Ion Transport in Solvent-Free Polymers

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1. Introduction

Solid electrolytes comprise a widely varied set of materials in which the ionic conductivity σ is far higher than that of typical ionic solids such as NaCl. The conductivity of typical solid electrolytes lies in the range ($10^{-6} \lesssim \sigma \lesssim 10^{-1}$ S cm^{-1}) characteristic of dilute aqueous ionic solutions.[1] Solid electrolytes include refractory covalent solids such as β-alumina [$(Na_2O)_x \cdot 11Al_2O_3$], soft ionic crystals such as AgI, glasses such as Ag_2GeSe_3, and among the most recently discovered and investigated species, polymer–salt complexes.

Within the past 2 decades, the area of electroactive polymers has become one of the most challenging and fruitful realms of polymer science. Both electronically conductive polymers and polymeric electrolytes have been prepared and studied in a large number of laboratories, and a good deal of both synthetic and mechanistic knowledge about these new polymer materials has been gained. While these species share some of the properties of more usual conductive systems such as metals, semiconductors, and ionic solutions, the polymeric structure provides a new set of conditions, so that a number of new features appear in the electrical response. While reviews of the polymeric ionic conductors recently have appeared,[2-6] we are not aware of any currently available overview of polymer electrolytes for a general chemical audience. This article will attempt to survey, very selectively, the polymer electrolyte field; our emphasis will be on the chemistry, the structural situation, and the conductivity response.

Table I categorizes the classes of solid electrolytes that have been extensively investigated. The classification is subjective; a number of intermediate situations occur and still other solid electrolytes do not fit into any of these categories. The ceramic framework materials are characterized by high Debye temperatures and melting points; in these substances, which are generally oxides or chalcogenides, conductivity is due to mobile ions hopping among energetically favorable sites in the potential fixed by the framework. The soft framework materials have far lower Debye temperatures and melting points; they are often halides, in which the conduction is due either to ion hopping or to liquid-like diffusion of one ionic sublattice. The class of polymeric electrolytes is substantially different from the first two; polymeric materials show fast-ion behavior only above the glass transition temperature and are generally softer, compliant materials. As will be discussed extensively in section 4, in polymer electrolytes the motions of the polymer host are responsible for ionic mobility; the ions move only if polymer segments also undergo fairly large-amplitude excursions. Below the glass transition, such chain motion does not occur, and ionic conductivity drops to very small values. This behavior stands in sharp contrast to framework inorganic electrolytes, where motions of the framework simply provide activation energy for ionic conduction through structural channels in the framework.

A number of polymer-based systems exhibit ionic conductivity. Our emphasis will be on solvent-free polymer–salt complexes, where interest really began with the pioneering studies of materials based on alkali metal salt complexes with poly(ethylene oxide), or PEO, reported by Wright[7-9] and by Armand[10,11] in the 1970s. Other types of ionically conductive polymer systems have been prepared and are of great interest. These include solvent-swollen systems such as poly(vinyl alcohol)/H_3PO_4[12] in which quite high conductivities are observed, due largely to ionic motion in solvent-rich regions of the swollen polymer host. Ionic motion is also seen in polyelectrolytes such as Nafion,[13] in redox polymers,[14] and in intercalated electronically conductive polymers such as lithium-doped polyacetylene. Traditional solvent-swollen polyelectrolytes such as Nafion or sodium poly(styrenesulfonate) are best thought of as concentrated solutions in which one ionic species is very large and multiply charged and the mobile ion is solvated. In recent work, both polar solvating groups and charged groups have been covalently incorporated into the polymers (see section 5d).[15-21] Redox polymers[14] such as poly[Os(bpy)(vpy)$_2$(ClO$_4$)$_x$] (x = 0–3, bpy = bipyridyl, vpy = vinylpyridyl) consist of mixed-valent complexes covalently attached to the polymer chains along with counterions (such as halides or nitrate) that

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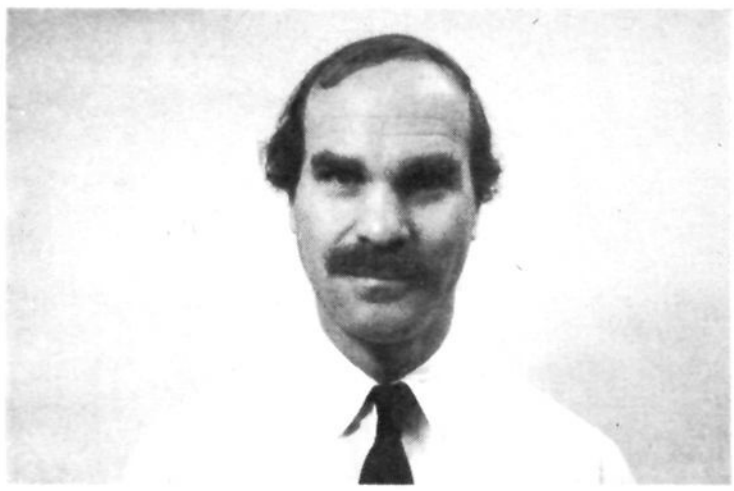

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move along the solvent-swollen polymer in response to electronic hopping among the mixed-valent metal sites. These are mixed ionic–electronic conductors. Intercalated electronically conductive polymer systems such as lithium polyacetylide or $(Si(pc)O)_n^+I_3^-$ (pc = phthalocyanine)[22] are much like the redox polymers. However, the electronic motion is of band, rather than hopping, type; once again they are mixed conductors (electrodes) rather than ionic conductors (electrolytes).

The remainder of this article deals with solvent-free polymer electrolytes based on polymer–salt complexes. Section 2 is devoted to the preparation of these materials, and section 3 to their structure. Section 4 presents a discussion of the conductivity in these polymer electrolytes, concentrating on measurements and on the interpretation of ionic mobility. Section 5 discusses several particular examples of polymer electrolytes. Finally, section 6 gives a brief outlook on current problems.

2. Formation of Metal Salt Complexes

The polymer electrolytes with which we are principally concerned are complexes of alkali metal salts, denoted MX, with polymer hosts. Both the precursor salt and the neat polymer are solids, so that the complex-forming reaction

$$m\mathrm{MX} + (\text{–RY–})_n \rightarrow (\mathrm{MX})_m\cdot(\text{–RY–})_n \qquad (1)$$

where (–RY–) denotes the polymer repeat unit, is a solid/solid reaction. As with most other reactions of this type, the kinetics of (1) are unfavorable, even when the complex is stable. Although other schemes for accelerating (1) have been employed, including intimate grinding/mechanical mixing,[23] by far the most common method has been to dissolve or suspend both the MX salt and the host polymer in a common solvent and then to remove the solvent, producing the solvent-free polymer electrolyte in either bulk or thin-film form.[24] Care must be taken to purify the starting materials and (especially in the case of hygroscopic lithium electrolytes) to exclude water. Acetonitrile and methanol have been the solvents most commonly used. If the polymer–salt complex is partly crystalline, both the morphology and the transport properties of the electrolyte material produced may vary with choice of solvent.

Clearly, reaction 1 will be thermodynamically favorable ($\Delta G°$ negative) only if the Gibbs energy of solvation of the salt by the polymer is large enough to overcome the lattice energy of the salt. In general, one then expects a close relationship between the ability to form homogeneous complexes and the ability of the monomer to dissolve the salt. Work by the Grenoble and Evanston groups has shown that for a given polymer host a fairly sharp demarcation line may be established between salts that can and cannot form complexes; the latter simply have too large lattice energies (compare Table II). In addition to the very important lattice energy considerations, a number of other criteria that determine the possibility of forming complexes have been described. These include the following:[11,34–38] (1) A high concentration of polar (basic) groups on the polymer chain is needed to solvate the salt effectively. (2) The cohesive energy of the polymer cannot be too high, and its flexibility, as indicated by a low glass transition temperature, should be quite high, so that reorientation of the local coordination geometry, to achieve effective solvation, may be achieved.

Most polymer electrolytes are based on oxygen-containing monomers, including ethers in poly(ethylene oxide) and poly(propylene oxide) and polysiloxanes, carbonyl in poly(vinylpyrrolidone) or poly(ethylene succinate), and hydroxyls in poly(vinyl alcohol). Other Lewis base groups have been employed, including nitrogen in poly(ethylenimine) and sulfur in poly(alkylene

TABLE I. Classes of Solid Electrolytes

ceramic framework materials		soft framework materials		polymers[a]	
crystalline species	glasses	crystalline species	glasses	partly crystalline	amorphous
$LiAlSiO_4$	$LiAlSiO_4$ (glass)	AgI	AgCl/AgI/CsCl		
β-alumina ($(Na_2O)_x \cdot 11Al_2O_3$)	$Ag_{2x}GeSe_{2+x}$	Ag_2HgI_4		LiSCN·PEO	LiSCN-MEEP
		PbI_2		$NaCF_3SO_3$·PEI	
Na_2SO_4					$NaCF_3SO_3$·PPO

[a] PEI = poly(ethylenimine), PEO = poly(ethylene oxide), PPO = poly(propylene oxide), MEEP = $-(N{=}P(OC_2H_4OC_2H_4OCH_3)_2)_n$.

