks and Blends

The blending and cosolubilization of PEO with other polymers has been adopted as a strategy for both suppressing crystallinity and enhancing the mechanical stability of PEO complexes. For example, Shigehara [39] formed blends of PEO with the perfluoro-polyelectrolytes Nafion and Flemion giving an ambient conductivity of 10^{-5} S/cm. Gray and coworkers [40] polymerized styrene in the presence of a P(EO)$_{10}$-LiCF$_3$SO$_3$ and found marked increases in physical strength for only small deterioration in ionic conductivity when 40 vol% polystyrene was present. Recently, Chiang et al. [41] reported the preparation of interpenetrating networks of PEO 400 with epoxy formulations. For formulations incorporating 20-30 wt% of epoxy resin and P(EO)$_{10}$-LiClO$_4$, films having good mechanical properties and conductivities $\simeq 10^{-4}$ S/cm at ambient temperature were prepared.

THE MECHANISM OF CONDUCTION

As discussed above, ionic transport in amorphous PEO-based systems can be described empirically by the VTF equation. An equivalent free-volume treatment which has been adopted by Cheredame [42] and by Watanabe and coworkers [30] uses a form of the Williams-Landel-Ferry (WLF) equation,

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

where the logarithmic term is the logarithm of the ratio of conductivities at temperatures T and the glass-transition temperature T_g and the constants C_1 and C_2 may be expressed [42, 30] as functions of the critical free volume for migration of the carrier ions and the free volume available at T_g. This approach allows comparison between the ionic conductivity and the dynamic mechanical properties through the familiar WLF relationship [43],

$$\log\left(\tau_T/\tau_{T_g}\right) = C_1'(T - T_g)/(C_2' + T - T_g),$$

where the logarithmic term is the logarithm of the ratio of the dynamic mechanical relaxation times at temperatures T and T_g. Cheradame and Le Nest [44] and Watanabe et al. [30] point out that the respective C parameters are approximately the same for ionic conduction and mechanical relaxation (i.e., $C_1 \simeq C_1' \simeq C_2'$). Furthermore, C_1 and C_2 are approximately independent of the diffusing salt for various lithium, sodium, and potassium halides and thiocyanates in PEO-urethane networks [30]. This suggests that charge carrier mobility is controlled by polymer segmental mobility, a similar conclusion to that from the Arrhenius behavior [6]. This is consistent with the charge carriers being associated with the moving segments or being present as ionic aggregates commensurate in size to the critical hole size for segmental mobility.

MacCallum, Tomlin, and Vincent [45] studied the molal conductance, Λ, of $LiCF_3SO_3$ and $LiClO_4$ in solution in PEO 400 according to

$$\Lambda c^{0.5} = (\Lambda_1{}^\circ/\beta_2{}^{0.5}) + (\Lambda_2{}^\circ \beta_3 c/\beta_2{}^{0.5}),$$

where $\Lambda_1{}^\circ$ and $\Lambda_2{}^\circ$ are the limiting molal conductances of the salt A^+, B^- and the hypothetical electrolyte $A_2 B^+, AB_2^-$, respectively; while β_2 and β_3 are the association constants for the AB ion pair (uncharged) and the triple ion aggregates, respectively. Linear plots of $\Lambda c^{0.5}$ versus c were obtained,

whence β_2, β_3, and the concentrations of free ions, ion pairs, and the triple ions were evaluated. MacCallum and coworkers concluded that above salt concentrations of approximately 0.01 mol/dm^3, between 50 and 85% of the salt was present as ion pairs, and the majority of the current was carried by the triple ions. The latter were present as 27% of the triflate salt and 41% of the perchlorate at 0.1 mol/dm.

The nature of the charge on the current carriers in PEO-based polymer electrolytes is a matter of some controversy at present. Ion transference numbers have been determined by a number of groups using a variety of techniques, including NMR [46-48], radiotracer methods [49], complex impedance measurements [50, 51], and potentiometric measurements [52]. Since salt solubility in PEO involves cation coordination by the polyether, the anion is expected to be the most mobile species. This expectation is generally borne out, but a wide range of cationic transference numbers ranging between approximately zero and approximately 0.5 have been reported. Cheredame and coworkers [53] used Tubandt's method, by which mass transfer through membranes is determined directly by weighing, to measure cationic transference numbers in PEO-urethane networks containing LiClO$_4$. The values observed ranged between ~0.45 and 0.03 and were found to decrease both with the concentration of salt and the molecular weight (400-5000) of the PEO between the network junctions. These results are consistent with the positive ions being mostly present as multiple ions since both an increase in salt concentration and in the length of PEO segments should promote the tendency for aggregation in quasi-crystalline arrays which nucleate around the PEO helix. The metastable, low-melting structures observed by Lee and Wright using DTA in PEO 600-NaI networks are probably developments of the type of aggregates present in networks at lower salt concentrations.

