Conductivity in Polymer Ionics

Dynamic Disorder and Correlation

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Theoretical constructs are developed for discussing diffusivity and conductivity in polymer ionic materials. Such materials are characterized by extensive disorder, either static (lack of long-range order) or static and dynamic (lack of long-range order with short-range order evolving with time). Beginning with a dynamic percolation model, we show that, in general, so long as the mean-square displacement of the charged particle obeys a certain growth law, the observed charged-particle motion will be diffusive, both in the ballistic regime, corresponding to electronic motion with strong scattering, and in the ionic-hopping regime, corresponding to dynamic disorder renewal of the hopping situation. Some general behaviour for transport under these conditions is predicted, including definite statements about the frequency dependence of the conduction, the relationship between the growth law in a single interval and the growth law for observation times long compared to scattering or renewal times, and the behaviour in the neighbourhood of the percolation threshold for the static problem. Interpretations are suggested both for ion and electron-hopping situations.

A statistical thermodynamic model is developed for analysis of contact ion pair formation and its effect on conductivity in ion-conducting polymer systems. In this model, the energy (due to solvation and polarization) favouring formation of a homogeneous complex in which the cations are solvated by the polymer host, competes with an entropic term favouring the separated structures (free polymer and contact ion pairs). We derive general conditions for this phase separation, and an expression for the number of polymer-bound, homogeneously solvated ions. We show that this number will, in general, decrease monotonically with increase in temperature, due to entropic favouring of the phase-separated material, this is reminiscent of the lower consolute temperature phenomenon in liquid mixtures.

1. Introduction

Polymer conductive ionics, or polymeric solid electrolytes, are the newest and most actively investigated area of solid electrolytes.[1-6] These materials were first developed at Sheffield,[7,8] Grenoble[9] and Evanston[10] in the 1970s, and interest in them is now very widespread indeed. Part of this interest arises from possible applications as electrolyte materials in electroactive devices; the remainder arises from their intrinsic scientific interest as dynamically disordered solid materials exhibiting ionic diffusivity of a magnitude more characteristic of that of ionic liquids or solutions.

The class of polymer conductive ionics now includes, in addition to the originally prepared and investigated polymer-salt complex materials,[7-10] solvent-free polyelectrolytes[11-13] and mixed ionic-electronic conductors.[14-16] The mixed conductors

really lie outside the scope of our discussion here, although a number of other contributions to this Faraday Discussion will centre on so-called redox polymers, a specific example of such materials.[17,18] Similarly, we will not discuss polyelectrolytes *per se*, though solvent-free polyelectrolytes in fact exhibit behaviour very similar to the polymer-salt complexes, differing only in the transference-number behaviour. Our discussion, then, like most of the experiments reported to date in the field, will centre on simple polymer-salt complex materials.

These solvent-free polymer ionics are generally prepared by dissolving or suspending the polymeric host material and a uni-univalent salt in a joint solvent and then driving off the solvent to prepare either a bulk material or a thin film of the polymer-salt complex. That a new compound, rather than a simple physical mixture, has been prepared is obvious from such physical characteristics as glass-transition temperature (it generally increases, by at least 60 K), viscosity, relaxation time and vibrational spectra. The simple chemical reaction

$$P(ru)_n + MX \rightarrow P(ru)_n \cdot MX \qquad (1)$$
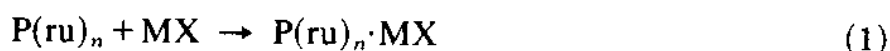
represents the formation of the complex, where MX is the salt, ru is the repeating unit of the polymer and n gives the relative stoichiometry of repeating units to salt. In the earliest materials to be studied, the repeating units were polyethers, with Lewis-base oxygens in the backbone. In particular, polyethylene oxide(PEO)- and polypropylene oxide(PPO)-based materials were studied extensively in the 1970s. More recent work is concentrated on more flexible polymer materials, including in particular so-called comb polymers, in which a very flexible backbone such as siloxane[19-21] or phosphazene[22,23] is substituted with short-chain oligoethers to provide the Lewis-base sites for complexing to the alkali M.

The polymer-salt complex electrolyte indicated on the right-hand side of eqn (1) can be structurally quite intricate. It has been convincingly demonstrated experimentally that the homogeneous elastomeric amorphous phase of the polymer-salt complex in fact provides the conductivity; partially crystalline phases reduce overall ionic mobility.[1-6,24] We will therefore concentrate, in our discussion, on ion dynamics in the homogeneous elastomeric (melt) phase.

Much of the intrinsic interest in these materials arises from their unusual conduction mechanism. In sharp contrast to ionic conductors based on crystalline solids or glasses, in these materials the Walden relation, stating that diffusivity is proportional to inverse viscosity, holds quite well. In this sense, these materials are more like liquid electrolytes, or ionic fluids, than like characteristic solid electrolytes. The applicability of the Walden relation argues that the polymeric host environment actively promotes ionic transport in these substances. This is in fact true, as will be detailed in Section 3, and comprises the basis for mechanistic understanding of transport in these substances.

Just as the polymer electrolytes differ from crystalline and glassy conductors because of the importance of host-chain dynamics in promoting transport, so they differ from simple liquid electrolytes such as aqueous solutions or molten salts, because the host itself is a high polymer, and exhibits the slow relaxation times, long-range correlations and high configurational entropies characteristic of high polymers.

The earliest suggestions for describing mechanistically the transport in these materials were based on simple hopping models, taken from crystalline solid electrolytes.[8] Such models were introduced for several reasons, partly because the earlier materials (such as PEO), were in fact partially crystalline. The fundamental assumption of these suggestions, that ionic motion occurred in structurally fixed pathways, is incorrect. A number of experimental observations demonstrate clearly the unusual and interesting mechanistic behaviour of ionic transport in these complex materials. Examples include:

(1) For a number of these substances, there is a linear relationship between the logarithm of the conductivity, and the logarithm of the so-called shift factor,
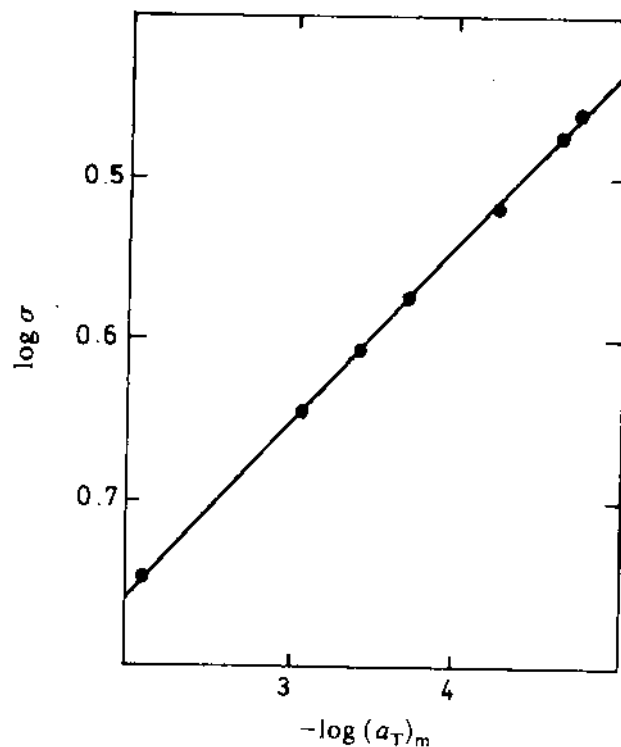
Fig. 1. Correlation between the shift factor a_T describing physical relaxation and the conductivity for PEO networks, with low concentrations of salt. The direct proportionality, with slope of unity, implies conductivity inversely proportional to viscosity, as assumed in the Stokes-Einstein relationship or Walden relationship. From ref. (25).
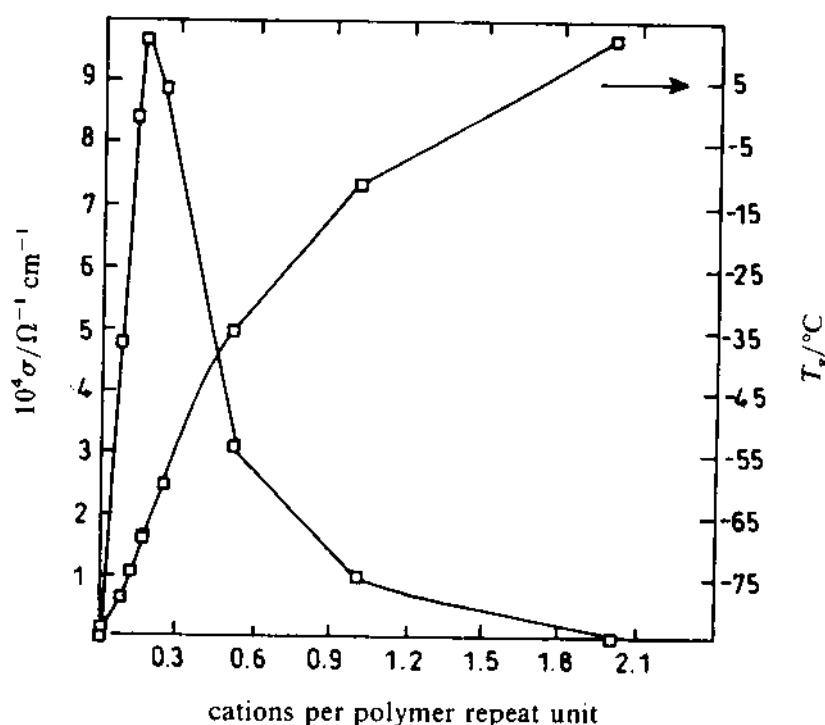

Fig. 2. Conductivity and glass-transition temperature of MEEP complexes containing $AgCF_3SO_3$. Note that the glass-transition temperature increases monotonically with salt concentration, and that the ionic conductivity maximizes at relatively low salt concentration. From ref. (22).

which describes structural relaxation in polymeric systems. Such correlation, measured by the Grenoble group,[25] is illustrated in fig. 1.