TABLE II. Salts That Form Complex Polymeric Electrolytes with PEO[a]

	Li^+	Na^+	K^+	Rb^+	Cs^+
F^-	no	no	no	no	no
	1036	923	821	785	740
Cl^-	yes	no	no	no	no
	853	786	715	689	659
Br^-	yes	yes	no	no	no
	807	747	682	660	631
I^-	yes	yes	yes	yes	yes
	757	704	644	630	604
SCN^-	yes	yes	yes	yes	yes
	807	682	619	616	568
$CF_3SO_3^-$	yes	yes	yes	yes	yes
	725	650	605	585	550

[a] The numbers reported are the lattice energies of the salts (in kJ/mol). "Yes" indicates polymer–salt complex formation and "no" indicates the lack of complex formation. The stair-step line indicates the division between complex formation and separate phases.

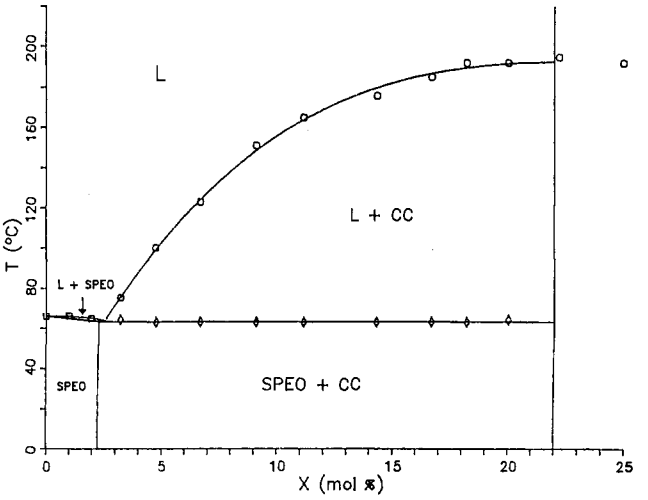


Figure 1. Phase diagram for the PEO–NaSCN system. X denotes mole fraction of NaSCN, L denotes liquid or elastomeric phase, and cc denotes crystalline complex. SPEO is semicrystalline PEO with NaSCN in the amorphous phase. From ref 43.

sulfides). In general, Lewis base character on the complexing host species is required to coordinate the cation of the salt and thus provide a favorable Gibbs energy of polymer–salt interaction.

3. Structure

Poly(ethylene oxide), or PEO, which has received the most attention as a host for electrolyte formation, is a semicrystalline material with about 60% of the bulk being crystalline at room temperature and the remainder present as an amorphous elastomeric phase. This phenomenon of partial crystallinity carries over to many of the polymer–salt complexes. Thus the problem of structure of the polymer electrolytes can be discussed at two levels: the macroscopic identity and arrangement of crystalline and amorphous phases and the microscopic arrangement of atoms in the polymer and polymer–salt complex.

The morphology of the crystalline phases can be observed with an optical microscope. For both PEO and PEO complexes the form of the polycrystalline phase is often dendritic or spherulitic.[39,40] It is not so easy to determine phase diagrams for the polymer electrolytes as it is for simple inorganic substances, because the kinetics of crystallization can be very slow and because a certain amount of randomness is inevitable in many polymer systems. These complications lead to apparent violations of the Gibbs phase rule and to experimental problems in determining the liquidus and solidus boundaries. Despite these problems it has been possible to obtain useful and revealing phase diagrams for several PEO–salt systems.[41-44] These phase diagrams demonstrate the presence of compounds having discrete ratios of PEO polymer repeat units to formula units of the salt. For example, the phase diagram for the PEO–NaSCN system (Figure 1) demonstrates the presence of a compound with the composition P-$[(EO)_{3.5}NaSCN]$.

There is considerable diversity in notation used to represent the phases, but the one used here appears to be the most consistent and unambiguous. In this scheme P denotes a polymeric unit of unspecified size, and EO indicates the ethylene oxide repeat unit. Thus in the formula given above there are 3.5 ethylene oxide (OC_2H_4) units per NaSCN.

As with the properties of free polymers, the properties of the polymer–salt complex appear to have little if any variation with polymer molecular weight once a suitably high molecular weight has been achieved. This demonstrates that the polymer motions relevant to ionic conductivity are not the gross backbone diffusion of the polymer backbone, which scale like M^{-2} (M = molecular weight) but rather the side-chain segmental motions, which are independent of molecular weight above a certain molecular weight.

It was clearly demonstrated by Berthier and coworkers that ion transport preferentially occurs in the amorphous phase of PEO–salt complexes.[45] Thus the gross morphological structure of PEO–salt complexes may play a role in determining the ion transport, because in the process of long-range diffusion an ion will have to circumnavigate the crystalline regions. This unfavorable influence on ion transport is mitigated in some applications by the structural integrity that the crystalline phase lends to the bulk polymer–salt complex. However, cross-linking of the amorphous polymer host appears to provide a more favorable solution to the structural integrity of the bulk polymer (section 5c).

At the atomic level, detailed structural information on the solvent-free electrolytes remains an important but elusive goal. Although interest has shifted from

TABLE III. Structures of Some Salt Complexes Inferred from X-ray Fiber Diffraction

PEO material	structural features	diffraction ref
$P[(EO)_4KSCN]$	K^+ outside PEO helix	46
$P[(EO)_3NaI]$	Na^+: 30 at 2.24–2.61 Å $2I^-$ at 2.94–3.16 Å	47
$P[(EO)_4HgCl_2]$	Hg^{2+}: 2 nearest-neighbor Cl 2 nearest-neighbor O	a

[a] Iwanoto, R.; Saito, Y.; Ishihara, H.; Tadokoro, H. *J. Polym. Sci., Part A-2* **1968**, *6*, 1509.

partially crystalline materials to amorphous polymer–salt complexes, oriented fiber diffraction studies on polycrystalline materials have provided useful insight into the structures of polymer–salt complexes. It is important to recognize that the oriented fiber technique does not provide the degree of structural precision ordinarily associated with structures determined by single-crystal X-ray diffraction. The oriented fiber X-ray studies indicate the expected coordination of the cation to the oxygen atoms in the polyether and association of the cation and anion.[46-48] The most detailed X-ray diffraction study to date was conducted on 100 reflections and indicated that in $P[(EO)_3NaI]$, three ether oxygens and two iodide ions are coordinated to each sodium ion.[47]

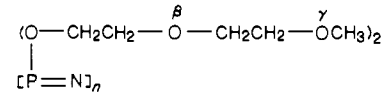
Extended X-ray fine structure analysis (EXAFS) has been explored as a means of probing the nearest-neighbor environment of the cation in some poly(ethylene oxide)–salt complexes; however, the technique has proven to be of rather limited utility because radial distribution patterns contain a broad single feature.[49,50] Apparently, inhomogeneity of the coordination environment and/or thermal motion present severe limitations on the application of this technique.

Infrared, Raman, and NMR spectroscopies have provided useful insights into the structures and dynamics of the solvent-free polymer electrolytes. Direct evidence for the polymer–cation interaction is available from the observation of a cation vibration in the ether cage. These far-IR studies confirm the general model of coordination of the cation by the ether oxygen atoms in poly(ethylene oxide) and related comb polymers (polymers with many short side chains).[37,51,52]

The degree of ion pairing has also been inferred from vibrational spectroscopy. In particular, the perturbation of vibrational modes for polyatomic anions has demonstrated ion pairing between BH_4^-, NCS^-, or NO_3^- and alkali metal cations.[51-53] Strong ion pairing is indicated in the case of sodium borohydride in poly(ethylene oxide), whereas ion pairing was not detectable with the BF_4^- ion. In keeping with these observations the borohydride salt complexes are much poorer ionic conductors. The problem remains as to whether one can effectively employ infrared spectroscopy to differentiate the degree of cation interaction with poorly coordinating anions such as BF_4^- and $SO_3CF_3^-$. As discussed in section 4, it is highly likely that strong ion association occurs in the polymer electrolytes containing these ions, but spectroscopic evidence concerning the nature of the interaction is lacking.

Vibrational spectroscopy also has provided valuable information about polymer conformation, coordination of polar groups to cations, and secondary interactions such as hydrogen bonding.[16,54,55] There is considerable scope remaining for further research in this area. In addition to the use of vibrational spectroscopy for structural and dynamic information, infrared spectroscopy is particularly sensitive for the detection of trace water and it should be more widely used in polymer electrolyte research because water can exert a substantial influence on ion transport properties.