FURTHER DEVELOPMENTS

Notwithstanding the uncertainties in cation transport numbers, solid-state batteries incorporating lithium electrodes have been developed [54-58], and the possibility of using these devices as rechargeable power sources has been demonstrated. The construction involves a thin film (50-100 μm) of PEO or modified PEO-salt electrolyte sandwiched between a lithium foil anode of similar thickness and a composite cathode of either V$_6$O$_{13}$ or TiS$_2$ mixed with PEO and acetylene black in various types of laminar arrangement. The PEO-salt electrolytes have EO:salt ratios of 10-20:1, and most published re-

sults refer to batteries which operate at temperatures above ~80°C. They generally deliver between 2 and 3 V at current densities up to ~2 mA/cm^2. However, power densities in excess of 100 W/dm^3 and energy densities in excess of 100 Wh/kg[1] have been demonstrated, and the cells may be charged/discharged for more than 100 cycles without significant deterioration in performance.

Other recent developments in PEO-based systems include the preparation of complexes with salts of divalent ions such as Zn^{2+}, Mg^{2+}, and Ni^{2+} [59, 60]. Electrochemical cells have been constructed from these materials although ionic conductivities are generally reported to be lower than for univalent salts and give cell currents of several microamperes. Skaarup and coworkers [61] recently reported composite, mixed-phase solid electrolytes consisting of Li_3N dispersed in $P(EO)_{10} LiCF_3SO_3$. Ambient conductivities $\simeq 10^{-5}$ S/cm are reported.

Systems analogous to the PEO complexes but based on the structurally related poly(propylene oxide) (PPO) chain have been investigated by Watanabe and coworkers [62]. This material has the distinct advantage over PEO in that, due to the atactic placement of the substituent methyl group, its salt complexes are invariably amorphous and thus require no chemical modification to suppress crystallinity. However, in general, PPO complexes have conductivities which are 5-10 times lower than the corresponding amorphous PEO structures. Watanabe concluded that ionic mobilities in PPO are similar to those in PEO and that the lower concentrations of charge carriers in the former must be ascribed to a greater degree of ionic association. This may presumably be accounted for by a lower local dielectric constant in PPO, deriving from the additional hydrocarbon in the structure.

PEO COMPLEXES WITH ALKALI SALTS OF ORGANIC ACIDS

The molecular model for the crystalline PEO complexes with Na$^+$ or Li$^+$ ions, which is suggested by Chatani and Okamura's structure for PEO-NaI (Fig. 2), consists of a low-pitch helix of PEO having cations spaced at regular intervals. The intervals are readily adjusted between approximately 0.36 and 0.42 nm to accommodate various anions according to their dimension along the fiber axis. This interval should comfortably accommodate the thickness of the aromatic ring in planar organic anions which should stack alongside the helices (Fig. 9), and suggests the possibility of preparing a wide range of novel complexes with PEO provided that the electrostatic components of the lattice energies of the free salts are not too high. In many aromatic anions, electron delocalization should ensure that this condition is met.
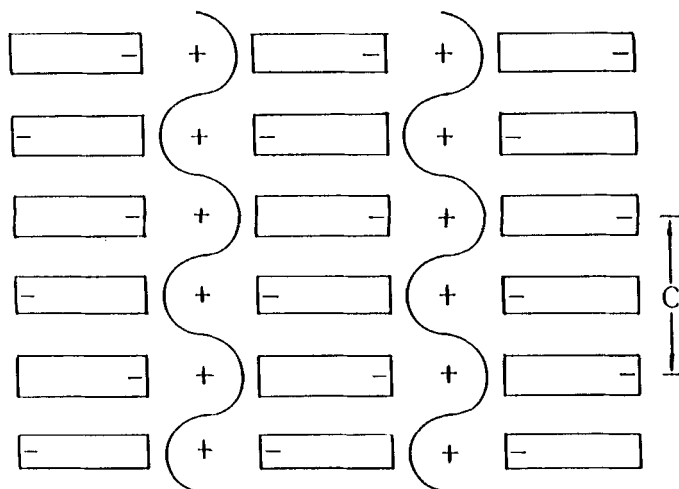
FIG. 9. Schematic diagram for structure of PEO-alkali ion complexes with aromatic anions (cf. Fig. 2). Fiber repeat distance, c, is adjustable over the range $\sim$0.72 ca $\sim$0.84 nm [11, 18].

