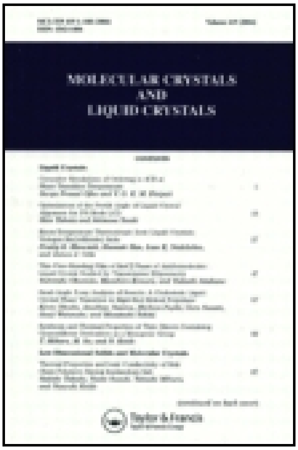

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Charge Carrier Mobility in Polymer Materials: Mechanisms in Polymer Electrolytes, and Relationships to Electronic Conductors

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Charge Carrier Mobility in Polymer Materials: Mechanisms in Polymer Electrolytes, and Relationships to Electronic Conductors

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Generalized renewal (or continuous-time random walk) models provide a systematic way to describe the dependence of conductivity in polymer systems upon the dynamical motions of the host material. For polymer electrolytes, dynamic disorder hopping models, or dynamic percolation models, provide an attractive kinetic description of the transport. In this picture, the mobility of an (assumed independent) ionic carrier is proportional to the inverse mean renewal time, or structural relaxation time, of the host material. Since structural relaxation times generally display WLF type behavior, so does the ionic conductivity in polymer electrolytes. In electronically conductive redox polymers, the mobility is determined by a hopping process, and should to lowest order be independent of microscopic renewal and relaxation times of the host material. In band type electronically conductive polymers, the renewal time can be identified with the scattering time, and more rapid renewal results in decreased carrier mobilities.

Some formal results, and interpretations of ionic conductivity in polymer electrolytes, are stressed.

INTRODUCTION

While polymers have traditionally been of major interest as bulk structural materials, within the last three decades important applications of electroactive polymers have been developed in many laboratories.[1] Such electroactive polymers constitute the most exciting current areas of polymer science, and form the basis of most of the papers at this conference. Although the majority of interest is centered on electronically conductive polymers,[2] ionically conductive polymers form an interesting set of materials, with important promise for applications in the area of solid electrolytes and solid electrodes, as well as in sensor and electrolyzer

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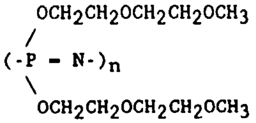
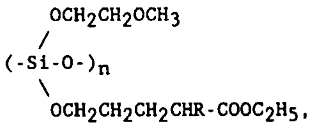
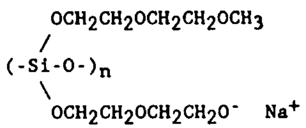
applications. Intrinsically, ionically conducting polymers are of interest from the point of view of ionic motion in an immobile solvent[3]: because of their large molecular weight, the polymeric hosts are strongly entangled, and do not exhibit real translational diffusion at any reasonable rate.

In the polymer electrolytes, first described by Wright in the early 1970's,[4] ions move within polymeric hosts. The ionic carriers, compared to electrons, are massive; they strongly polarize the host, and require motions of the polymer structure itself to become mobile. Most commonly, polymer electrolytes are prepared simply by making a complex between a uni-univalent salt, such as $LiCF_3SO_3$, and an amorphous, pure, high molecular weight, polymeric host containing Lewis base sites. Typical host polymers include those listed in Table I. The thermodynamic driving force for the formation of the complex is the complexation of the cation by the Lewis base groups on the polymer main chain or side chain.[5] In the design of polymer electrolytes, mechanistic arguments (discussed in Section II) led to the early realization that the most highly conductive polymer electrolytes tend to be those in which the main chain or side chain segmental motions occur most easily, which occurs in materials with low glass transition temperatures.[6]

Polyelectrolytes differ from polymer electrolytes in that charge carriers of one sign (either + or −) are localized in groups covalently bonded to the backbone. Typical polyelectrolytes are also listed in Table I; they have been less extensively investigated than the polymer electrolytes, but if low enough glass transition tem-

TABLE I

Typical host polymers for polymer electrolytes or polyelectrolytes

	(Name)
$(-CH_2-CH_2-O-)_n$	PEO
$(-CHCH_3-CH_2-O-)_n$	PPO
 $(-\overset{OCH_2CH_2OCH_2CH_2OCH_3}{\underset{OCH_2CH_2OCH_2CH_2OCH_3}{P}}=N-)_n$	MEEP
 $(-\overset{OCH_2CH_2OCH_3}{\underset{OCH_2CH_2CH_2CHR-COOC_2H_5}{Si}}-O-)_n$,	R = p-nitrothiophenoxy
 $(-\overset{OCH_2CH_2OCH_2CH_2OCH_3}{\underset{OCH_2CH_2OCH_2CH_2O^- \quad Na^+}{Si}}-O-)_n$	

peratures can be achieved (either intrinsically or by plasticizing with a small molecular weight oligomer), then the polyelectrolytes can exhibit relatively high ionic conductivities with unit transference number for the mobile ion.[7]