Recently, very useful information on the structure and dynamics of polymer electrolytes has been obtained by NMR spectroscopy. For example, both chemical shift and spin–lattice relaxation time data from ^{13}C NMR have shown that the likely region of coordination of Li^+ to the comb polymer MEEP is at the oxygen atoms designated β and γ in structure 1.[56] Aside from



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structural information, NMR has proven to be very useful for the determination of the dynamics of the polymer–salt complexes. Spin–lattice relaxation data provided the first conclusive demonstration that ion motion preferentially occurs in the amorphous phase,[45,57-58] and pulsed field gradient NMR studies provide detailed information on the diffusion coefficients for NMR-active nuclei.[58,59]

4. Ion Transport

a. Measurement

In the characterization of the electrical properties of a solid electrolyte the most basic and useful information is the total conductivity and the fraction of this conductivity that is attributable to each charge carrier. There is a broad class of materials in which both ions and electrons are mobile; these interesting materials will be discussed later in this review. In the electrolyte materials with which we are now dealing, conductivity occurs by the migration of ions. The measurement of ionic conductivity, or ion transport as it is often called, is nontrivial, because of resistance to ion flow at the electrode–electrolyte interface. In general, it is much more difficult to establish a low-resistance interface for ion flow than for electron flow. This problem is largely surmounted by the use of ac impedance spectroscopy, which is described in-depth elsewhere.[60,61] For the purposes of this review it is adequate to note that the measurements are often made with the electrolyte sandwiched between a pair of electrochemically inert electrodes (Figure 2); a sinusoidal potential is applied and the magnitude (A) and phase shift (ϕ) of the current (I) are measured. Thus the sinusoidal dependence of the current with time (t) is given by

$$I = A \sin(\omega t + \phi) \quad (2)$$

This measurement is repeated at a series of frequencies which typically may range as low as 10^{-4} Hz to as high as 10 MHz. From these data it is possible to extract the conductivity and dielectric constant of the bulk electrolyte sample. Information on the resistance to interfacial charge transport also can be determined. This analysis follows along lines originally proposed by Cole and Cole[60] and developed in detail by Macdonald.[61,62] The raw data referred to above can be

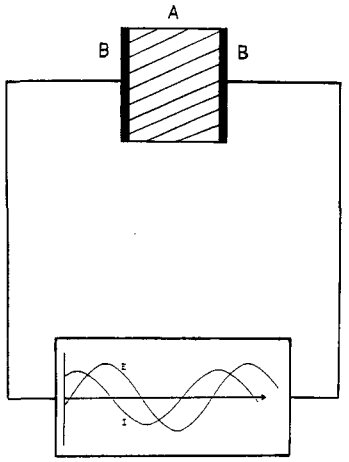


Figure 2. Schematic of an ac impedance experiment. B = electrode, A = polymer electrolyte, E = imposed potential, I = measured current response.

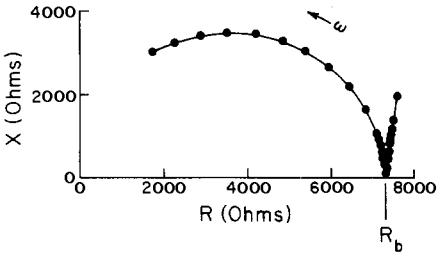


Figure 3. Complex impedance spectrum (Cole–Cole plot) obtained on $(MEEP)_4LiI$ at 20 °C between Pt electrodes. Frequency range 100 Hz to 3 MHz. X is the imaginary impedance (Z'' in eq 4) and R is the real impedance (Z' in eq 4). R_b represents the bulk resistance of the electrolyte sample.

used to express the ac current vector (I^*) in terms of real (I') and imaginary (I'') parts:

$$I^* = I' + jI'' \qquad j = \sqrt{-1} \tag{3a}$$

and a similar expression applies to the ac potential:

$$E^* = E' + jE'' \tag{3b}$$

The ac impedance, $Z^* = E^*/I^*$, also can be expressed as a real and imaginary part:

$$Z^* = Z' + jZ'' \tag{4}$$

In a Cole–Cole plot, now commonly referred to as an impedance spectrum, the real part of the impedance (Z') is plotted against the imaginary part (Z'') for data collected at a series of frequencies (Figure 3). In favorable cases various features of the impedance spectrum can be interpreted in terms of the response of the bulk polymer whereas other features arise from the electrode–electrolyte interface. The bulk resistance of the electrolyte (R_b) is one of the quantities that can be derived from such a plot. The value for the resistance of the sample (R_b) along with thickness of the sample and electrode area yields the resistivity of the sample or its inverse, the conductivity. Table IV presents some typical values for the total ionic conductivity for a range of electrolytes, as well as some more familiar electronic conductors, which are included to put the electrolytes into perspective.

The identity of the charge carriers and the fraction of the current carried by each is a more subtle issue that is still not well resolved in most studies of solvent-free polymer electrolytes. This issue was addressed by physical chemists around the turn of the century for

TABLE IV. Typical Conductivities[a]

material	conductivity
$P(EO)_{12}LiClO_4$	5.6×10^{-6}
$P(PO)_9LiCF_3SO_3$	2.2×10^{-5}
$(MEEP)_4LiCF_3SO_3$	1.0×10^{-4}
$RbAg_4I_5$	6×10^{-1}
Ge[b]	5×10^{-2}
Cu[b]	5.6×10^{5}

[a] Results in S/cm. Values at 312 K. [b] Electronic conductivity.

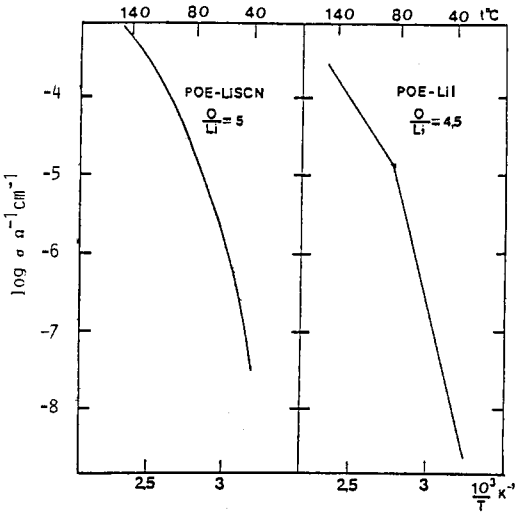


Figure 4. Arrhenius-type plots for log σ vs T^{-1} for PEO complexes of LiI and LiSCN. The curved behavior for PEO-LiSCN fits the VTF relation of eq 7. The double Arrhenius behavior from PEO-LiI corresponds to the conduction of the partially crystalline and elastomeric phases. From J. M. Chabagno, Thesis, Grenoble, 1980.

liquid electrolytes. They devised simple but elegant methods for the determination of transference numbers, which are generally designated as t_+ or t_- for the fraction of the current carried by the cation and anion, respectively.[63] The measurement of transference numbers, or transport numbers as they are also called, is experimentally more difficult with the solid electrolytes than their solution counterparts,[5] but measurements of fair quality have been made and the general picture for a variety of polymer electrolytes is that somewhat over half of the current is carried by the anion and therefore less than half by the cation. A major issue that is not yet well resolved is the nature of the mobile species. With monovalent ions in dilute aqueous solution the isolated cation and anion are the charge carriers. But the much lower dielectric constant of the polymer host in the solvent-free polymer electrolytes should be conducive to strong Coulombic interaction between ions. In the salt concentration range generally studied in polymer electrolytes, the primary charge carriers may well be ion triplets, quintets, and so on. A recent detailed study of ion transport in fluid solutions of short-chain poly(ethylene oxide) provides strong evidence for the importance of ion clusters in the solid electrolytes.[24]

b. Temperature and Pressure Dependence

The temperature dependence of the conductivity of polymer electrolytes indicates an activated process. Thus the conductivity increases with increasing temperature, and Arrhenius behavior often provides a good representation of the data (Figure 4). On closer in-

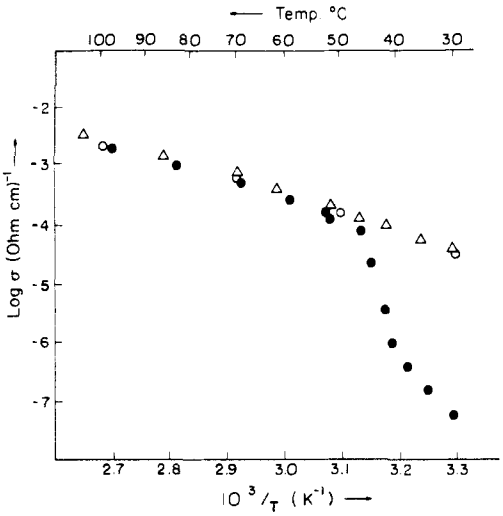


Figure 5. Temperature–conductivity plots for P-[$(EO)_8NH_4SO_3CF_3$]. The darkened circles represent data obtained by heating the partially crystalline sample from room temperature. The rapid rise in conductivity corresponds to the crystalline to elastomer transition. (△) Cooling curve in which a metastable elastomeric phase persists below 45 °C. (○) Heating curve for the metastable elastomer. From ref 44 and 91.

spection, changes in slope and curvature of the log σ vs $1/T$ plots are often observed. An abrupt change in slope can generally be traced to a phase change in the polymer–salt complex.[11] Of somewhat greater interest is the curvature observed in the conductivity plot for most amorphous polymer electrolytes when data are collected over a wide temperature range (Figure 4).