Accordingly, Siddiqui and Wright [63] and Mussarat and coworkers [17] prepared a range of complexes with various sodium and lithium phenolates and naphtholates and with sodium acrylate. These complexes were characterized by WAXS and by DTA. The DTA traces showed both the lower and higher temperature endotherms in the same temperature regions as for the inorganic complexes but, in addition, some complexes prepared with high molecular weight PEO had pronounced exotherms, suggesting some molecular reorganization in the temperature region between the two endotherms (see Fig. 1h).

Complexes from freshly prepared methanol solutions with "hydrophobic" anions (i.e., acrylate, phenolate, or naphtholate ions with only hydrocarbon substituents such as alkyl or phenyl) were not deposited from solution in the normal spherulitic morphologies but were deposited as thin films having self-organized "macrodomains" of uniaxially oriented structure when viewed between crossed polarizers (Fig. 10a). Macrodomains 0.5 cm in dimension have been observed, and they may readily be row-nucleated by lightly shearing the solution prior to removal of the solvent.

The formation of macrodomains clearly points to the presence of lyotropic organization as precursor complexes in solution. As discussed above, precursor complexes in low polarity solvents also give rise to the more stable forms
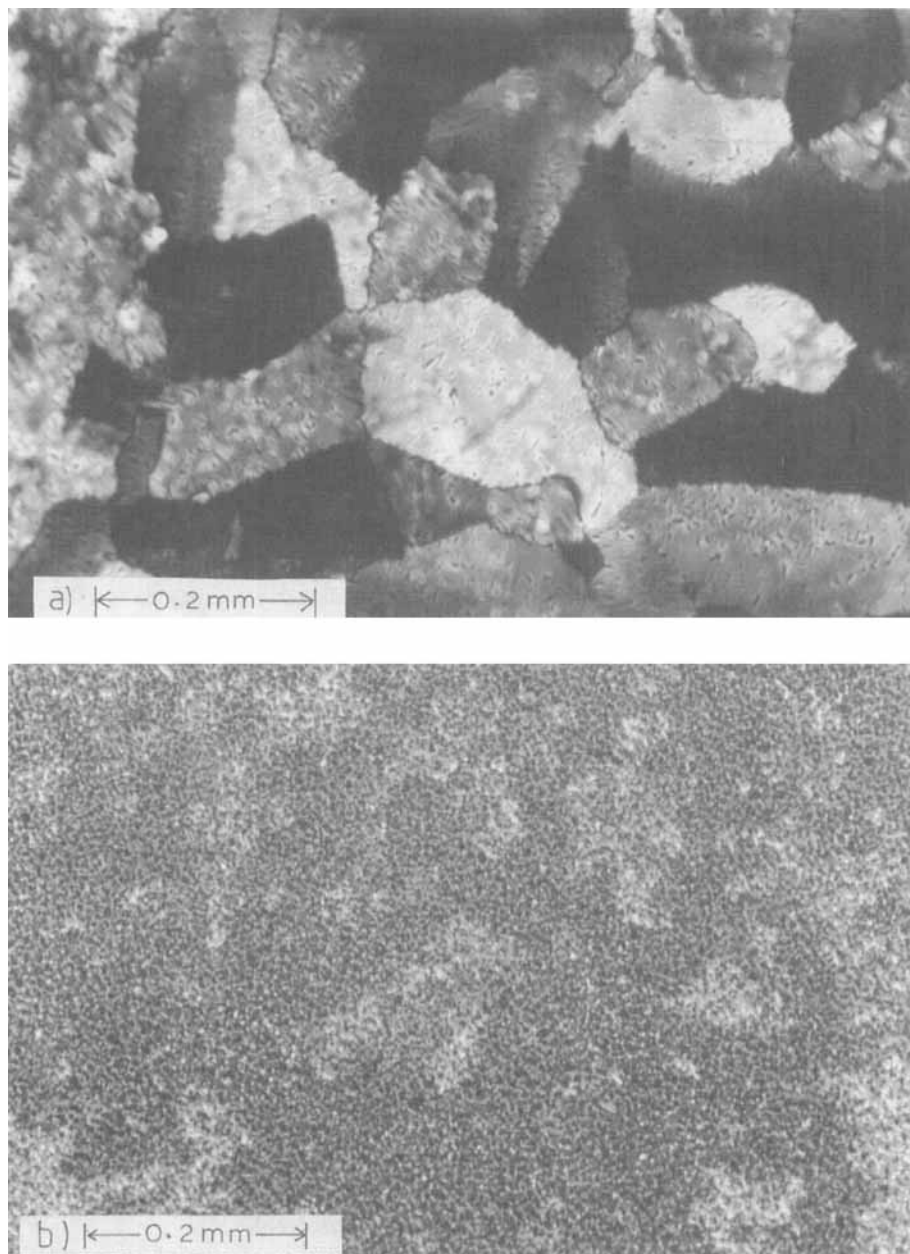
FIG. 10. Optical micrographs of P(EO)$_3$Na 2-naphtholate between crossed polarizers. a) Deposited from methanolic solution and b) after heating above ~60°C.