(2) Upon change in stoichiometry, conductivity exhibits a highly non-monotonic behaviour with salt concentration. An example, for phosphazine-based material, is shown in fig. 2.
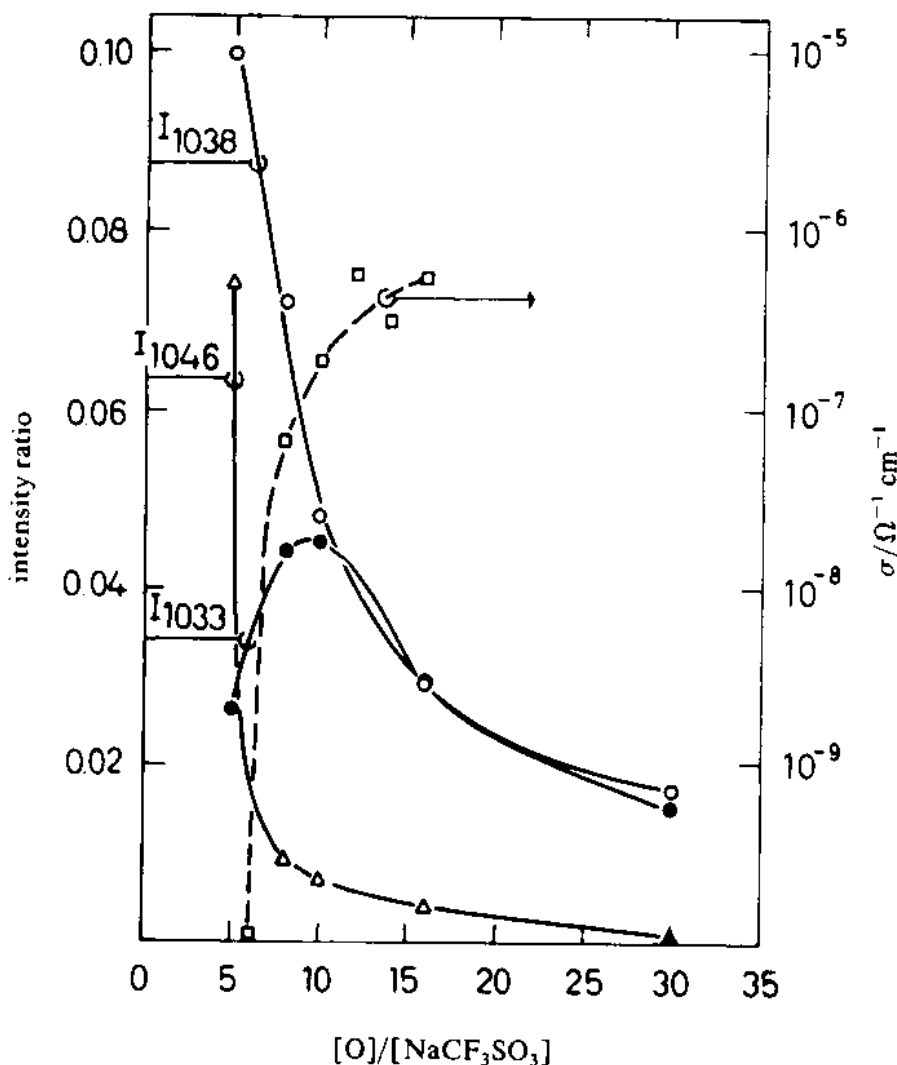
Fig. 3. The relative intensities of the vibrational components of the SO_3 symmetric stretch in the triflate ion *versus* inverse salt concentration for modes due to free ions (●), ion pairs (○) and multiple ion aggregates (△).[41] The right-hand scale shows ionic conductivity. Note the reduction in free ions for either high or low salt concentrations. The measurements were made in polypropylene glycol, based on vibrational spectra. From ref. (41).

(3) The number of free ions in such materials changes non-monotonically as a function of concentration. An example, based on observations[22] of vibrational spectra, is shown in fig. 3.

(4) In hosts such as PPO, which have relatively lower stability constants for formation of Lewis acid–base adducts with the alkali, a 'salting out' phenomenon is observed at high temperatures, with the crystalline salt precipitating from the complex, which was homogeneous at lower temperatures.[26]

(5) Addition of crown ethers or cryptates, which form tight cages around the cation, results in increased conductivity[27,28] as a function of temperature, shown in fig. 4.

Our aim here is to discuss microscopic models for describing such behaviour. Observations (1) and (2) can be understood straightforwardly on the basis of the diffusion of independent ions in a dynamically disordered polymer host, and are the subject of sections 2 and 3. The last three results are due to the Coulomb interaction of the ions in the material, which corresponds to a highly concentrated Coulomb fluid. Their explanation is more complex, but some steps in that direction are made in Section 4. Finally, Section 5 gives a current view of mechanistic behaviour in these ionic materials, and relates them to other conduction processes in polymers.
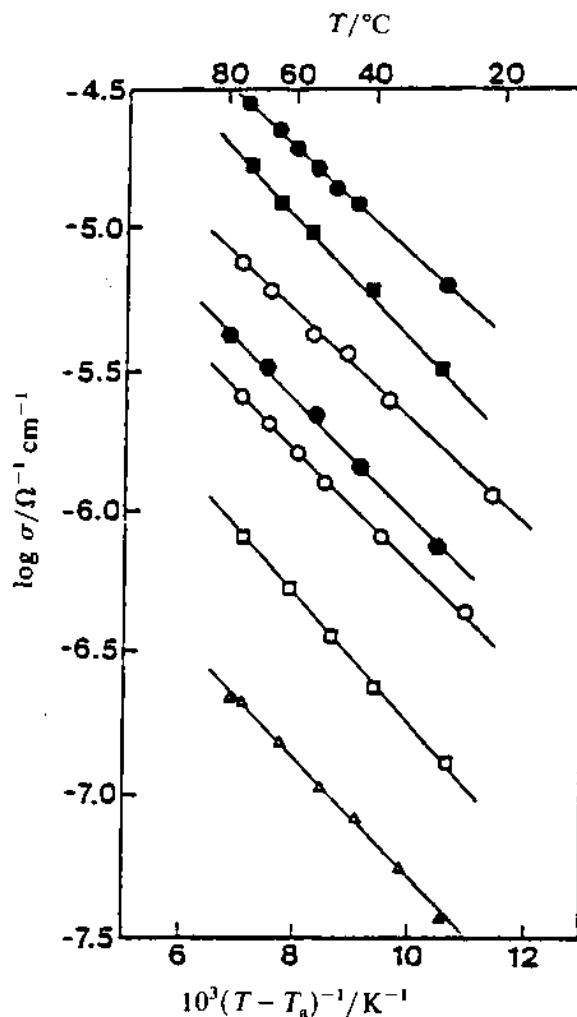
Fig. 4. Temperature dependence of the conductivities for a sulphonate polyelectrolyte based on a siloxane backbone, with increasing amounts of polyelectrolyte charge. The symbols △, □ and ○ indicate 20, 30 and 50% charged groups on the comb backbone, respectively, with Na^+ as the mobile ion. The symbols, ●, ○, ● and ■ are the conductivities measured after adding tetra-ethylene glycol, dimethyl tetra-ethylene glycol, MPEG and 18-crown-6, respectively, at a 1:1 concentration ratio to sodium cation. Note the increase in conductivity, due to the break-up of contact ion pairs, on adding sequestering agents. From ref. (61).

2. Some Experimental Observations: Requirements for Mechanism

We consider single-phase, homogeneous elastomeric polymer-salt complex materials. These exhibit purely ionic diffusivity and conductivity. The materials in question contain no small-molecule solvents, with the polymer phase itself acting as a solvent for the salt MX. The materials are characterized by both static and dynamic disorder. The static disorder simply arises from the structure and morphology of the polymer chain itself. These materials are non-crystalline, and although the polymer may exhibit helical regions (as PPO does), no crystalline phases occur; no crystalline scattering patterns are seen either in optical microscopy or X-ray scattering.

The dynamic disorder is a slightly more complicated process. Polymer ionics, unlike glassy ionic materials, are always studied well above their glass-transition temperature, T_g. While the glass transition is a rather complicated phenomenon, at temperatures exceeding T_g, the local structure is in fact molten, with rapid changes in local bond and dihedral angles. The materials above T_g are soft and plastic, exhibiting high viscosities and solid-like physical properties. These arise from the entanglements of the long chains; very short-chain materials flow easily above T_g, and would not normally be considered solids. While static disorder (the absence of crystallographic long-range

order) is found in the glassy materials such as sodium silicate, these glasses do not exhibit dynamic disorder: in glasses, local metrical information is preserved in time. In dynamically disordered systems, like liquid water or polymer electrolytes, the nearest-neighbour, next-nearest-neighbour, next-next-nearest-neighbour, *etc.*, shells around a given atom or ion will change in time, as orientational and vibrational modes of low frequency and high amplitude are excited.