Polymeric electrolytes are soft materials, and one might therefore suspect that they would be easily compressible. Accordingly, several investigations[65-67] have been reported in which the ionic conductivity was measured as a function of pressure. The conductivity indeed is observed to decrease with increasing pressure, as expected on the basis of the free volume model, discussed below, or any other vacancy model. Activation volumes have been discussed, and the results have been used to suggest the nature of chain relaxations that aid ion motion.

c. Interpretation of Ionic Conductivity: Phenomenological Models

As mentioned in section 3, partially crystalline polymer electrolytes may have different degrees of crystallinity and a variety of morphologies. The multiphase behavior influences the transport by strongly reducing dc conduction and by introducing hysteresis effects as temperature is varied (Figure 5). It is clear from this figure that the higher conductivity occurs in the amorphous phase that is metastable at room temperature. The multiphase behavior presents complications for fundamental studies and for applications. To gain fundamental insight into the mechanisms of ionic motion in polymer electrolytes, we consider fully homogeneous amorphous polymer–salt complexes. These materials are in fact now of primary interest in the study of polymeric electrolytes. Particular examples include the phosphazenes, siloxanes, poly(propylene oxide), and cross-linked poly(ethylene oxide), to be discussed in section 5.

The conductivity of any material can be expressed in terms of the mobility μ by the relationship

$$\sigma = \sum \mu_i n_i q_i \tag{5}$$

where σ, μ_i, n_i, and q_i are respectively conductivity, the mobility of the i species, the concentration of carriers of the i species, and the charge of the i species. The polymer electrolytes contain no significant conjugation within the polymer backbone, and the salts on which they are based have negligible electronic conductivities. Thus one might suspect, and indeed several experimental measurements have shown,[68] that electrons or electron holes do not contribute to the summation in eq 5. Both cations and anions do, however, contribute and as discussed above, important questions concerning the relative mobilities (transference numbers) of the cationic and anionic carriers remain. Once again, this represents a complication in the simple interpretation of the temperature dependence of conductivity.

Experimentally, one observes fairly straightforward behavior of the temperature dependence of the conductivity in homogeneous electrolytes. The straight or curved lines observed when the conductivity is plotted in Arrhenius coordinates (Figure 4) can be fit, respectively, to the Arrhenius and VTF[69] forms

$$\sigma T = \sigma_0 e^{-E_A/kT} \tag{6}$$

$$\sigma T = \sigma_0 e^{-B/k(T-T_0)} \tag{7}$$

In the Arrhenius form, E_A is the usual activation energy, whereas in the VTF form, T_0 is a parameter to be determined, and B is a constant, whose dimensions are in fact energy, but which is not simply interpreted as an activation term; k is Boltzmann's constant. The early investigations of the groups in Grenoble generally showed curved plots, corresponding to VTF type behavior.[10,11,25-27] Cheradame and co-workers discussed these plots in terms of the chain segment mobility of the polymer host material.[25-27,30] They used the relationship, very common in discussion of polymer dynamics, of polymer chain viscosity to glass transition temperature that is summarized in the Williams–Landel–Ferry[70] relationship:

$$\log [\eta(T)/\eta(T_s)] = \log a_T = \frac{-C_1(T - T_s)}{C_2 + (T - T_s)} \tag{8}$$

where T_s is an arbitrary reference temperature, a_T is called the mechanical shift factor, and C_1 and C_2 are "universal" constants. Often the WLF equation is coupled with the empirical observation known as Walden's rule[63]

$$D\eta = \text{const}/r_i \tag{9a}$$

or equivalently with the Stokes–Einstein relationship

$$D = kT/6\pi\eta r_i \tag{9b}$$

where D is the diffusion coefficient and r_i is the radius. If in addition the Nernst–Einstein relationship

$$\sigma = DNq^2/kT \tag{9c}$$

where N is the number of carriers and q is the charge, is employed, then one can rewrite the temperature dependence of the conductivity in the WLF form:[70]

$$\log \frac{\sigma(T)}{\sigma(T_s)} = \frac{C_1(T - T_s)}{C_2 + (T - T_s)} \tag{10a}$$

To a good first approximation, eq 7 and 10a hold quite well for a series of polymer electrolytes. On the basis

of this, Cheradame's group has argued that WLF behavior is the rule in polymer electrolytes and, therefore, that the fluidity (inverse viscosity) of the polymer chain segments largely determines the conductivity.

The WLF form of eq 8 was, in fact, originally[70] based on the empirical VTF form[69] of eq 7, but written for the fluidity (η^{-1}) rather than for σT. The equivalence of eq 10 to the VTF form is easy to show and provides an identification of the parameters in the form

$$C_2 = T_s - T_0 \tag{10b}$$

$$C_1 = B/k(T_s - T_0) \tag{10c}$$

where the constants C_1 and C_2 refer to eq 8 and represent the mechanical shift factor.

The WLF and VTF equations themselves are empirical generalizations, rather than the result of any theoretical approach. As is clear from Figure 4, they describe the thermal dependence of σ quite well. In an attempt to understand how the conductivity mechanism works, quasi-thermodynamic theories,[71-76] originally developed to deal with molten salts and neat polymers, have in fact been applied with some success to consideration of transport properties in polymer electrolytes. These theories are based on considerations involving the critical role of the glass transition temperature T_g and of the so-called "equilibrium" glass transition temperature T_0. Above T_g, the polymeric material becomes macroscopically rubbery rather than glassy.[71-76] Mechanistically, this is understood by considering that a local environment on any given polymer chain becomes liquid-like at the glass transition. Therefore, it is only the thermal energy in excess of the glass transition temperature that provides actual mobility of the local polymer chain segments. In this sense, one is not surprised that the Arrhenius behavior, involving inverse temperature, is replaced by the VTF involving the inverse of $T - T_0$. The concept of equilibrium glass transition temperature T_0 is based on the kinetic feature of T_g: depending on the rate of cooling, one can observe different glass transition temperatures, and T_0 is idealized as the temperature at which all "free volume" vanishes or at which all polymer segment motion disappears or at which the excess configurational entropy of the material vanishes. The theoretical scheme which treats T_0 in terms of volume is called the free volume theory,[71,72] and that which treats it in terms of entropies is called the excess entropy or configurational entropy model.[73,74]

The free volume model, although subject to various trenchant criticisms[75-79] for the discussion of ion transport (to be discussed below), is the simplest way to understand the polymer segment mobility. It states that as temperature increases, the expansivity of the material produces local empty space, free volume, into which ionic carriers, solvated molecules, or polymer segments themselves can move. The overall mobility of the material, then, is determined by the amount of volume present in the material. The free volume is calculated according to the simplest model, by the usual statistical argument of maximizing the number of ways in which the volume can be distributed.[71] One then obtains, for the diffusivity D, the form

$$D = BRT \exp(-V^*/V_f) \tag{11a}$$

where B and V^* are constant and V_f is the free volume.

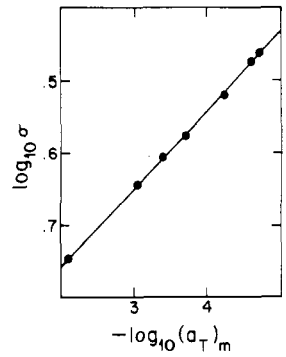


Figure 6. Correlation between the conductivity and the shift factor a_T (of eq 8) for PEO networks with low concentrations of salt (less than one ion per oxygen). The direct proportionality, with slope of unity, implies that σ is inversely proportional to viscosity, as assumed in the Walden or Stokes–Einstein relations (of eq 9a,9b). From ref 32.

When the volume is expanded in terms of the volume at the glass transition temperature plus a linear term, the free volume theory yields the form[25,30,38]

$$D = D_0 T \exp\left(-\frac{a}{T - (T_g - C_2')}\right) \tag{11b}$$

where the constants a and C_2' are both inversely proportional to the free volume thermal expansion factor. Note that we can rewrite eq 11b as

$$D = D_0 T \exp\left(\frac{-a}{C_2 + T - (T_g - C_\Delta)}\right) \tag{11c}$$

with $C_2 \equiv C_2' - C_\Delta$. If one chooses $C_\Delta = 0$, the free volume argument thus yields the WLF relationship of eq 8. Alternatively, one can choose any other value of the arbitrary constant C_Δ; for instance, often one selects $C_\Delta \simeq 50$ K, relating D to $T_0 \simeq T_g - 50$ K, the so-called "equilibrium" glass transition temperature.