Polymer electrolytes can best be envisioned in terms of ionic motion in a macroscopically immobile solvent. Like ionic motion in ordinary solids, one might then expect the Walden relationship[8]

$$D\eta \sim \text{constant} \tag{1}$$

to hold, where D is the diffusion coefficient and η is an appropriate viscosity. The Walden relation has indeed been found to hold relatively well for polymer electrolytes, in sharp distinction to electronically conductive, band-type molecular metals such as TTF-TCNQ, or nickel phthalocyanine iodide.

Electronically conductive polymers, especially those based on such band-type materials as polyacetylene, polythiophene, poly(paraphenylene vinylene), polypyrrole, or poly(phthalocyaninate Si-O-), are neither expected nor observed to obey the Walden relationship. In these materials, the conductivity seems to be limited largely by defects or impurities or chain breaks, which must be overcome by either activation or tunneling. Redox polymers, on the other hand,[9] are based on hopping-type electronic conductivity, and should show temperature dependence arising essentially from activation. One fascinating issue then is the mechanistic distinction among these classes of transport, and how all three of these classes can be explained as particular limits of a general behavior. We believe that such an interpretation can indeed be derived, based on the general idea of reinitialization or renewal. Section II of this paper discusses the mobility mechanism in the polymer electrolytes. It stresses the mobility mechanism of individual ions, rather than conductivity, since the conductivity is complicated by the presence of ion pairing and Coulombic interactions among ionic carriers.[3,10] It demonstrates the observed behavior of the mobility as a function of temperature, and suggests interpretations in terms both of the quasi-thermodynamic picture based on free volume, and a microscopic model based on dynamic disorder (or dynamic percolation).

Section III discusses, in a conceptual manner, a unifying picture for charge mobility motion in electroactive polymers. Physical considerations suggest that, for any macroscopic measurement (low-frequency measurement), the existence of dissipative processes implies the validity of Ohm's Law, as well as a linear relationship between mean-square displacement and total elapsed time, corresponding to diffusive behavior. The charge transport can then be understood in terms of an average diffusion coefficient over long times, and if particular sorts of growth-law dynamics are obeyed,[11,12] one can obtain a general form for the diffusion coefficient in terms of a mean-square displacement within a given renewal (or waiting time) interval and the mean rate of renewal. The three limits of ballistic (i.e., quasi-free electron), diffusive, and spatially-limited (i.e., below the static percolation threshold) behavior then correspond to particular time dependences of the mean-squared displacement within a given renewal interval. Relationships to the temperature dependence of the charge transport, and generalizations to frequency dependence, are suggested.

II. POLYMER SALT COMPLEX ELECTROLYTES AND POLYELECTROLYTES: MOBILITY IN IMMOBILE SOLVENT HOSTS

Polymer salt complex electrolytes, as usually prepared, exhibit essentially no electronic conductivity.[3,5,13] Charge transport is divided between cation, anion, possible higher multiplet motions, with the exact balance being determined in a complicated way by interionic interactions and intrinsic mobility. For simplicity, we focus here on the dominant effect, which is simply the mobility of single ion carriers.

The initial mechanistic notion that ionic motion in polymer electrolytes occurred by hopping of ions within helical regions of the host probably arose because the first materials to be studied were semicrystalline polymers based on PEO. Subsequent investigations using NMR[14] and a number of other techniques[15] have established beyond doubt that the ionic conduction occurs in the amorphous elastomeric continuum regions of the polymer host. More importantly, such investigations have also shown a very close relationship between mobility, or conductivity, and the intrinsic mechanical properties of the polymer.

Typically, the conductivity when plotted in Arrhenius coordinates shows a curved behavior characteristic of mechanical or electrical relaxation properties of polymers themselves (and also characteristic of transport in liquid solutions). The characteristic curvature in such plots as Figure 1, is not entirely obvious over short temperature regimes, but in most polymer electrolytes over a long enough temperature range such curvature is manifest. Arithmetically, behavior of this kind can be described by

$$\mu = \mu_0 e^{-A/(T-T_0)} \tag{2}$$

where μ is the mobility, μ_0 is a characteristic prefactor, T_0 is a fitted temperature (often roughly 50° degrees below the glass transition temperature) and A is a pseudo-activation energy term. The temperature dependence in (2) is equivalent to that of the so-called WLF behavior:

$$-\log a_T = \frac{c_1(T - T_r)}{c_2 + (T - T_r)}, \tag{3}$$

where c_1 and c_2 are arbitrary constants, and T_r is a reference temperature. Furthermore, a_T, normally called the shift factor, is the ratio of the given mechanical property at temperature T to the same mechanical property at temperature T_r.[16]