Experimental studies, such as those already discussed in Section 1, place several stringent requirements on a mechanistic picture describing ionic mobility in these materials. Perhaps the most important observation is the necessity, as is clear from the relationship in fig. 1 between relaxation properties and conductivity, for the dynamical motions in the polymer host itself to promote ion transfer. In this sense, we deal with a coupled process between ionic motion and host dynamics. Angell[29-31] has provided a very useful description of the coupling between ionic diffusivity and host motion. He defines the decoupling index, R_τ by

$$R_\tau = \tau_s / \tau_\sigma \tag{2}$$

where τ_σ and τ_s are, respectively, relaxation times corresponding to conductivity and structural relaxation. In molten salts or liquid electrolytes, the structural relaxation is intimately connected with the conductivity relaxation and this ratio is roughly unity. As a molten electrolyte is cooled, if it forms a glassy electrolyte, below a certain fictive temperature,[32] at which the relaxation processes fall out of equilibrium, there will be a decoupling of the large-scale orientational (structural relaxation) modes of the host and the hopping diffusion of the ions. Thus, in typical glassy electrolytes, the decoupling index, R_τ, can approach values of 10^{12}, as relaxation times, or at least the longer relaxation times, approach a macroscopic size of the order of seconds, minutes or hours. In the polymer electrolytes, this ratio is generally of the order of unity; indeed, it will often fall below unity for concentrated electrolytes, as certain motions that contribute to structural relaxation do not promote ion transfer. This is evidence for interionic correlation, and will be discussed in Section 4.

That segmental motion of the polymer host is required to promote ion transport is obvious from a number of experiments. Perhaps the most striking is the fact that in many materials the thermal dependence of the conductivity can be expressed in the so-called Vogel-Tamman-Fulcher[1-6,33,34] form of

$$\sigma T = \sigma_0 \exp[-B/(T - T_0)] \tag{3}$$

where σ is the conductivity, B is a constant related to the inverse expansivity of the material, and T_0 is a reference temperature, generally *ca.* 50 degrees below the glass-transition temperature. This form was originally used to discuss the viscosity of polymeric materials; the fact that viscosity and conductivity are inversely related, essentially the physical content of the Walden relationship, suggests very strongly that structural motions of the polymer are required for diffusive motions leading to conduction. The explanation of a large number of other experimental facts, conveniently reviewed elsewhere,[1-6] also requires a dynamical coupling of the segmental motion of the polymer host with ion diffusion. Physically, the picture is simply that well defined passageways, or channels, such as are characteristic of crystalline ionic conductors like AgI or Ag_2S are simply not present in these soft polymeric substances. Rather, spaces for ionic motion to occur must form due to activated motions of the polymer host. This physical picture underlies free-volume theory,[35] the quasi-macroscopic model that has been extensively, and very usefully, employed in the polymer electrolytes field.[36,37]

Although host motions are required for conductivity, by themselves they are not sufficient. Thus, for example, the conductivity of $NaBH_4$ complexes in PEO is quite small,[38] as is, characteristically, ionic diffusion in most non-ethereal polymer hosts.

Thus, it appears necessary that the acid-base interaction between the polymer hosts and the salt is strong enough to cause solvation, but not so strong as to militate against exchange of the coordination environment of the mobile ion.

3. Independent Particle Transport: Dynamic Percolation Theory

Formulation of Model

The results of extensive experimental investigation of polymeric electrolytes, including those just discussed, place substantial constraints both on the mechanism of ion transport and on any model that might be formulated to discuss ion transport in these materials. Perhaps the most important result is that the motion of the ions is strongly dependent on segmental motion of the polymer host. This is clear both from the near-unity value of the decoupling index R_τ, and from the adequacy of the VTF form of eqn (3) in describing the conductivity. The equivalent WLF form,[39] it should be remembered, is originally defined for structural and relaxation properties; the close similarity of the dependence upon temperature of ionic conduction and polymer relaxation, as indicated in fig. 1, requires that the dynamics of the chain be linked to the transport process. Additionally, the fairly good relative agreement of the Nernst-Einstein relationship between conductivity and diffusivity, with no substantial correction factors,[40] argues that while interionic interaction effects may be important, they are to a first approximation not needed for understanding the dominant conductivity mechanism in most of these systems. This conclusion is underscored by recent spectroscopic experiments that demonstrate quite convincingly that contact ion pair formation, while important, is not dominant in determining the conduction.[41,42]

Based on these two ideas (coupled dynamics of ions and polymer hosts, and fairly weak dependence of conductivity on interionic interactions), it is reasonable to define an independent particle, hopping-type model for ionic motion. We will see later (Section 3) that such a model can be substantially generalized, and thus describe the physics of ionic motion fairly well. The simplest model, then, involves ionic hopping among sites, defined by simple geometry, in the continuous elastomeric phase of the polymer electrolyte. Note that, in contrast to crystalline ceramic electrolytes, or heavy-metal electrolytes like silver iodide, the sites are not fixed by the crystal structure, but are simply the nodes of a net arbitrarily defined within the continuous phase. The ions will then, under rather general conditions, obey a generalized master equation, or hopping-type equation, of the form:

$$\dot{P}_i = \sum_j (W_{ji}P_j - W_{ij}P_i). \tag{4}$$

Here P_i is the probability of finding a mobile ion at site i, and W_{ji} is the probability per unit time that an ion will hop from site j to site i. For simplicity it is generally assumed that W_{ji} is zero except between nearest-neighbour sites; in a continuous elastomeric network, this assumption is eminently justified. The sites are not necessarily defined in terms of any particular binding geometry; for cations, it is reasonable to assume that sites are defined by a locally attractive coordination environment of, say, tetrahedrally disposed oxygens or nitrogens. In contrast, for anion motion the sites are perhaps best defined simply in terms of sufficient geometric space to accommodate such large anions as triflate or tetraphenylborate. In either case, in any given metrically defined region of the continuous material, a stable site for ion occupancy may not exist at any given time; there may be insufficient volume for the anions, or inappropriate coordination environment for the cations. Under such conditions, the probability W_{ij} for hopping from site j to site i may be zero, if a favourable environment is not available

around site *i.* Under these conditions, it is appropriate to simplify the jumping probabilities as:

$$W_{ij} = \begin{cases} 0 & \text{probability } 1-f \\ w & \text{probability } f \end{cases} . \tag{5}$$

Here *w* is an average hopping rate between two sites available for ionic occupancy, and the relative probability of the site *i* being available is denoted *f.* The probability distribution of eqn (5) is essentially that of a random hopping model,[43] in which it is assumed that particles can hop between sites, with random jump probabilities chosen from some given distribution. The percolation model is highly appropriate for statically disordered systems, and has been extensively used in glasses, alloys and related materials.

The polymer electrolytes are always investigated at temperatures above T_g. In this regime, the materials are both statically and dynamically disordered; in terms of our percolation model, then, a pathway between two sites which was unavailable at a certain time may become available at a slightly later time, as segmental motions of the polymer chain change the local void volume and/or the local coordination environment. It is then appropriate to generalize the static percolation model given by eqn (4) and (5) to a dynamic percolation model or a dynamic disorder hopping model,[1,3,37,44–53] in which the assignment of any given hopping probability W_{ij} between sites *i* and *j* as available ($W_{ji} = w$) are unavailable ($W_{ji} = 0$) changes in time. The process by which such changes occur is referred to as renewal, or reinitialization, or reassignment and is characterized by a particular average time, called the renewal time, τ_{ren}. Just as one can define different (random) hopping models depending on the details of the distribution of the W_{ji}s and their values among different sites, so one can define different dynamical percolation models depending on how the renewal process occurs. The simplest renewal process assumes that on a given average interval τ_{ren}, the assignment of which jumps are available and which are unavailable instantly changes. The simplest dynamic percolation theory picture, then, involves use of eqn (4) and (5), describing the static percolation, with the additional feature that after a given time-interval the W_{ji}s are reassigned. This is fixed by the parameters *w, f,* and τ_{ren}. These can be related to such system parameters as ion size, free volume, temperature and pressure. In fact, the most important of these parameters is the renewal time, characterizing the rate of change of the availability of a given intersite hop. This rate of change is determined by the dynamics of the polymer host, and therefore τ_{ren} is simply a characteristic relaxation time for a polymer's configurational degrees of freedom.

This simplest dynamic percolation model has been rather extensively applied in discussing ionic motion in polymer electrolytes.[44–51] Some results and applications are discussed in the next subsection, and extensions of the model, which illuminate precisely what is and what is not important about the restrictions defined on this point, are discussed in the subsection following the next.

Results: Applications of Dynamic Percolation Models to Polymer Electrolytes

A number of very general results follow from the simple definition of the dynamic percolation model; we will first discuss these, then mention briefly some applications to experiments.