Figure 6, based on the results of Cheradame and coworkers,[25-33] shows that indeed there is a very close relationship between conductivity and polymer relaxation behavior. The shift factor a_T, whose logarithm is plotted along the abscissa, is the ratio of the mechanical relaxation time at temperature T_1 to that at a reference T_s, which is generally taken to be either the glass transition temperature T_g or the "equilibrium" glass transition temperature T_0. It is easy to show that if the WLF equation fits data well with a given reference temperature T_g and parameters C_1 and C_2, then it will fit the data equally well if a different reference temperature is chosen, provided that C_1 and C_2 are allowed to change. This close relationship between the relaxation property of the polymer host and the conductivities of the ionic solute very strongly suggests a relationship between the chain motion of the polymer and the diffusive or conductive mode of the ions. Such a relationship is also implied by the use of the Walden relation of eq 9a since the η refers to the viscosity largely determined by the polymer chain, whereas the D is the diffusion of the ionic solute. Several other facts also imply a close relationship between the segmental fluidity motions of the polymer and the ionic diffusivity motion of the salt. For example, when the conductivity is fit to the WLF form of eq 10a, the constants C_1 and C_2 very closely match the "universal" values found for

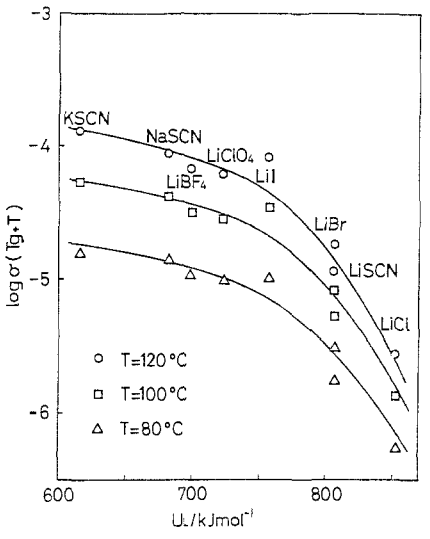


Figure 7. Conductivity at constant reduced temperatures $T_g + T$ as a function of the lattice energies of the incorporated salts. The dropoff in conductivity at high lattice energy is indicative of residual Coulombic attraction among the ions in the complex, reducing the effective number of current carriers and, therefore, reducing the conductivity. The measurements (ref 82) were made in PEO-based networks.

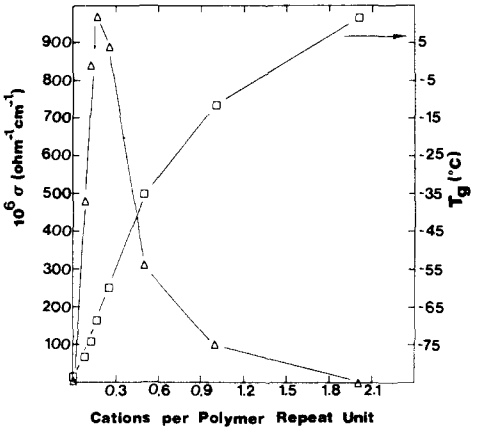


Figure 8. Dependence of conductivity (left ordinate) (at 70 °C) and of glass transition temperature (right ordinate, in °C) on concentration of salt in MEEP·$(AgSO_3CF_3)_x$ complexes. (MEEP = $-(N{=}P(OC_2H_4OC_2H_4OCH_3)_2)-$.) Note two effects on the conductivity: increased carrier number at low salt concentration, and higher glass transition temperature (less flexible chains, slower segmental motion) at higher salt concentration. From ref 83.

polymer physical properties.[19,25,27,28,30,43,81,82] Thus, for example, if T_s is chosen as T_g, characteristic values for C_1 range from 8.3 to 15.2 while those for C_2 range from 30 to 93 °C. These numbers, obtained from fitting the conductivity to the WLF form, should be compared with the "universal" values, $C_1 = 17.2$, $C_2 = 51.6$ °C, used to describe polymer physical properties (the shift factor a_T). The substantial deviation indicates that the simple relationship of Figure 6 is correct overall but that differences can occur in any given species. These differences reflect, for example, ion interaction effects.

In fact, it is the diffusivity or mobility rather than the conductivity of the ion which might be imagined to relate to the polymer chain motions. According to eq 5, the conductivity depends not only upon mobility but also upon the concentration of carriers. In extremely dilute solutions, it is generally fair to assume that all carriers are in fact available, so that the number n of eq 5 is simply the stoichiometric number of ions. In most polymer electrolytes, however, the concentrations are in fact much higher. For example, in P-[$(EO)_4$LiCNS], assuming a density of 1 g cm^{-3}, the concentration of salt is 4 M, and the mean distance between cation and anion is roughly 7 Å. Under these conditions, the ions do not move freely, and one might therefore suspect that the concentration of carriers, n, is dependent on the temperature, the stoichiometric concentration, and the physical properties of the polymer host. Although nearly all the early discussions of ionic conductivity in polymers were based on noninteracting carrier ideas,[10,11,35] it is clear in retrospect that the polymer electrolytes usually studied are in fact strongly concentrated electrolytes and that Coulombic interactions among the carriers will be crucial for determining the conductivity.[25] This can be clearly seen if one studies the conductivity of a number of polymer–salt complexes with the same polymer host and different solutes. If simple free volume theory were applicable, then the conductivity should be constant for constant $T + T_g$. Figure 7 shows a plot of such data, obtained by Watanabe and co-workers.[82] Note that there is a fairly substantial variation of the conductivity even at constant $T + T_g$ and that the conductivity decreases as the lattice energy of the parent salt increases, indicating that Coulombic attraction between anion and cation acts to reduce the effective number of carriers.

The effects of concentration variation,[25,80–84] qualitatively, generally follow the behavior seen in Figure 8: as the salt concentration increases starting from a dilute complex, the conductivity first increases and then, after attaining a maximum for a particular concentration, falls off quickly for more concentrated materials. Qualitatively, such behavior may be understood on the basis of eq 5: at low concentration, the carrier numbers increase as salt is added, so that n in eq 5 increases as does σ. (The expected dependence is sublinear due to effects of ion association.) At higher concentrations, the salt acts as a weak sort of cross-linker, raising the value of T_0. One then expects σ to drop with further increases of ion concentration. Angell and Bressel suggested[85] (for liquid solutions) that the conductivity can be expressed, following eq 11, in the form

$$\sigma \sim X \exp[-B'/(X_0 - X)] \qquad (12)$$

where X is the mole fraction of salt, B' is a constant, and X_0 is the concentration at which the isotherm temperature matches T_g. Once again, however, the presence of interactions within the polymer electrolyte makes itself clearly felt: the maximum conductivity of PEO-based solid electrolytes is much smaller (almost a factor of 100) than that of comparable aqueous solutions. Angell[86] attributes this to the effects of residual ion–ion interaction in the low dielectric constant polyether solvent.

The observed pressure dependence of ionic conductivity in polymer electrolytes is easily interpreted by free volume type concepts. Since the free volume V_f of eq 11a will decrease with applied pressure, one expects D to fall off exponentially as pressure is increased and free volume decreased. Alternative explanations,[38] however, can be given in terms of the configurational entropy or dynamic percolation models. In the latter cases, the pressure dependence of the conductivity is considered to arise largely from reduction in the extent of local segmental motion of the polymer chains. In a

free volume picture, the pressure dependence might arise from motion of ions into voids or of chain segments into voids.[25,87] Since, however, ionic conduction in these electrolytes is not critically dependent on ion size for the small ions usually studied,[83,88] free volume theory is usually invoked in terms of the volume required for motions of the polymer chain segments, rather than of the ions themselves.

The free volume model is intuitive and helpful. It has been subjected to thorough analysis in the context of ionic motion in fused salts, fluid solutions, and polymer electrolytes. Several shortcomings of the model have been pointed out in each of these contexts.[38,63,77] For example, free volume models give incorrect quantitative predictions of the pressure dependence of transport properties.[75] Occasionally even the sign is incorrect.[79] An improved model, based upon considerations of entropy fluctuations rather than volume fluctuations, was developed by Gibbs, DiMarzio, and Adam.[73,74] The model, called the configurational entropy model, leads to transport properties in agreement with the empirical VTF form of eq 7 or WLF form of eq 10a. Moreover, it correctly predicts pressure dependences and provides a satisfying description of T_0 as the temperature at which the excess configurational entropy vanishes. Angell[76-78] has pointed out quite clearly the advantages of configurational entropy, as opposed to free volume, interpretations of the VTF equation, but the appealing simplicity of free volume ideas has led to their widespread use in the literature.[25,32,80,81,89] Like the free volume model, the configurational entropy theory is quasi-thermodynamic, rather than microscopic. This is both a strength because of the direct relation to thermodynamic observables such as P, V, T, and S and a weakness since no microscopic mechanistic or equation-of-motion pictures are available.

d. Frequency-Dependent Conductivity: Dynamic Percolation and Relaxation

We have dealt thus far with the dc conductivity and its dependence on pressure, concentration, and temperature. The explanation of the motion mechanism invoked arguments based on the rates of segmental motion of the chains of the polymer host. Measurements of the characteristic time scales for segmental motion are therefore of interest. A number of measurements, including those of storage modulus and mechanical relaxation,[25,27,30,31,43,90] NMR relaxation,[33] dielectric relaxation and loss,[91,92] microwave measurement of ac conductivity,[91,93] Brillouin scattering,[94] and inelastic neutron scattering,[95] have been made to characterize the dynamic (frequency dependent) response of polymer electrolytes. The mechanical loss or mechanical relaxation measurements are generally interpreted in terms of WLF behavior, and, indeed the observed direct proportionality of mechanical relaxation and ionic conductivity, as illustrated in Figure 6, constitutes one of the most telling evidences for the dependence of ionic conductivity on chain motion. Relaxation times obtained from NMR studies also fit very well to the WLF relation as a function of temperature; Cheradame's group has found recently,[17,96] for example, that in polyelectrolytes with phosphorus cross-link sites and mobile Li^+ the ^7Li, ^1H, and ^{31}P NMR signals all fit WLF behavior very well, with identical values for the C_1 and C_2 parameters. Once again, this shows the dependence of ion transport on polymer motion. Angell and Torrell have recently used the width of the Brillouin peak to obtain the characteristic relaxation times for both glassy and polymeric ionic conductors[94] and to study the dependence on molecular weight of the polymer. They note that the mechanical relaxation times appropriate for description of segment motion and for use in the decoupling ratio R of eq 13 are not the global, macroscopic times, but rather local, microscopic times corresponding to small (roughly 1–10 Å) motions. The proper probes to obtain such relaxation times are local ones, such as NMR, light scattering, or dielectric relaxation. Poinsignon and Berthier[95] have recently completed quasi-elastic neutron scattering studies of polymer electrolytes; they obtain from the quasi-elastic half-width a time of roughly 10^{-10} s, which they identify as the time scale for segment motion.