of the $P(EO)_4$-$LiBF_4$ complexes and probably feature to a greater or lesser degree in the formation of most crystalline PEO-salt complexes. The inorganic complexes are deposited in spherulitic morphologies but the mesogenic nature of the planar aromatic anions together with poor ion solvation is apparently responsible for the lyotropic organization observed in these cases. Macrodomains have not been observed in lithium salt complexes from methanol presumably in consequence, at least in part, of stronger cation solvation.

On heating macrodomain material through 60-90°C, reorganization to a microdomain ($<$10 μm) texture takes place (Fig. 10b). This reorganization takes place over the range at which the onset of the mesophase is observed in the inorganic salt complexes and presumably also involves anion disorganization. However, as discussed above, large-scale morphological reorganization appears much slower and at higher temperatures in the inorganic cases (Fig. 3b). Melt recrystalization of the aromatic salt complexes results in well-defined spherulitic morphologies. Furthermore, complexes formed from planar aromatic ions bearing polar substituents, such as chloro- or cyano-, also form spherulites since anion solvation reduces the stability of precursor association with the polyether. However, thermotropic reorganizations are apparent in these materials also. These organo-salt-PEO complexes may thus represent a novel class of ionic polymer liquid crystals.

PEO-BASED MATERIALS DISPLAYING ELECTRONIC-IONIC CONDUCTIVITY

The possibility of constructing all-polymer cells, such as the $(CH)_x$ |PEO-NaI|$(CH)_x$ system proposed by Chiang [64], has aroused interest in the preparation of materials having mixed ionic-electronic conductivity which may assist interfacial ion transport between electrode and electrolyte. Blends of polypyrrole and PEO have been prepared by Inganäs and coworkers [65] and Owen and Minett [66]. The latter also prepared polypyrrole with pendent EO oligomers attached at the nitrogen atoms.

Conheeny and Wright [67] prepared polythiocyanogen $(SCN)_x$ by a "canal" polymerization which is brought about on exposure of fibers or particles of $P(EO)_3$-NaSCN to a halogen:

$$xP(EO)_3 NaSCN + 0.5xBr_2 = xP(EO)_3 NaBr + (SCN)_x.$$
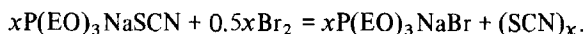
The reaction, which is strongly exothermic, may proceed via thiocyanogen gas $(SCN)_2$, and is conveniently controlled in a fluidized bed of dry N_2 when particulate polymer complex is used. Anisotropic particles of $(SCN)_x$ may
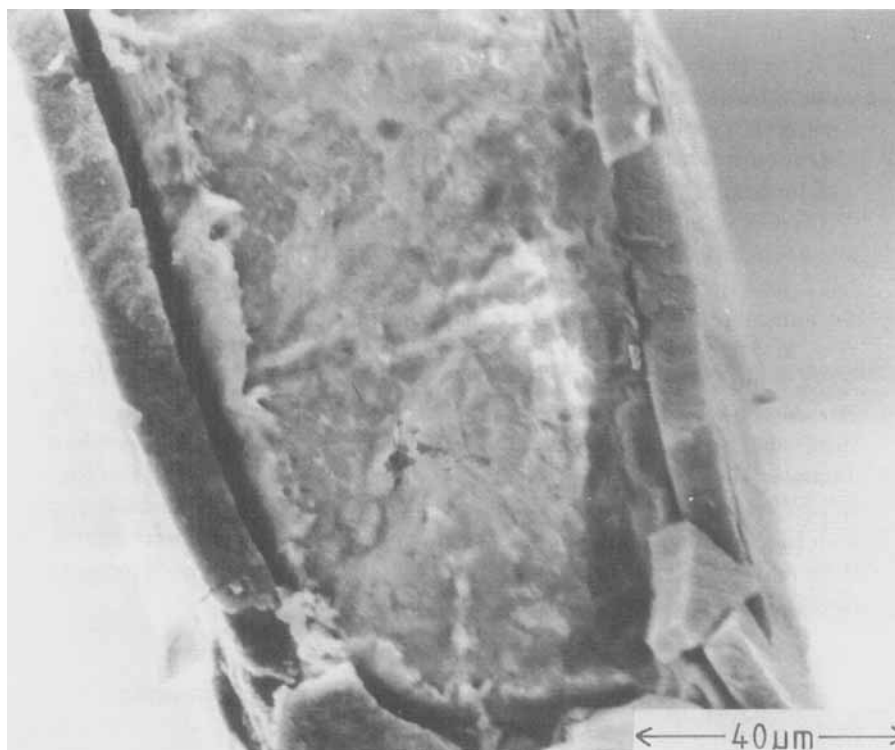
FIG. 11. Scanning electron micrograph of section of PEO/Na-tetracyano-quinodimethanide, lightly rolled and fractured in liquid nitrogen. (Photograph by J. A. Siddiqui.)

be isolated by extraction of the matrix polymer and salts in methanol. Following exposure to I_2 dopant vapor, the particles may be pressed between rollers to give films having conductivity $\simeq 10^{-6}$ S/cm. Additional exposure to small amounts of diethylamine increases the conductivity to $\sim 10^{-1}$ S/cm. The enhancement of the conductivity may perhaps be accounted for by promotion of electronic energy levels in the polymer, so reducing its ionization potential, following attachment of the diamine. However, retention of the PEO lattice resulted in marked decrease in conductivity.

Siddiqui and Wright [68] prepared electronic-ionic conducting films by exposure of $P(EO)_3$-NaI complexed films to tetracyanoquinodimethane (TCNQ) solution in a hydrocarbon solvent:

$$P(EO)_3\text{-NaI} + TCNQ = PEO/NaTCNQ + \tfrac{1}{2}I_2.$$
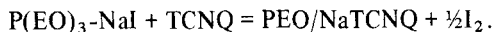
The structure of the films is not fully clear, but although NaTCNQ dissolves in amorphous phase PEO, microscopic and WAXS examination of the PEO/NaTCNQ films suggests that some of the NaTCNQ is present as microcrystals of dimensions $\sim 1\,\mu m \times 0.1\,\mu m$. Following the simple exchange reaction described in the equation, the I_2 is mostly lost to the solvent and the purple NaTCNQ material is confined to surface layers $\sim 10\,\mu m$ in thickness. The films thus constitute a composite sandwich of ionically conducting PEO electrolyte between electronic-ionic conducting surfaces (Fig. 11). The ambient temperature conductivity of the PEO/NaTCNQ surface layers is estimated to be $\simeq 10^{-3}$ S/cm.

However, exposure of the films to I_2 vapor over several days brings about a change in appearance of the films to a lustrous gold and an increase in conductivity to ~ 1 S/cm. This corresponds to the formation of an NaTCNQ-I_2 complex salt with a different WAXS spectrum and conductivity superior to the simple salt. However, the PEO/NaTCNQ-I_2 films have conductivities which are a hundredfold greater than compacted pellets of the complex salt. Prior treatment of the $P(EO)_3$-NaI films with I_2 allows deeper penetration of the TCNQ into the film, presumably by protecting the mobile neutral TCNQ molecule from rapid exchange with I^- ion and the precipitation of the less soluble salt. Similar composite structures may also be prepared by exchange of TCNQ with I_2-treated PEO-NaSCN films. The interaction of electronic and ionic conducting processes in these films is under further investigation.

ACKNOWLEDGMENTS

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