(1) For any observation time, t_{obs}, that is long compared to the renewal time, the ionic motion in any dimensionality is always diffusive.[44,45] This is illustrated in fig. 5, in which it is clear that, although over a short time compared to the renewal time, the mean-squared displacement can become asymptotically constant (for a system below the static percolation threshold), the renewal process
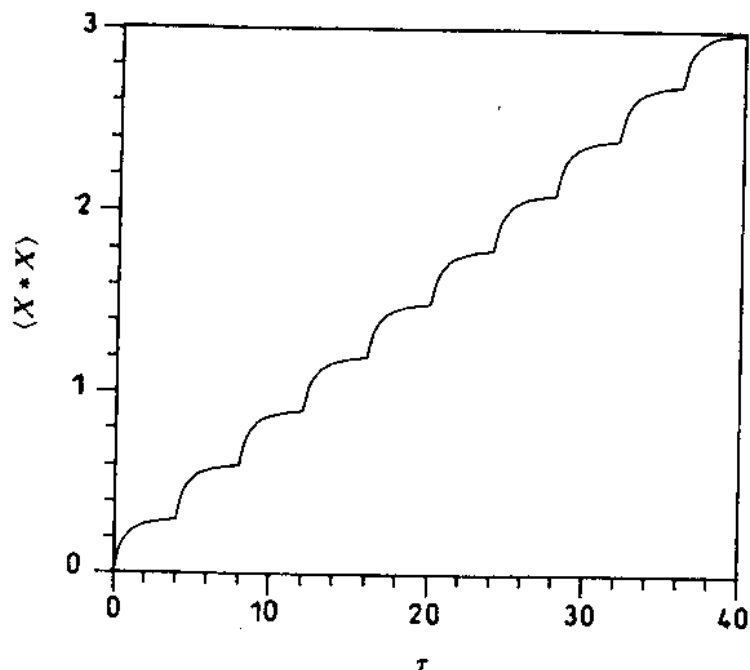
Fig. 5. Mean-square displacement as a function of time, for dynamic percolation on a one-dimensional chain. Notice that within each small interval (of relative size 5 time units) the transport becomes limited by the size of the connective cluster, but over many renewal epochs mean-square displacement is indeed linear in temperature. From ref. (44).

permits concatenation of such motions resulting in overall diffusive behaviour, with mean-squared displacement proportional to time. This has been shown to hold in any integer dimensionality.

(2) For motion in one dimension, the closed-form result of eqn (6) holds for the diffusion coefficient[44,49]

$$D = \frac{a^2 f^2}{2(1-f)^2 \tau_{ren}}.$$ (6)

Here a is the mean distance between sites. Dependence on f describes essentially how far an ion travels before the renewal process must occur, and the dependence on $1/\tau_{ren}$ arises from the renewal process itself.

(3) In static percolation models, there is generally a percolation threshold, that is there exists a value f_{th} below which diffusion is not observed.[43] No such thresholds exist in renewal models, consistent with experimental observation; nevertheless, a remnant of the threshold behaviour is found in that the value of the diffusion coefficient changes substantially in the region of f_{th}.[47,49] This is more extensively discussed in the next subsection.

(4) The frequency-dependent diffusion coefficient can be rigorously related to the diffusion coefficient D_0 in the analogous static percolation lattice [*i.e.* the problem defined by eqn (4) and (5) without renewal] by the analytic continuation formula[45]

$$D(\omega) = D_0(\omega - i/\tau_{ren}).$$ (7)

This formal result can be quite important, since closed-form expressions often exist, on different lattices with different hopping probabilities, for the mean-squared displacement or static percolation coefficient.

(5) If certain reasonable assumptions are made relating viscosity to the relaxation, a Walden product can be obtained as:

$$D\eta = mc^2 \langle x^2 \rangle_{\tau_{ren}} f / a^2. \qquad (8)$$

Here c is the speed of sound in the elastomer, and the notation $\langle x^2 \rangle_{\tau_{ren}}$ indicates mean-squared displacement in a single renewal interval. The Walden product is thus predicted to be only weakly temperature dependent, and to depend upon such material properties as the speed of sound and the segment length. The near constancy of this product is in agreement with the results of fig. 1, and with the near constancy of the decoupling ratio R_τ (which, assuming the validity of Nernst–Einstein relationships, is essentially proportional to the Walden product).

(6) The predicted dependence of the diffusivity of system properties is entirely dominated by the dependence upon the polymer renewal relaxation time τ_{ren}. This is in agreement with experimental results. Indeed, it can be shown in general that[44,47]

$$D = n_d \overline{\langle r^2 \rangle_{\tau_{ren}} / \tilde{\tau}_{ren}} \qquad (9a)$$

where $n_d = 1/2d$ with d the space dimension of the hopping net, and the brackets and bar corresponding to averaging over a thermal ensemble and the distribution of renewal times, respectively. The $\langle r^2 \rangle_{\tau_{ren}}$ is for a single renewal interval.

(7) If the conductivity is plotted as a function of frequency on a log–log plot (fig. 6) one notices substantially different behaviour for the mean polymer host and the elastomeric ionic conductor. At frequencies above *ca.* 10 GHz these two responses are essentially identical; this may reflect displacive motions of charges or dipoles within the polymer host. For lower frequencies, only the ions themselves continue to respond diffusively over longer and longer time scales. Thus the response of the neat polymer drops essentially to zero, while that of the electrolyte flattens out to an asymptotic value at low frequency, corresponding to the d.c. diffusion arising from the renewal process. This is shown in fig. 6, where the results of the dynamic percolation model are contrasted with experiment.[51]

(8) Depending on the size of the continuous region over which static percolative diffusion can be observed, the overall diffusivity or conductivity show different dependences upon the renewal rate. This is illustrated in fig. 7, showing two limits. In the small cluster limit (fig. 7) the mean-squared displacement, assuming no unavailable bonds, would be very much larger than the mean size of the connected cluster. Under these conditions, renewal is clearly necessary for diffusion to occur, and the diffusion coefficient is given by eqn (9a). On the other hand, if the connected cluster is large enough that the mean-square displacement for simple hopping in the given time is smaller than the extent of the connected cluster, one expects the motion to be independent of the dynamic renewal process. Under these conditions one finds, as expected,

$$D = D_0 \approx w \langle r^2 \rangle n_d. \qquad (9b)$$

Note here that the result is indeed independent of the re-initialization in the host. Eqn (9a) and (9b) describe, respectively, conduction in polymer electrolytes above T_g and the glassy solid electrolytes below T_g. In the former case, dynamic host motion is necessary to promote ionic diffusivity, whereas in the latter case dynamic diffusion occurs in a relatively fixed host environment, promoted by thermal motions of the host.

(9) The result (9a) implies that

$$\log \left[\frac{\sigma(T)}{\sigma(T_s)} \right] = \log \left[\frac{\tau_{ren}(T_s)}{\tau_{ren}(T)} \right] + \log \left[\frac{T_s}{T} \frac{F(T)}{F(T_s)} \right] \qquad (10a)$$
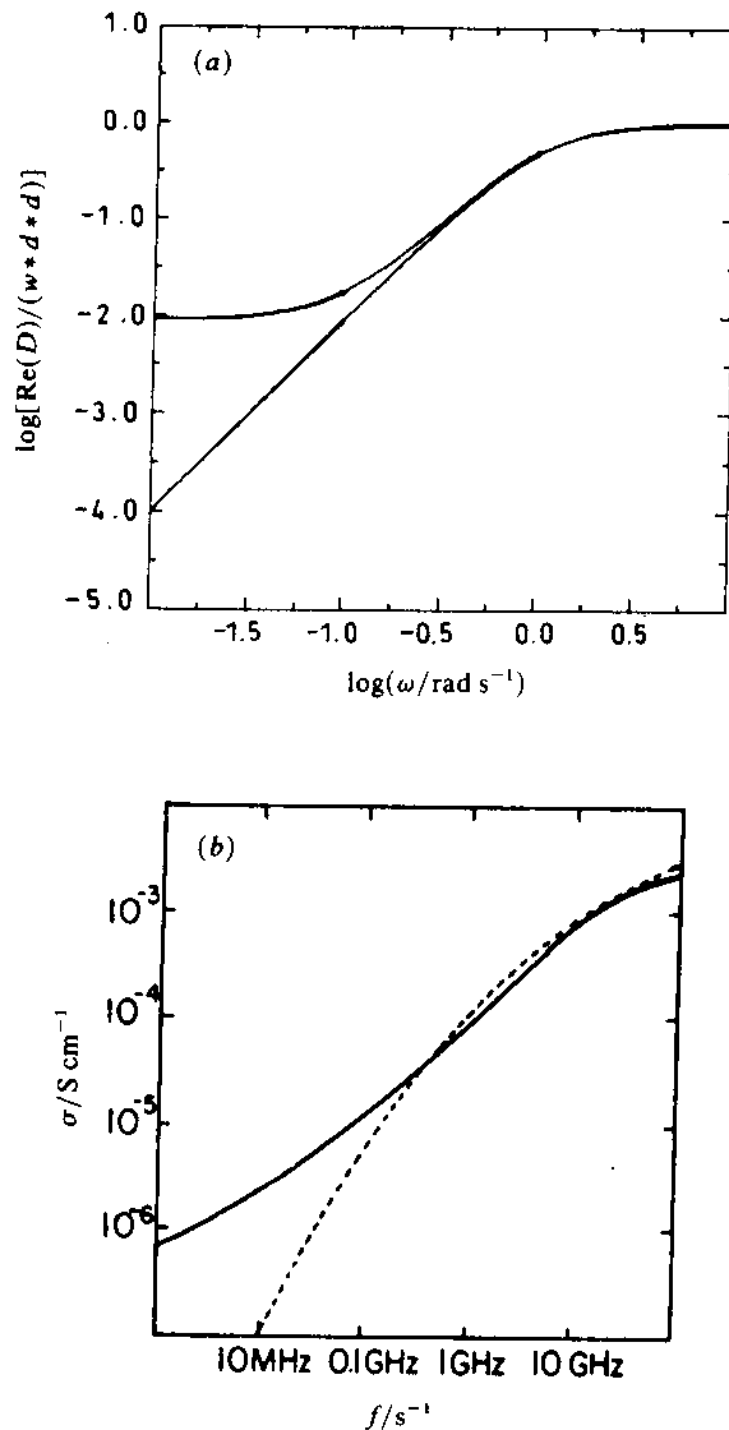
Fig. 6. (*a*) Calculated frequency-dependent conductivity for a simple dynamic percolation model. The lower line is the diffusion coefficient without renewal, the upper line that with renewal. (*b*) For comparison, the frequency-dependent conductivity of pure PEO (- - - - -) and PEO salt complex (—) at 22°C. Only the salt ions are capable of long-distance diffusive motion, corresponding to renewed diffusion. From ref. (51).

where $F(T)$ is the correlation factor correction to the Nernst-Einstein relationship. Writing the shift factor as

$$\log [\eta(T)/\eta(T_s)] = \log [\tau(T)/\tau(T_s)] \qquad (10b)$$

the combination of (10*a*) and (10*b*) explains the linear curve of fig. 1, if correlation corrections to Nernst-Einstein are relatively unimportant.