Relaxation processes in amorphous condensed-phase systems such as fused salts of polymers often show a wide spectrum, or distribution, of characteristic relaxation times. Different experimental measurements, depending upon precisely how the experimental probe couples to the system under study, can observe different relaxation processes. This is clearest with NMR, where the resonance frequency selects which nucleus is being monitored, but it is true in general that different experiments will measure different components of the relaxation time distribution. Thus neutron scattering probes chiefly motions of the protons, Brillouin scattering senses relaxation of the phonon modes, etc. The measurements of frequency-dependent conductivity $\sigma(\omega)$, as obtained from microwave measurements, and of dielectric relaxation are sensitive to the motions of charged species, including both mobile ions and dipoles on the polymer. Since the important polymer movements for promoting ionic transport involve motions of polymer segments that contain dipolar Lewis base groups, the relaxation processes measured by electrical probes are probably the most relevant ones for interpreting the conductivity although, as we have already stated in connection with Figure 4, it appears that most measurements of relaxation processes yield similar temperature dependence.

Polymer solid electrolytes conduct very poorly near or below their glass transition temperatures; above T_g, the local polymer chain motion is in fact liquid-like and rapid. Angell[77,78] has generalized these concepts to differentiate two types of amorphous solid electrolytes. He defines a decoupling ratio R as

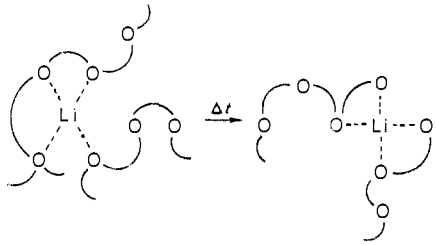
$$R = \tau_s/\tau_\sigma \tag{13}$$

where τ_s is a structural relaxation time and τ_σ ($\simeq e_0\epsilon_\infty/\sigma_{dc}$, where ϵ_∞ is the optical dielectric constant) is an electrical, or conductivity, relaxation time. For glassy electrolytes, which are used at temperatures below their glass transition temperature T_g, R can be of the order 10^{13} (since τ_s can be[97] of the order 200 s at T_g), whereas for polymer electrolytes, useful above T_g, R can approach or even drop below unity. If R were close to unity, it would indicate that the ionic motion and the structural relaxation occur on the same time scale, thus suggesting that their rate-determining steps are the same. Angell[78,94] has noted that for polymeric solid electrolytes $R \simeq 10^{-3}$, which implies (since it is

substantially less than unity) strong residual ion–ion coupling, resulting in reduced conduction. For our purposes here, however, the most striking aspect of the decoupling index is that it is much closer to unity than was true for the glasses, again indicating a very close relationship of structural relaxation process (due to chain motion and reflected in τ_s) and conductivity (inversely proportional to τ_σ).

The substantial change in the value of R, from $\sim 10^{13}$ in glasses to near unity in soft polymer electrolytes, must in part be due to the low frequencies and large amplitudes associated with polymer segment motion in the elastomeric phase above T_g. In an ionic conducting glass, as in a covalent crystal, only small charges in the local geometry are, in general, associated with ionic motion into a vacancy. In these polymer materials, in contrast, very large changes in the local geometry are brought about upon complexation of a cation. For the cation to move, subsequently, the segments complexing it must first exchange the primary coordinating atoms, and such motions require segmental mobility.

Druger, Nitzan, and Ratner[38,87,89,98–101] have developed a dynamic percolation model for description of ion transport in polymer electrolytes. This is a microscopic model that characterizes the ionic motion in terms of jumps between neighboring positions. For anions, which are not strongly solvated by the polymer host, such a description is straightforward. For cations, the local coordination environment evolves slowly, as a single $M^+ \cdots B$ (M^+ = metal ion, B = Lewis base site on polymer) linkage is changed at a time;[36,37] the "jump" of a cation then corresponds to a completed exchange of one ligand. This process is sketched in structure 2.



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The rate of "jumping" (that is, of ion motion) between any two "sites" (that is, between two different positions in the material) is then represented in terms of simple first-order chemical kinetics, using the so-called master equation

$$dP_i/dt = \sum_j (P_j w_{ji} - P_i w_{ij}) \qquad (14)$$

with P_j the probability to be on site j and w_{ji} the rate of ion motion from site j to site i.

The dynamic percolation model takes into account the dependence of ionic motion rates on the fluidity, or rate of segmental motion, of the polymer host. A characteristic rate of renewal, $\lambda = \tau_{ren}^{-1}$, is defined, which characterizes the rate at which a motion pathway from one site to another becomes available for the ion to move. In ordinary (static) percolation theory,[102] applied, for example, to electron hopping in amorphous metals, the rates w_{ij} of eq 14 are taken to be

$$w_{ji} = 0 \quad \text{probability } 1 - f$$
$$w_{ji} = w \quad \text{probability } f \qquad (15)$$

with w being some average rate. For polymer electrolytes above T_g, the segmental motion changes the local coordination environment of the ion with a characteristic time τ_{ren}, so that a jump which is unavailable (because the chains are improperly arranged) at time t can become available, because the chains have reoriented, at time $t + \tau_{ren}$. The mathematical statement of this motion is that the assignment of probabilities w_{ij} as zero or w changes on the time scale τ_{ren}.

The dynamic percolation model is characterized by the parameters f, w, and τ_{ren}. These can be related to the phenomenological models,[38,87] so that these parameters are defined in terms, say, of free volume. The dynamic percolation model has several interesting features, among the most important of which are the following:[5,38,87,89,98–101]

1. For observation times long compared to the renewal time, the motion is always diffusive. That is, the mean-squared displacement is always proportional to time. This is observed for polymer electrolytes but is not true of ordinary, static, nonrenewing percolation models.

2. The diffusion coefficient is, in general, proportional to $\langle\lambda\rangle$, the average rate of renewal. This corresponds well both to the wealth of experimental data indicating that the ionic motion is modulated by the segmental motions of the polymer host and to the expectation, based on a value of the decoupling index R of eq 13 close to or less than unity, that structural reorganization and conductivity arise from the same underlying motion mechanism.

3. It is possible to show in great generality that

$$D_0(\omega + i\lambda) = D(\omega) \qquad (16)$$

That is, the diffusion coefficient at frequency ω in the renewing (dynamic) percolation problem may be found from the diffusion coefficient in the static (nonrenewing) percolation problem, analytically continued to frequency $\omega + i\lambda$.

4. The factor f, giving the number of available jumps, will be substantially different for cationic (strongly solvated) and anionic (weakly solvated) motions. The transference numbers might reflect this difference. The study of polyelectrolytes, in which only one ionic species moves, will be a good test of this feature of the theory.

One interesting application of the dynamic percolation model has been in understanding the problem of frequency-dependent conduction in the accessed microwave range 1 MHz $< \omega <$ 37 GHz. Brodwin and collaborators have measured these conductivities for a number of polymer electrolytes;[35,91,93] qualitatively, one expects that either the hop time $\tau_h = w^{-1}$ or the renewal time τ_{ren} might lie within the microwave range. The general behavior observed for homogeneous polymer electrolytes involves an initially flat response followed by a rise to a peak value. As Figure 9 shows, the dynamic percolation model fits these data quite well. At low frequencies (long times), only the ions that experience the renewal process exhibit $\langle r^2\rangle \sim t$, so that only the ions contribute to σ. In the partly crystalline sample, below $\sim$1 MHz a significant dropoff is observed in σ, again describing limitations to long-range motion of ions due to poorly conducting crystalline regions; to obtain the fit shown in the figure, two renewal times were involved, one for crystalline, the other for amorphous regions. At higher frequencies (shorter

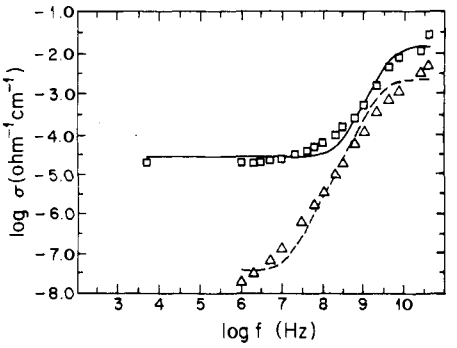

Figure 9. Room temperature plots of observed microwave conductivity as a function of frequency for amorphous P-[$(EO)_8NH_4SO_3CF_3$] (□) and pure PEO (△). The lines are the fits to experimental data of the dynamic percolation model. From ref 91 and 44.

times, smaller distances), there is a contribution to the observed signal both from the response of the polymer and from the ions themselves. Indeed, at high enough frequency (above ~100 MHz), the conductivity of the complex becomes comparable to that of PEO itself, since excursions of dipolar groups on the polymer chain contribute to σ. At even higher frequencies, into the infrared, inertial effects should destroy the response, so that at very high frequency, the conductivity σ should go to zero. The dynamic percolation model, like any hopping model, contains no inertial effects and thus predicts, incorrectly, that at very high frequencies the conductivity $\sigma(\omega)$ becomes flat (frequency independent but finite).