The relationship between mechanical shift factors, or relaxation times, and mobilities or conductivities is very consistent. Typical data are shown in Figure 2 for observations on crosslinked networks based on polyethylene oxide.[17] This close relationship between mechanical properties for relaxation and ionic conductivity indicates clearly that the ionic motion is indeed modulated by the dynamics of the polymer host. A myriad of other measurements, ranging from strong correlations between ionic conductivity and glass transition temperature through dynamics of cocrystallization[8] to variation of conductivity with polymer molecular weight, again show clearly that the conductivity is limited by solvent renewals or relaxation times.

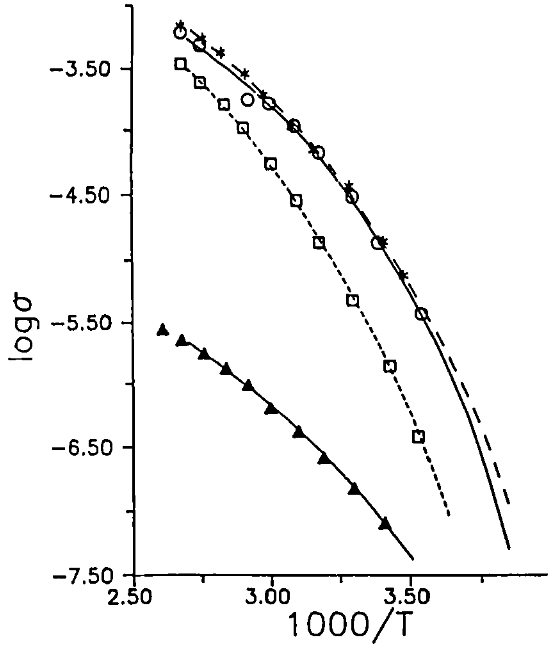


FIGURE 1 Temperature dependent conductivity for polymer-salt complexes of amorphous PEO. O, $PEO_{25}NaCF_3SO_3$; *, $PEO_{25}NaSCN$; , $PEO_8NaCF_3SO_3$; Δ, $PEO_{25}NaCH_3SO_3$. Lines are data fitted to the VTF equation. [K. E. Doan, B. J. Heyen, M. A. Ratner and D. F. Shriver, in press.]

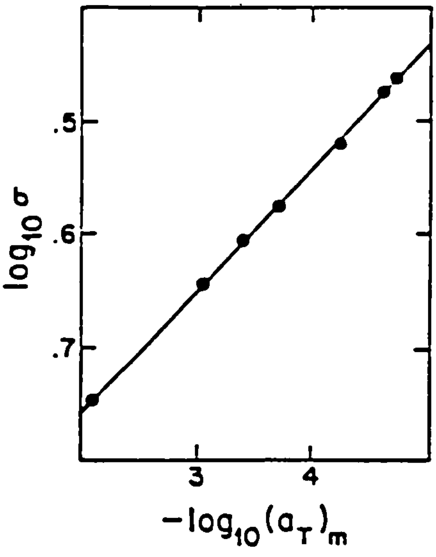


FIGURE 2 Correlation between the conductivity and the shift factor a_T for PEO networks with low concentrations of salt (less than one ion per oxygen). From Reference 17.

The simplest mechanistic explanation is given in terms of free volume theory.[19] According to the free volume model, the rate of polymer motion, and therefore the ionic conductivity that it controls, is governed by the requirement that there be sufficient free volume for the polymer segments to move. The mobility will then be given by

$$\mu \sim e^{-V^*/V_f(T)}, \tag{4}$$

where V* is a minimum free volume, and $V_f(T)$ is the free volume at temperature T. Expansion of the denominator of the exponential around T_0, the temperature at which the free volume vanishes, gives

$$\mu \sim \exp\left[-A/(T - T_0)\right] \tag{5}$$

with the identification of A as:

$$A = \frac{V^*}{\left(\frac{\partial V_f}{\partial T}\right)\Big|_{T_0}} \tag{6}$$

thus the pseudo-activation energy A is given as an inverse expansivity; this leads one to suspect that the pseudo activation energy should be largely determined by the expansivity of the polymer host, independent of the ion or any energy factor; this rough constancy has in fact been observed for many materials.[20]