Other applications of the dynamic percolation model, including comparison of semicrystalline and fully amorphous materials,[54] frequency dependence,[50,54] relation to
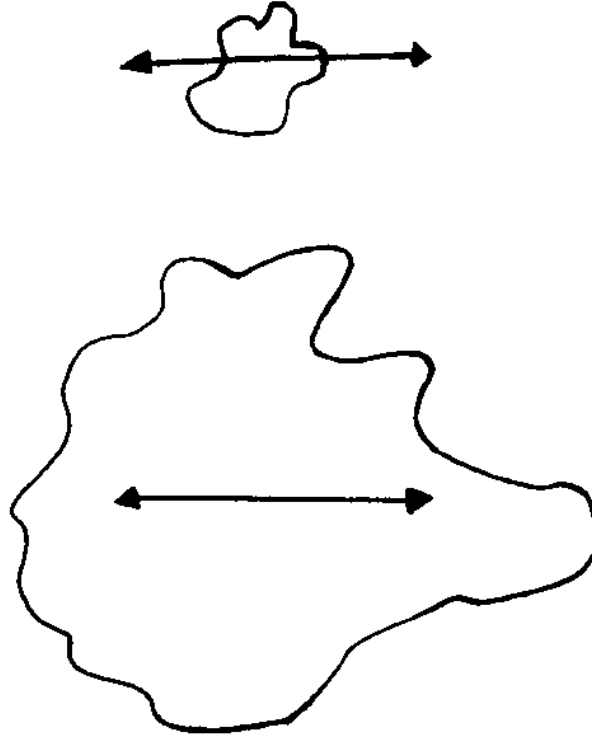
Fig. 7. Different diffusion limits for dynamic percolation. In the upper cartoon, the blob representing the mean connected cluster is small compared to the line, representing root-mean-square displacement within a renewal epoch. Under these conditions, conduction will be proportional to the inverse renewal time. The lower cartoon shows the opposite situation, with large mean connected cluster. Under these conditions, the medium will renew before the local connected region is filled and D will be independent of the renewal time.

quasimacroscopic transport theories,[37] threshold behaviour and the importance of correlations,[47-50,53] are discussed in later papers on dynamic percolation.

Aspects and Extensions of the Dynamic Percolation Model

In addition to the specific applications discussed above, the dynamic percolation model has been extended to apply beyond the simple independent hopping of particles on a regular lattice. A number of generalizations have in fact been published. Perhaps the most important conclusions to be drawn from these generalizations are as follows.

The important results, particularly in the analytic continuation rule, the diffusive nature of the transport and the monotonic increase of diffusion coefficient with frequency for low frequencies, can be shown to hold under much more general condtions. One can relax the site model, permit certain correlations among the different renewal processes and allow the renewal times to be chosen from nearly arbitrary distributions.[45,46,49,50] In fact, the only real requirement for these general results to hold is that the displacements obey a particular growth law.[50] The growth law is illustrated in fig. 8, showing an arbitrary function, F, such as the mean-square displacement for a specific sequence of renewal or reassignment events. Analytically, it can be expressed as:

$$F(t) = g(\tau_0) + \sum_{i=1}^{N} f(\tau_i).$$

(11a)

Here $g(\tau)$ is the growth that would be observed, without further renewal, starting from an arbitrary time 0, before which random renewal had been an on-going process. $f(\tau_i)$
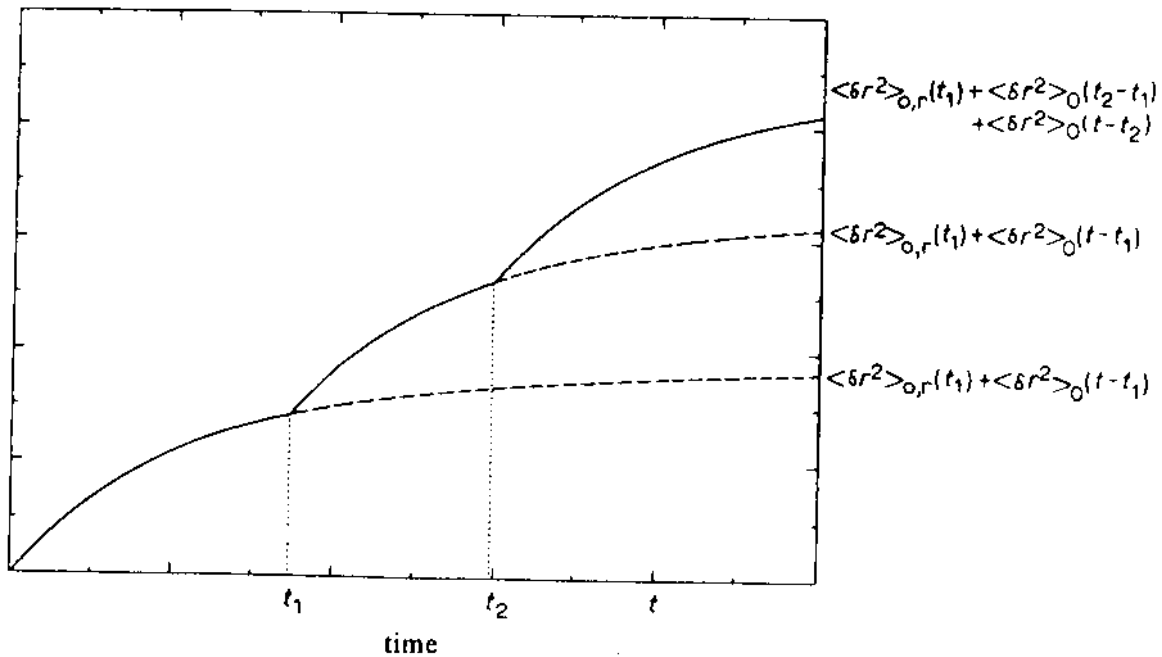
Fig. 8. An illustration of the growth law for mean-square displacement. The solid lines represent the mean-square displacement addition within each time interval. Notice that the growth law, in the sense that the mean-square displacement is additively incremented within each time interval, is obeyed. From ref. (50).

of t is the growth that would be observed without further renewal, starting from a previous renewal at $t = 0$. The time sequences are defined by

$$\tau_i = \begin{cases} t_i & i = 0 \\ t_{i+1} - t_i & 0 < i < N. \\ t - t_N & i = N \end{cases} \quad (11b)$$

Physically, fig. 8 and eqn (11) mean that a particular property (F might, for example, be associated with mean-square displacement) grows by addition of finite increments, and these finite increments depend upon time intervals. The behaviour illustrated in fig. 8 is precisely that expected for ionic diffusion in a dynamically disordered medium (including both polymer electrolytes and liquid solution), and therefore the growth law will hold, and the results of the simplest dynamic percolation model will be applicable, for these situations also. The growth law clearly does not require a lattice with sites, nor approximations involving either the correlation of subsequent renewals or the distribution of renewal times. An alternative proof that important results of dynamic disorder hopping apply under more general conditions can be derived in quantum mechanics, starting with the linear response expression for the conductivity. One can then show that the analytic continuation rule of eqn (7) will hold if and only if the velocity auto-correlation functions satisfy

$$\int^{\beta} \langle v_\xi(0) v_\eta(t + i\hbar\alpha) \rangle \, d\alpha = \exp(-\lambda t) \int_0^{\beta} \langle v_\xi(0) v_\eta(t + i\hbar\alpha) \rangle_0 \, d\alpha. \quad (12)$$

Here ξ and η represent space variables x, y or z, λ is the inverse mean renewal time, $\beta k_B T = 1$ and the expectation values on the left and right sides are evaluated in a renewing lattice and a static lattice, respectively. The importance of eqn (12) lies in providing yet a further generalization of dynamic disorder motion to quantum behaviour. For example, fig. 9 shows the effective renewal as a function of time for two situations. The upper situation corresponds to hopping-like transport, in which the mean-square displacement is beginning to flatten out asymptotically with time, before renewal occurs.
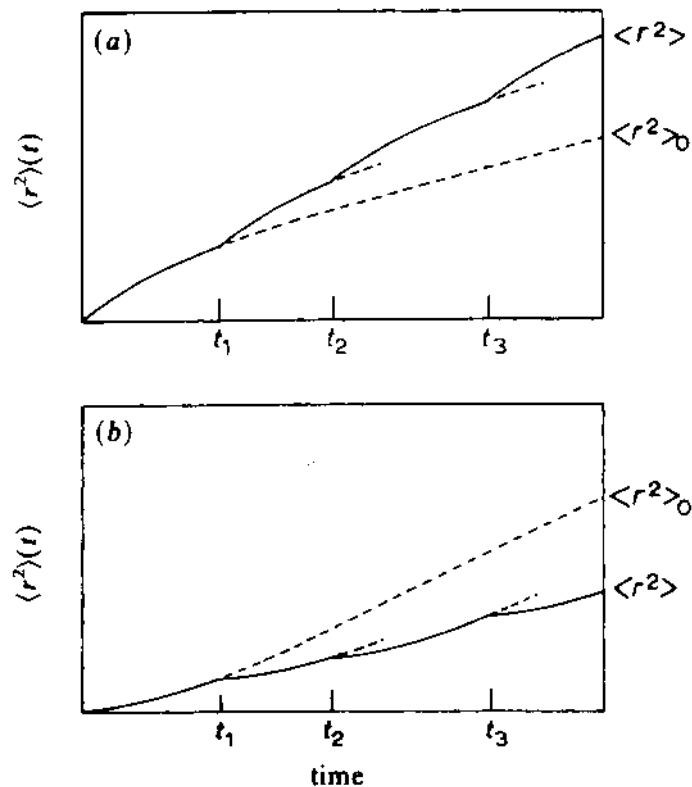
Fig. 9. The effective renewal times, at t_1, t_2, ... (a) on a concave-down and (b) on a concave-up mean square displacement $\langle r^2(t)\rangle_0$ dependence, corresponding relatively to hopping-like (ionic) and coherent or ballistic (electronic) transport. Notice that the growth law is obeyed in both cases, guaranteeing diffusive conductivity along times. From ref. (50).