The dynamic percolation model has also been applied to understand the frequency-dependent conductivity in partially crystalline P[(EO)·NaSCN].[100] There, a distribution of renewal times was necessary to fit the observed conductivity; this is quite reasonable, since one expects far faster renewal, hence better conduction, in the amorphous regions compared to crystalline ones.

Applications of the dynamic percolation model to polymer electrolytes are discussed in detail elsewhere.[38,87,101] While the model does have the attractive feature of including the effects of segment motion on ionic conduction, it does not directly include interionic interaction. Thus while it is the best microscopic model currently available for understanding ionic conduction in polymer electrolytes, it is inadequate in several ways (no inertial dynamics, no interionic interaction). A great deal remains to be done in understanding, on any reasonable microscopic level, ionic motion in these materials.

5. Specific Polymer Conductors

a. Complexes of Linear and Branched Polymers with Salts

Poly(ethylene oxide) complexes of alkali metal salts have been studied much more extensively than any other solvent-free polymer electrolytes. As discussed in sections 3 and 4, ion transport occurs primarily in the amorphous phase, so the partial crystallinity of most of these PEO complexes is an unwelcome complication when studying the conductivity response of the material. As shown in Figure 5, the conductivity is low for the partially crystalline compound and as the crystalline phase melts the conductivity increases dramatically. Commercial poly(propylene oxide) is not stereoregular and is therefore noncrystalline; however, the commercial material includes a cross-linking agent, which represents an unwanted impurity for fundamental studies. Nevertheless, there is an extensive literature on the electrical properties of PPO–salt complexes.[11,80,105] A very promising linear polyether that does not have the problems of crystallinity consists of medium-chain poly(ethylene glycols) linked by methylene groups. By this device the OC_2H_4 repeat units are interrupted by OCH_2 units, thus preventing crystallization. The conductivities of the $LiSO_3CF_3$ complexes are high at room temperature.[104] Many other linear polymers with polar groups have been investigated as polymer hosts for electrolyte formation,[5,6] such as sulfides,[106] ketonic oxygens,[54,107] and imines.[41,103] Poly(ethylenimine) is a close analogue of poly(ethylene oxide) and it shares with PEO the complications of multiphase behavior.[41,103] Closely related branched polymers such as branched poly(ethylenimine) also have been investigated. Branched poly(ethylenimine) is an amorphous material and therefore generally superior to its crystalline linear counterpart as a host for polymer electrolyte formation.[55]

b. Complexes of Comb-like Polymers with Salts

The realization that high conductivity in polymer electrolytes is dependent on local thermal motion of polymer segments led to the exploration of comb polymers as hosts for polymer electrolyte formation. The general concept is to utilize a flexible backbone and attach to this short-chain polar oligomers capable of complexing alkali metal salts. These ideas led to the synthesis and characterization of polyphosphazene, polysiloxane, and polyitaconate comb polymers containing short-chain polyether side chains.[83,108-112] Salt complexes of the phosphazene polymer have been fairly extensively investigated and are found to have much higher conductivity at room temperature than poly(ethylene oxide)-based electrolytes. The somewhat less flexible polymethacrylate comb polymers also have been investigated.[113]

c. Network Polymers with Salts

From a practical standpoint amorphous linear polymers are inconvenient because they tend to flow at somewhat elevated temperatures. This nuisance can be remedied in fundamental studies by proper design of cells for electrical measurements, but it is a serious drawback for potential commercial applications where long-term dimensional stability is required. Cheradame and co-workers provided a solution to this problem by the synthesis of network polymers consisting of cross-linked poly(ether glycols).[24-33] If the degree of cross-linking is kept low or if flexible cross-links are employed, segmental chain motion is not significantly impaired and salt complexes of these network polymers have conductivities that are superior to those of the crystalline linear polymers.[24,33] Cross-linked siloxane and phosphazene comb polymer electrolytes are found to have good mechanical properties with little sacrifice in conductivity.[108c,114] It also has been shown that amorphous materials with high conductivity can be prepared by radiation cross-linking poly(ethylene oxide)–salt complexes above their melting point.[115]

d. Polyelectrolytes

The comparable conductivities of anions and cations in the solvent-free polymer electrolytes discussed so far have led to the exploration of polyelectrolytes in which charged groups are bound to the polymer. Most solvent-free polyelectrolytes, such as sodium poly(styrenesulfonate), are hard materials with high T_g and low conductivity. Potentially a hard plastic may be rendered flexible (increased in free volume) by the addition of a plasticizer. Attempts to introduce standard plasticizers into sodium polystyrene led to materials that were unstable with respect to phase separation. However poly(ethylene glycol) plasticizers were found to give stable materials.[15,16] Judging from infrared data the stability of these systems arises from hydrogen bonding between the glycol OH group and the sulfonate group. One of the principal lines of interest in polymer electrolytes is their wide potential window of redox stability but the presence of OH groups is detrimental to this electrochemical stability. However, the glycol-containing polyelectrolyte suggests that suitable materials might be prepared by covalently linking short-chain poly(ethylene oxide) groups to the polyelectrolyte. Recently comb-like polyelectrolytes have been reported with anionic or cationic groups as well as short-chain polyethers attached to the backbone. These short chains provide self-plasticization, so that no added plasticizer is needed.[96,20,116]

e. Proton-Conducting Polymers

Polymer electrolytes that transport protons have been examined for several types of materials. Solvent-swollen polyelectrolytes have long been recognized as excellent protonic conductors.[13] In addition, poly(vinyl alcohol)/phosphoric acid/water films[12] have been studied and show relatively high protonic conductivity. Water-containing Nafion in the proton form at room temperature reaches a conductivity of 0.01 S cm^{-1}. These materials conduct better with higher water content, and, as suggested by Slade et al., the proton motions are probably more similar to those in systems of sorbed water than to ionic conduction in solvent-free polymer electrolytes.[13]

Recent work by Armand and co-workers has focused on rigorously anhydrous PEO/H_3PO_4 materials, cast in thin-film form from tetrahydrofuran/acetonitrile solution.[117] These differ from the solvent-containing materials and are far closer to the alkali polymer electrolytes. They show VTF rather than Arrhenius behavior (eq 7 rather than eq 6) for the temperature dependence of the conductivity and attain conductivity maxima near 10^{-1} S cm^{-1} near 100 °C. Armand's group has also investigated polyamide electrolytes, including nylon 6 and acrylamide, complexed with H_3PO_4 and cast into films from methanol. These materials are of real interest for electrochromic or sensor applications, showing $\sigma \sim 10^{-4}$ S cm^{-1} at ambient temperature and proton transport numbers t_+ roughly equal to 0.9. These phosphoric acid/polymer materials degrade if wetted, so that rigorously anhydrous conditions must be maintained.

A decade ago, Hoel and Grunwald[118] investigated protonic conductivity in polybenzimidazole films. They found proton conductivity on the order of 10^{-4} S cm^{-1} at room temperature. Unlike the polymers discussed elsewhere in this review, this is a rigid material with a T_g that exceeds room temperature. Therefore the mechanism of conduction is likely to be quite different from that in the softer low-T_g materials discussed here. Another interesting difference between this material and others reviewed here is the relative insensitivity of the bulk conductivity to the presence of moisture.

f. Polymer–Salt Complexes Containing Dipositive Cations

The overwhelming majority of studies of solvent-free polymer–salt complex electrolytes have focused on 1:1 electrolytes (anion and cation singly charged); recently, systems with doubly-charged cations have been studied.[119-122] Reports largely center on PEO materials, though transport in polyphosphazenes containing Sr^{2+} has been measured.[83] In the PEO-based complexes, problems have been encountered with residual water content, history-dependent properties, and partial crystallinity. Nevertheless, some of these complexes do show rather high conductivities; with well-defined amorphous samples, estimated transport numbers indicate that these are largely anion conductors.[123] An interesting report by Moryousseff et al. indicates the presence of a "mixed-cation effect", in which a sample of $P[(EO)_{30}CaBr_2CaI_2]$ has higher conductivity than $P[(EO)_{15}CaBr_2]$ or $P[(EO)_{15}CaI_2]$.[124]

g. Mixed Ionic and Electronic Conductors

Polar polymers of the type used in polymer electrolytes also have been shown to be useful for the preparation of mixed conductors in which ionic conductivity and electronic conductivity coexist. The concept is to incorporate alkali metal salts of an electronically conducting anion, such as a polyiodide, into the polymer host. In a material of this type the ions will be mobile and the polyiodide may serve as an electronic conductor. Starting with an alkali metal iodide in the polar polymer, a pure electrolyte results, and as successive increments of I_2 are added, the conductivity increases and electronic conductivity eventually predominates.[125] The electronic conductivity transition in these materials is analogous to the metal–insulator transitions that can be achieved in certain metal oxides as the oxygen partial pressure is changed.[126]