This is characteristic of diffusive hopping transport. On the other hand, fig. 9(b) shows a coherent-like transport situation, corresponding to scattering in band conduction. Here the mean-square displacement without renewal is quadratic in time; the renewal process in fact reduces the expected growth in the mean-square displacement, in sharp contrast to the diffusive situation. The applicability of dynamic disorder hopping models in both the quantum (coherent)[56] and classical (hopping) cases makes the results useful both for ionic conductors and for electronic conductors of relatively short mean free path, such as redox polymers and molecular metals.

While correlations in the renewal process will generally have rather small effects on the growth law and the diffusion coefficient, spatial correlations in the renewal pattern can in fact change the rate substantially. Harris *et al.*[55] show by means of simple simulations that if bond renewals are restricted to occur between nearest-neighbour sites, the d.c. conductivity is reduced relative to that for random renewal since the carrier must occasionally wait for the slower renewal chain of events before it can proceed along the chain. More recent work has extended these considerations substantially, by examining a situation in which there are two renewal processes. The first corresponds to a simple fluctuation of each site with a characteristic renewal rate $1/\tau_{ren}$ between open and closed, or available and unavailable, positions. The second renewal process corresponds to pairs of adjacent bonds interchanging their status as available or unavailable; this rearrangement occurs at a rate α. The interchange is related to models such as the Grotthus picture for proton transport in hydrogen-bonded systems, in which case the rotation of water molecules permits protonic hopping.

Granek and Nitzan and others[47,49] have analysed a renewal problem containing such processes in the effective medium approximation. Fig. 10 shows, for a two-dimensional square lattice, the effective medium rate of transport as a function of the bond filling factor, f, for the situation in which only adjacent-bond interchange is permitted (τ_{ren} goes to infinity). Notice that the threshold, which for the two-dimensional square lattice
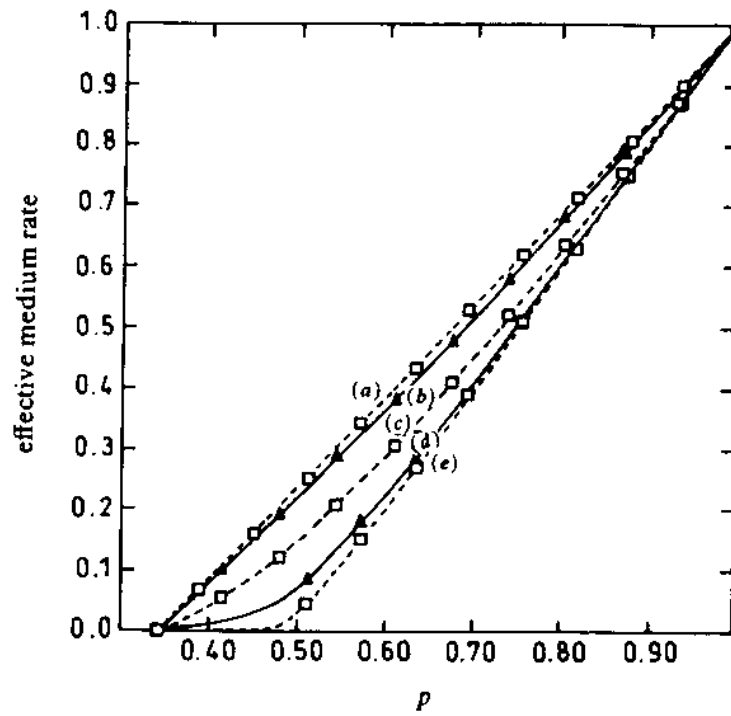
Fig. 10. The effective medium diffusion rate as a function of p (equivalent to the f of text), the percentage of available bonds. The static percolation threshold for this square lattice system is at 0.5; notice that the dynamic renewal process (in this case corresponding to correlated renewal, the exchange of nearest-neighbour bonds) drops the percolation threshold to much lower values of p. The different curves are for different rates of interchange of status (open $\rightleftarrows$ closed) between adjacent jumps; this rate increases by a factor of 3750 from (e) to (a). From ref. (47) and (49).
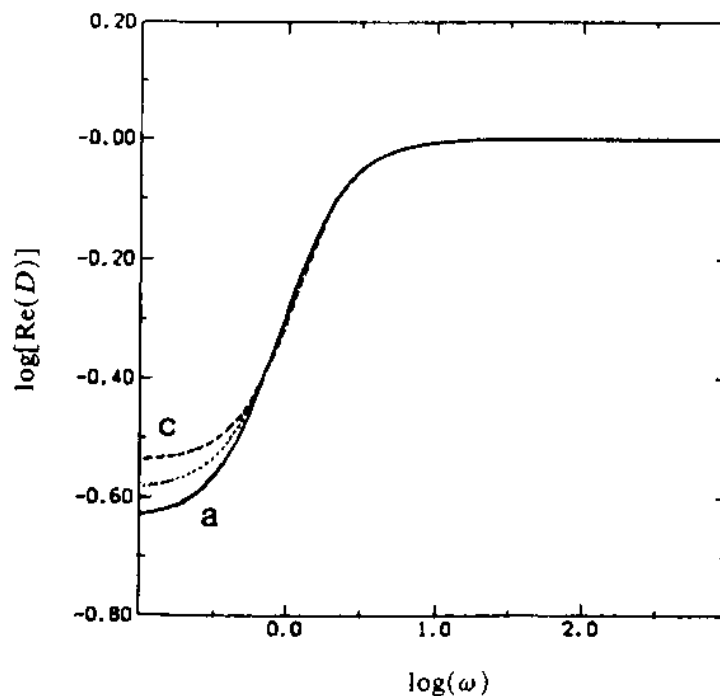

Fig. 11. Calculated frequency-dependent conductivity for dynamic percolation, or for general growth-law diffusion. The different curves have slightly different renewal processes, but the generalized behaviour (flat near the origin, monotonically upward, flattening out at high frequencies) is common for all growth law or renewal processes. From ref. (50).

occurs at $f = 0.5$ in the static, $\alpha = 0$ limit, is downshifted to $f \approx 0.34$. This threshold is independent of the actual magnitude of α, so long as $\alpha \neq 0$. Notice that for increasing α, the effective medium transport rate increases montonically, as expected, with increasing α; for large enough α, this increase is unimportant.

Some generalized results on the frequency dependence of dynamic percolation models follow from the growth law itself.[50,53] Fig. 11 shows the calculated dependence of the diffusion coefficient on frequency. The high-frequency, asymptotically flat result is an artifact of the hopping model, since any real conductivity must eventually roll over and vanish as the mobile species, due to its inertia, cannot follow the instantaneous reversals of the field. The more important behaviour is the relatively flat slope at very low frequencies, becoming monotonically upward in the intermediate frequency range. While it is generally true that any hopping model must yield an increasing diffusion coefficient with frequency at low frequencies,[57] the general roll-over behaviour observed in fig. 11 will always hold in dynamic percolation models.

Thus the dynamic percolation model has been extended to deal with situations far beyond the original simple picture discussed at the beginning of this section. While correlations among renewals can affect the diffusivity, unless such correlations are very strong[47,49,53,55] the effects are quite small. This is not necessarily true with correlation effects among the ions, arising from Coulombic forces.

4. Ionic Correlation Effects: Coulomb Interactions

Characteristically, the ionic concentration in polymer–salt complex electrolytes is roughly one molar, and the mean distance between ions is of the order of 6 Å. This means that all ionic motion is within a relatively strong Coulomb field of other ionic particles, and therefore that the material can be considered as a solvated Coulomb fluid, rather than a simple set of independently hopping particles. Under these conditions, one seriously questions not only the simple independent particle description of diffusivity which underlies both the free-volume theory and the dynamic percolation model just discussed, but also any simple extension in terms of ion-pair formation. Indeed, spectroscopic studies, both in liquid polymer hosts[58] and in actual polymer electrolytes,[31,38,41,42,59] indicate strongly that independent ions, ion pairs, ion triples, and higher ion multiples can be observed. Moreover, the experimental data seem to argue that both solvent-separated ion pairs and tight, or contact, ion pairs exist in these materials. Before proceeding to some simple theoretical considerations concerning ionic interactions in polymer electrolytes, we discuss some of the critical experimental observations.

Greenbaum and collaborators[13,26] noted that complexes based on PPO, when heated, often broke down into a remaining complex phase and isolated salt crystals. This was not so clearly observed in the more strongly solvating PEO, nor has it been repeated in ionic conductors of stronger solvating ability, such as the comb polymers. Nevertheless, the observation itself indicates that, especially with weakly solvating hosts, there is a substantial thermodynamic driving force at higher temperatures toward the formation of separated salt structures and polymer host (the latter possibly containing some salt).

Cheradame suggested[34] early on that one could modify the simple WLF form of eqn (3) for the conductivity, by including an activation form relating the stoichiometric concentration of ions to the concentration of mobile ions. This results in:

$$\sigma T = \sigma_0 \exp\left(-\Delta E_F / RT\right) \exp\left[-B / (T - T_0)\right] \tag{13}$$

where ΔE_F is the activation energy involved in forming mobile ions from immobile ions. It was suggested that this is the energy necessary to break up ion pairs, to produce free carriers. This form has been used in several subsequent investigations,[60] and indeed

Watanabe reports[60b] values of the activation energy ΔE_F, of the order of 0.3 eV for polypropylene oxide electrolytes.

More recent investigations, as well as older investigations in the general solvation literature, indicate that the situation may in fact be more complicated. Thus, Torell has discussed[31,41] vibrational spectra in terms not only of concentration effects, as indicated in fig. 3, but also of temperature dependence. Indeed, she suggests that the number of contact ion pairs actually increases with temperature; this is consonant with the spirit of Greebaum's observation of salt precipitation. Extensive work in the simpler situations of ethereal solvents has also shown that the concentration of contact ion pairs, as opposed to looser solvent separated ion pairs, in fact increases with increasing temperature.[61]

That ion pairs are relevant to conductivity in ionic conductors has been demonstrated several times, notably in the early work of Shriver and collaborators in PEO hosts.[38] These studies show that ions, such as BH_4^-, spectroscopically demonstrating contact pair formation yielded much less conductive complexes than ions such as BF_4^-, for which no vibrational spectroscopic evidence for pairing occurred. Analogously, several workers have shown (compare fig. 4) that addition of a sequestering agent, capable of fully and selectively solvating the cation, can often increase the ionic conductivity.[27,28,61] One obvious argument is that the chelating agent, such as 18-crown-6, tetraethylene glycol or various cryptands, form such a tight sheath around the cation that no contact ion pairs can in fact be formed. Watanabe suggests[36] that remnant cation–anion attractions, whose strength is indicated by the cohesive energy of the parent salt, can actually reduce overall ionic conductivity in polymer–salt complexes. Finally, as has already been pointed out, the value of considerably less than unity for Angell's decoupling index R_τ might well indicate reduction of conductivity by means of Coulombic attraction to counterions.

From the viewpoint of simple thermodynamics, the free-energy of desolvation to form pairs can always be written

$$\Delta G_p = \Delta U_p - T \Delta S_p \tag{14}$$

where the subscript p indicates pair formation, and enthalpies and energies are taken to be equal. Simple thermodynamics then suggests

$$(\partial \Delta G_p / \partial T)_{pressure} = -\Delta S_p. \tag{15}$$

Thus, the stabilization of the homogeneous complex in free energy will become less favourable with increasing temperature, if the entropy for the contact ion-paired, or salt-separated, material is in fact greater than the entropy of the homogeneously distributed ionic complex.

To assess, then, the free-energy for desolvation to form ion pairs is necessary to evalaute both the energy term ΔU_p and entropy term ΔS_p. An actual derivation of these terms, involving some fairly elaborate arithmetic, is given elsewhere.[62] We recap here the important physical points involved, and discuss how this theoretical approach relates to experiment.

We first consider the energetics involved. Generalizing the approach of Debye, Hückel and Onsager,[63] we can consider forming a dipole within a cavity in the uniform fluid of charges. For the polymer electrolytes, however, the concentrations are in fact extremely high. The inverse Debye screening length is given by

$$k = \sqrt{(4\pi \Sigma_i n_i q_i^2 / \epsilon k_B T)} \tag{16}$$

with n_i the charge density of carriers with charge q_i and ϵ the static dielectric constant. For most polymer electrolytes, the high concentration makes this inverse Debye length of the order of 1 bohr^{-1}.† This means that the usual expansion, to first order in inverse temperature,[63,64] is no longer justified. Instead, one must treat the problem numerically

† 1 bohr = $5.291\,77 \times 10^{-11}$ m.

to evaluate the energetic contribution ΔU_p of eqn (14). Our preliminary calculations[62] indicate that for the complex electrolytes of interest, for which the concentration is near one molar, the energetic term will always favour separation of the contact ion pairs, to form solvated ions. This of course is evaluated in the continuum–cavity model, and ignores specific solvation effects and the molecularity of the solvent. These latter would in general tend to favour pair separation even more strongly,[65] so in the absence of entropic terms contact pairs would not be very favourable even at high concentrations. This is in accord with a number of experiments, which indicate that at relatively low temperatures contact ion pairs are less probable than quasi-free ions.

One caveat must be remembered: specific energetic interactions may in fact overwhelm the solvation stabilization of separated pairs, and result in contact pair formation. This has been observed with very small anions[39] such as BH_4^-, and with very strong Lewis-base anions, such as tetra-alkoxy aluminates.[27] Also, simple mass action suggests that the equilibrium

$$M_{solvated}^+ + X^- \xrightleftharpoons[]{\text{polymer solvent}} MX \tag{17}$$

will in fact favour the right-hand side (contact ion pairs) to a greater extent as the overall concentration of salt increases. This is in accord with the simple physical expectation, as well as the observations of Torell, Smid, Shriver and others. Finally, we should remember that 'quasi-free' in this context means that the ions are separated to their stoichiometric average distance. In highly concentrated salt solutions, this average distance will be a number *ca.* 6-10 Å, rather than the large separations familiar from dilute electrolyte situations.

The temperature dependence of ion pairs really depends, as suggested in eqn (15), on the entropic changes that arise from the formation of contact pairs. A very simple statistical model has recently been developed[62] to characterize this entropy change, and it suggests [in agreement with most experiments, and contrary to the implication of eqn (13)] that with increasing temperature contact ion pair formation, and salt separation, might in fact be favoured.

This model is based upon the effective cross-linking between polymer strands brought upon by coordination to the alkali cation. Such cross-links reduce the configurational entropy of the polymer chain, and thereby the overall configurational entropy of the system. While this effect will be exaggerated in polymer systems, it will hold even in polar solvents, where strong coordination to cationic metal species will substantially limit the translational entropy, and orientational entropy, available to the solvent itself. This extra entropic contribution will be proportional to the number of such cross-links. If we denote by n_p^f the number of free polymer segments, then this entropic contribution can be written $n_p^f \ln \lambda$, where λ is the contribution to the entropy from each free polymer strand; that is, if the free polymer strands are complexed, and therefore immobilized, the entropy cost will be proportional to $n_p^f \ln \lambda$.

We consider then, the formation of contact ion pairs according to the simplified relation

$$pc + a \rightleftharpoons p + ac. \tag{18}$$

Here we have denoted by p, c and a, respectively, polymer segments, cations and anions. When reaction (18) proceeds to the right, the cation complexed by the polymer strand decomplexes and forms a contact ion pair. The polymer segments and cations can then exist in two states: we denote by n_c^b, n_c^f, n_p^b, respectively, the number of bound (to solvent) cations, the number of free (unsolvated) cations and the number of bound (complexed) polymer segments. Since the total number of segments and ions must be conserved, we have

$$N_p = n_p^f + n_p^b \tag{19}$$

$$N_c = n_c^b + n_c^f \tag{20}$$

where N_b and N_c are, respectively, the number of polymer segments and the number of cations (equal to the number of anions). There will then be three independent stoichiometric variables: N_c and N_p describe the overall make-up of the material, and $n_b = n_c^b = n_p^b$ is the number of bound (complexed) cation–polymer segment pairs.

The energetic component for the free-energy can be defined by setting the zero of energy as the fully uncomplexed material (separated salt and polymer). Then we can write the thermodynamic energy term as

$$-\Delta U_p = \varepsilon n_b \tag{21}$$

where we expect the constant ε to be negative, corresponding to energetic favouring of the formation of the homogeneous polymer salt complex. If ε were in fact positive, the thermodynamic driving force for complexation would not exist, and the complex would never form. Indeed, it was noted early on in studies of PEO materials that for salts of sufficiently high lattice energy, there is not sufficient energy gain on complexation to overcome the cohesive energy of the lattice, and complexes simply never do form.[8,10] If indeed the constant ε is negative, then the energy will be minimal when all cations are complexed, and no contact ion pairs exist.

Using simple combinations, the entropy can be written as

$$S/k = \ln \left\{ \frac{N_p! \, N_c! \, (\lambda)^{n_p^f} N_s^{(n_b + n_c^f + n_p^f)}}{n_p^f! \, n_c^f! \, n_b!} \right\}. \tag{22}$$

Here the factorial quantities simply refer to the division of polymer segments and cations among the two categories free and bound; the λ-dependent term is the extra entropy contribution that arises when the polymer segments are not limited by being complexed to cations. The term proportional to N_s is simply a volume term, that arises from all the different ways to distribute bound pairs, free cation segments and free polymer segments over all the sites in a lattice model of the system. (We have already discussed extensively in Sections 2 and 3 that although no real lattice exists in these systems, an effective lattice can be defined simply as a spatial net in the amorphous material.) This form is reminiscent of the term in the Sackur–Tetrode equation in which the entropy is proportional to the number of particles times the logarithm of the volume per particle: the role of the volume is taken by N_s, the number of sites. In fact, this simple form is valid only in the dilute limit, which we can assume here since the lattice spacing is entirely arbitrary.