Thermopower measurements on the poly(ethylene oxide)–sodium polyiodide system demonstrate that holes are the conductors in these materials. Although further details on the mechanism of conduction must be worked out, it is probable that an atom-transfer mechanism occurs, similar to that discussed by Gileadi for polyhalides in fluid solution.[127]

In the range of iodine concentrations over which both the ionic conductivity and electronic conductivity can be measured, it is found that increasing electronic conductivity is accompanied by increasing ionic conductivity.[128] It is not clear as yet whether this phenomenon arises from changes in polymer segmental motion or the influence of mobile electrons (or electron holes) on ion motion. The latter phenomenon was predicted by Huggins and Huggins[129] based on the earlier work by Wagner.[130] They consider the case of only two carriers (one ionic, the other electronic) and point out that in the case in which the ionic carriers are

more numerous but the electronic carriers are more mobile, a substantial enhancement of the chemical diffusion constant is expected.

Charge-transfer ions other than polyiodides can be used to provide the electronic conductivity in these mixed conductors. Interesting materials have recently been studied by Wright,[131] who prepared P[(EO)$_n$LiA], where LiA is an organic acid salt or charge-transfer salt (that is, the A^- species can be $TCNQ^-$, chloranil$^-$ or phenoxy$^-$). He has observed electronic conductivities as high as 10^{-1} S cm^{-1}. The conductivity is activated, and when the material was drawn and oriented, the conductivity increased appreciably, as the conducting states of aromatics became more favorably aligned for electronic overlap.

h. Inhomogeneous Systems

Structural polymers are often based on the copolymerization of monomers or on polymer blends, to achieve good mechanical properties. In these materials the two polymers involved in the blend exist as a physical mixture of separate phases held together with physical forces and not chemical bonds. Motivated largely by a desire to improve the structural integrity of polymer electrolytes, investigations of polymer blends as electrolytes have been carried out. Often these polymer blends consist of a polar polymer providing the conductive paths, and a more rigid structural polymer, such as polystyrene[132,133] or poly(vinyl acetate).[134] Another set of popular structural materials is based on block copolymers. Again, good structural properties often result. A very interesting aspect of these materials is the range of microstructures that can sometimes be achieved by the phase separation of the components. For example, sheetlike and rodlike structures of one polymer in a matrix of the other can be achieved. Block copolymers that undergo distinct phase separation have been investigated as polymer electrolytes, but as yet detailed studies of morphology and directional conductivity have not been reported. Block copolymers with both structural integrity and good conductivity have been prepared.[135]

Solid inorganic phases within the polymer electrolyte have been investigated. A moderate amount of an insulating phase, alumina, has been found to have little influence on the electrical properties of PEO electrolytes.[136] In battery development, extensive use has been made of composite electrodes, in which a polymeric electrolyte such as P[(EO)$_n$LiCF$_3$SO$_3$] is intimately mixed with a solid inorganic cathode material such as V_6O_{13} or TaS_2.[137,138] These materials are electronic conductors via the inorganic phase and ionic conductors in the polymer phase. Although a torturous path for charge migration must exist with resulting percolation limitations,[137] these composites appear to be effective cathode materials.[138]

6. Problems and Prospects

A great deal has been learned about solvent-free polymeric electrolytes since the first reports by Wright 15 years ago on the high conductivity of PEO complexes. Our picture of conductivity mechanisms has evolved from independent cation hopping among fixed sites in the crystalline region to strongly correlated diffusive motion by both ions in an amorphous solvated Coulombic fluid. Important developments have taken place in the areas of polymer hosts, of mechanistic interpretation of the conduction, of polymer blends, comb polymers, and copolymers, of microionics preparation, and of battery building and testing. Both the level of understanding and the preparation of new materials have progressed substantially.

Probably the most complex feature of these materials is the high concentration of charged species, which results in strong Coulombic correlations of charge carriers. In particular cases, this can lead to carrier trapping in ion pairs or higher multiplets, thus substantially reducing the conductivity. Even in other situations, the residual Coulombic interactions are important. They lead to correlation factors in the Nernst–Einstein relation (eq 9c), where the number N of carriers is not the stoichiometric concentration N_0 of ions, to off-diagonal friction coefficients in a Langevin description of the pulsed field gradient NMR measurement of diffusion,[139] and to a decoupling index R of eq 13 becoming less than unity. Curiously, the very high concentration of ions may make the problem a bit easier than in the analogous case of lower concentration (~0.1–1.0 M) solutions, where the ions can range from tightly ion paired to roughly independent and where the theoretical description is very complicated and seriously lacking.[63] When the concentrations become as high as they are in these polymer electrolytes, most carriers are strongly coupled to counter charges, and the situation is very similar to that of a solvated fused salt (always remembering that the solvent, here, is a polymer, whose own internal motion time scale acts as a gate for the ionic motions). In analogous glassy electrolytes, the so-called weak-electrolyte model[140–143] has been very useful. In this model, emphasis is placed on the carrier number term n_i, rather than the mobility factor μ_i, in eq 5; in fact, the mobilities of all free ions, once they can act as carriers, are essentially identical. The scheme is called the weak-electrolyte model because mass action type relations are used to obtain the carrier numbers.

The relative importance of interionic interactions on the structural and transport properties of the polymeric electrolyte is probably the most active current research topic in these materials. Some reports indicate[144] that the Nernst–Einstein relation of eq 9c works very well over a broad temperature range, thus implying that the correlation factors for diffusion and for conduction are very similar. But, as already indicated, several experiments, including pulsed field gradient NMR studies of diffusion, show strong ionic correlation effects. From a modeling viewpoint, it will be important to modify the currently used pictures (free volume, configurational entropy, dynamic percolation) to include correlation effects.

The outstanding experimental problems are connected with the precision and specificity of structural and dynamic information. From the structural standpoint we have evidence for coordination of the polymer polar groups to the cation and some for ion pairing, but we lack detailed knowledge of coordination numbers and geometries. Similarly, the dynamical information often is based on the response of the bulk material, which may not be directly related to microscopic models for conductivity. For example, dielectric properties can be measured and related to relaxation times but the

detailed connection with motions at an atomic level are lacking. The problems are similar to those that remain unsolved for electrolyte solutions. However, experience with fluid electrolytes indicates that further progress can be made with more extensive use of multinuclear NMR spectroscopy, which has already contributed substantially to our knowledge of both structure and dynamics of polymer electrolytes. More detailed information on diffusion coefficients, polymer structure, and relaxation times for the constituent nuclei in polymer electrolytes can help to test structural and dynamical models. Other techniques that have not been fully exploited for the study of polymer electrolyte dynamics include ultrasound measurements, Brillouin scattering, and variable high-frequency conductivity. Recently, kinetic electrochemical measurements were made on electroactive ions in polymer electrolytes.[145] The kinetic electrochemical methods can be used to determine diffusion coefficients for electroactive ions, thus facilitating the study of how ion charge, size, and concentration influence ionic diffusion.

There are many synthetic opportunities in the area of polymer electrolytes. The combination of the synthesis of new polymer electrolytes with electrical measurements may lead to new electrolytes that are selective ion binders and transporters. Other synthetic challenges include the preparation of polyelectrolyte systems that have high ionic conductivity in the absence of solvents or plasticizers. Materials of this type would have a transference number of 1 for the mobile ion, with a resulting simplification of the interpretation of the transport process. Mixed ionic–electronic conductors based on salts in polar polymers have only recently been reported and considerable scope remains for the synthesis of these new materials and studies of their charge transport mechanisms.

Although our review has concentrated on the phenomenology and theory of polymer electrolytes, a few words on applications are in order because substantial impetus for the study of solvent-free electrolytes has come from the prospects for utilizing them in advanced electrochemical devices, such as high energy density batteries. To our knowledge, there are no batteries on the market that incorporate polymer electrolytes, although development projects are under way in several different countries.[146–152] Experience demonstrates a low success rate and long development times for new high energy density batteries but the potential rewards are huge.

The properties of polymer electrolytes such as their high compliance, good adherence to electrodes, and the possibility of fabricating the polymers into thin films are attractive not only for batteries but for many other electrochemical devices. A variety of such applications have been proposed, including electrochromic displays,[153] electrochromic windows, solid-state photoelectrochemical cells,[154–156] and sensors. In addition, a recent paper from Wrighton's laboratory describes the utilization of a polymer electrolyte in an electrochemical transistor.[157] Finally, polymer electrolytes are convenient media for electrochemical experiments under unusual conditions such as high-vacuum photoelectrochemistry.[158]

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