Inserting the energy and entropy expressions of eqn (21) and (22) into the thermodynamic form of eqn (14), and minimizing the energy with respect to the constitutive parameter, n_b

$$\partial F/\partial n_b = 0 \tag{23}$$

we obtain the temperature dependence of the number of bound pairs as

$$\exp(\varepsilon/kT) = \frac{N_P N_C - n_b(N_p + N_c) + n_b^2}{\lambda n_b N_S}. \tag{24}$$

This can be solved for n_b itself, yielding:

$$n_b = \tfrac{1}{2}\{N_P + N_C + \lambda \exp(\varepsilon/kT) N_S \pm \sqrt{([N_p + N_C + \lambda \exp(\varepsilon/kT) N_s]^2 - 4N_P N_C)}\}. \tag{25}$$

This is, then, the desired expression for the temperature dependence of the number of ion pairs. Taking derivatives and rearranging, we obtain

$$\frac{\varepsilon \lambda n_b N_s \exp(\varepsilon/kT)}{kT^2} = \left(\frac{\partial n_b}{\partial T}\right)[N_p + N_c - 2n_b + \lambda N_s \exp(\varepsilon/kT)]. \tag{26}$$

Since ε is in fact a negative quantity, and the factor in the second parenthesis on the

right-hand side of eqn (26) must be positive, we have

$$\frac{\partial n_b}{\partial T} < 0. \tag{27}$$

This shows, in agreement with experiment, that the number of cations bound to the polymer, and therefore not tied up in contact ion pairs, decreases with temperature. This is in agreement with the experiments, both those showing the number of contact ion pairs increasing with temperature, and those observing actual segregation of salt with increase in temperature.

The general phenomenon of phase separation with increase in temperature is contrary to naive interpretations of entropy in terms of disorder, since fully dispersed phases would appear to have lower distributional order, and therefore higher distributional entropy, than partially separated phases. On the other hand, precisely such behaviour occurs in liquid mixtures exhibiting lower consolute temperatures;[66] we suggest that perhaps the same sort of energy contributions (configurational entropy decreases with increasing temperature overwhelming simple arguments) may be operative in such thermodynamic systems. In any case, such a model appears entirely reasonable for the polymer salt complex electrolytes, and the simple model contained in eqn (18)–(22) does yield, in agreement with experiment but in contrast to arguments based solely on energy [such as the negative value of ε or the activated form of eqn (13)], that ion pair formation will be increased with rising temperature.

Several obvious limiting cases of eqn (25) for the number of complexed cations can be derived. When ε/kT becomes very large, $n_b = 0$. This is reasonable, since under these conditions there is an energy cost associated with separation of cation and anion, and this energy is unavailable. A second obvious limit is when ε/kT becomes a very large negative number. Under these conditions, n_b is equal to the smaller of N_p and N_c. Once again this is reasonable; at very low temperatures the cations will be entirely complexed if the energy change is negative for complexation. The third obvious limit is the high-temperature limit, where ε/kT vanishes. Here n_b also vanishes, since at very high temperatures only the entropic terms are important, and the entropic terms favour formation of contact pairs according to eqn (18).

This thermodynamic model is simple and reasonable, and gives the correct experimental observations. The important fundamental inputs to the model are the energy difference upon solvation of a contact ion pair, called ε and the entropic penalty involved in complexation associated with the λ term of eqn (22). For any given substance, a generalized Debye–Hückel treatment is available to calculate ε; a number of terms can contribute to λ, including configurational entropy of the polymer, and even vibrational entropy, since vibrational frequencies are higher in complexed solvents (either polymeric or small molecule) than in free solvents. The term involving configurational entropy reduction upon complexation would suggest that at smaller chain lengths the entropic favouring contact ion pair formation, and salt separation, should be reduced. Notice that λ and ε enter the expression for n_b only in the combination $\lambda \exp(\varepsilon/kT)$. Thus $kT \ln \lambda$ is in some sense equivalent to ε, and a change in the value of λ from $\lambda < 1$ to $\lambda > 1$, like a change in ε from negative to positive, favours decomplexation and ion-pair formation; this agrees with the interpretation of λ as an increase factor for the number of configurations available to the free solvent.

5. Comments

Polymer ionic materials are always characterized by the presence of static disorder, arising from the disordered polymer host. Above the glass-transition temperature, they additionally have dynamic disorder, by which we mean that the local environment of any given site will undergo substantial change with time, due to liquid-like local motions.

These two types of disorder have important roles to play in determining charge transport in these polymeric materials.

For temperatures above T_g, we are in the realm of dynamic disorder. Here substantial changes in the local structure arise; this change in the local geometry results in 'renewal' processes, or reinitialization processes, which can modulate either ion transport (in electrolyte materials) or electron transport. Examples of electron transport modulated by dynamic disorder include situations in which ion motion is needed to provide homogeneous doping, as in a large class of doped conductive polymer systems.[67] A second example is provided by redox processes on polymer-modified electrodes; for example, recent work from several groups[68,69] has utilized a network of donor–acceptor relays, or electron-transfer modulators, suspended along a polymer chain leading from a modified electrode to a redox active terminating group, such as a redox enzyme. Under these conditions, the relays along the chain (for example, ferrocene/ferrocenium sites) can provide efficient ET pathways from the redox enzyme to the electrode; the electronic motion is promoted by large-scale motions of the host polymer chain, which permit the sites to become close enough for efficient hopping transport to occur. Thus, very flexible chains, with low glass-transition temperatures, such as are provided by siloxanes, have proven optimal for the design of such relay systems. The role of dynamic disorder in promoting ion transport in polymer electrolytes and polyelectrolytes has been extensively discussed in Sections 2 and 3.

For temperatures below T_g, local ionic sites undergo quasiharmonic vibrations, and no easy diffusion pathways will exist. Electrons can still move, but such motion occurs in largely static structures. Under these conditions, electron transfer over very short distances is ballistic or band-like. Scattering processes can then lead to growth laws, with the conductivity being diffusive over long times [as is clear from fig. 9(b)]. Under these conditions, the temperature dependence arises from the scattering problems, but the diffusive transport is due to the growth law.[50,56]

Thus the role of static and dynamic disorder in promoting charge transport in polymer ionics can vary from situations reminiscent of glass-like substances ($T < T_g$) to those more characteristic of liquids ($T > T_g$). Charge-transport mechanisms in polymer ionics are unusual, and understanding requires models, like the dynamic disorder hopping model discussed in section 2, that differ substantially from those more appropriate for crystalline solids.

Polymer ionics contain charged species, and therefore the issue of Coulombic interactions among charge sites is highly relevant. For doped polymers in the glassy state below T_g, Mott-type transitions[70] are possible. Under these conditions, the ions are not mobile, but electrons or holes can be, if the local screening length becomes comparable to the hopping distance. Analogous ideas are relevant for ion hopping in these materials, if appropriate pathways for long-range ion transfer exist.[71]

In polymer electrolytes and polyelectrolytes, Coulomb interactions are important because they can lead to segregation of charged species either as ion pairs or as more highly charged multiples, and thus impede conductivity. If the lattice energy of the salt, or the inter-ionic Coulombic interaction attraction, is too large no complexes will form, no ions will become free and relatively low conductivity will be observed. If, on the other hand, the solvation energy is strong enough, formation of contact ion pairs will be energetically unfavourable compared to solvent-separated pairs, leading to quasi-free ions and substantial ionic conduction.[59-61] Solvation energy clearly must be larger than the ion-pairing stabilization, as indexed by the lattice energy of the parent salt. If the stabilization energy to separate the contact ion pair is very large, the material will remain a homogeneous conductive substance over broad temperature ranges. If, on the other hand, the stabilization energy is smaller, entropic effects can lead to instability of the separated pair compared to contact ion pairs, and to the formation of contact ion pairs (with concomitant reduction in the number of charge carriers) with increasing

temperature. Such a situation can be described by a quasi-thermodynamic model, as discussed in Section 4. The overall temperature dependence, then, of the mobility and the concentration terms will differ: the mobility will increase with temperature according to the usual VTF, but the number of free carriers may decrease with temperature due to ion-pair formation at higher thermal energies.

For very low concentrations of ions, the inverse Debye length will be small, and a simple analytic extension of Debye-Hückel theory can be used to estimate the energy involved in separating charged pairs.[62] For the concentrations appropriate for most polymer electrolyte systems, however, the inverse screening lengths are quite large (of the order of 1 bohr^{-1}), and the analytic treatment (involving expansion in the smallness parameter proportional to inverse temperature)[64] is no longer valid. Under these conditions the energy of solvation stabilization must be calculated numerically. The dominant concentration effect for many systems will come from raising the glass-transition temperature due to effective cross-linking of polymer strands arising from ion complexation; this decrease in mobility dominates the stoichiometry dependence of conduction in most regimes.

Perhaps the most interesting theoretical insight arising from the models discussed here is that there are significant commonalities in the charge transport processes due to ionic and electronic motion in polymer ionics. The effects of the dynamical events and the growth law as well as Coulomb interactions are similar in both sorts of materials. The dynamic and static disorder of the polymers is the dominant effect on all dynamical processes, including charge transport. In this sense, the polymer ionic materials offer an interesting continuum of behaviour, ranging from liquid-like transport in the high-temperature regime (where dynamic motions of the solvent are involved in the charge transport) to glass-like, hopping behaviour for temperatures below the glass-transition temperature.

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