The free volume model, while very attractive conceptually, does have some difficulties. There are some situations in which the dependence of conductivity on pressure does not in fact follow the free volume model. More importantly, the microscopic interpretation for the free volume model is not at all clear, since neither V*, nor the free volume itself, is rigorously defined. Also, the free volume picture is a macroscopic one; it does not take into account the microscopic structure of the material. Accordingly, a more microscopic model has been developed to describe mobility in polymer electrolytes. This model,[11,12,21-28] which has been called dynamic disorder hopping or dynamic percolation theory, is closely related to the continuous time random walk model of Scher and Lax,[29] originally developed to discuss carrier transport via hopping between impurities in semiconductors. According to this model, as applied to polymer electrolytes, the motion of the ion from one site to another is governed by three factors. First, there is a static probability p that the motion between two sites be allowed. Second, there is an intrinsic jumping rate w between two sites when such a transition is indeed allowed. Finally, there is a renewal rate $\lambda = \bar{\tau}_{ren}^{-1}$, which describes the rate at which the assignment of a given transition between two sites as either allowed or unallowed changes; the renewal time $\bar{\tau}_{ren}$ is the average time it takes for one renewal to occur after a previous renewal.

In this dynamic disorder model, then, the probability $P_i(t)$ of observing an ion on site i is given by the master equation

$$P_i(t) = \sum_j (W_{j\to i}(t)P_j(t) - W_{i\to j}(t)P_i(t)), \tag{7}$$

where the sum runs over all other sites $j \neq i$, and W_{ji} is the probability per time unit of jumping from j to i. For the special case of a dynamic percolation (rather than dynamic disorder) model, the jump rates are distributed according to:

$$W_{i\to j}(t) = \begin{cases} w & \text{probability } p \\ 0 & \text{probability } 1-p \end{cases} \tag{8}$$

Equations (7) and (8) themselves define simple percolation models; the dynamic disorder is accounted for by allowing the reassignment of any particular $W_{i\to j}$ as unallowed or allowed to change in time, over a characteristic time $\bar{\tau}_{ren}$. This renewal time model has been extensively investigated and applied to the behavior of polymer electrolytes.[11,21-28]

The focus of attention here is on several particularly striking predictions of the dynamic percolation model. 1) In dimensionality d, it can generally be shown that the diffusion coefficient, whenever the carriers do not interact, is given by

$$D = (2d)^{-1}\langle \bar{r^2}\rangle_0/\bar{\tau}_{ren} \tag{9}$$

Here $\bar{\tau}_{ren}$ is the mean renewal time, and $\langle \bar{r^2}\rangle_0$ indicates the mean-squared displacement attained within a given renewal interval (for an ensemble of non-renewing systems) averaged over the distribution of renewal times. This result holds for the dynamic percolation model, for dynamic disorder hopping models, and for a number of closely related model situations.[12] In polymer electrolytes in particular, one has the general thermal behavior

$$\bar{\tau}_{ren} = \bar{\tau}_0 \exp\,[A/(T - T_0)]. \tag{10}$$

When this is substituted into (9), one obtains the observed WLF type behavior of Equation (5).

2) Equation (9) and its consequences were originally derived from behavior on a lattice of percolating type. It has since been shown that the result applies also when the motion occurs in a continuum rather than on a lattice, and when the renewal events are dynamically correlated in time.[12] On the other hand, when the renewal events are correlated in space, one observes very different behavior.[27,30] For example, the simple dynamic percolation model of Equations (7) and (8), with renewal occurring randomly subject only to the probability constraint that a fraction p of bonds be available, always yields diffusive behavior in the long-time limit: that is, for times long compared to the mean renewal time, the mean-squared displacement is linear in time, independent of the value of p.[24] In the limit where renewal time goes to infinity, and one has static percolation, the observation time cannot be long compared to the renewal time, and one observes the usual behavior of ordinary percolation models;[31] for this case below the percolation threshold p_{th},

with $p < p_{th}$, there is no connected cluster of sites, and diffusion is not observed. While there is no percolation threshold in the simple dynamic percolation model, when the hopping rate assignments are correlated between successive renewal intervals such thresholds can in fact occur.[27,30,32] For example, Figure 3 shows that calculated renewal jump rate as a function of available sites p for a situation in which renewal occurs only by bond exchange; that is, in this two-dimensional square net, the assignment of any bond status as available or unavailable alters only by random interchanges of status with a nearest neighbor bond. This correlated renewal results in the appearance of a second percolation threshold at p less than the static percolation threshold. Intuitively, such a result makes sense; the ion must now wait longer times for a pathway to become available, and eventually, for a small enough number of available bonds, diffusive behavior may become impossible.

3) In general, one can show[24,33] that an analytic continuation rule of the form

$$D(\omega, \lambda) = D(0, \omega - i\lambda) \tag{11}$$

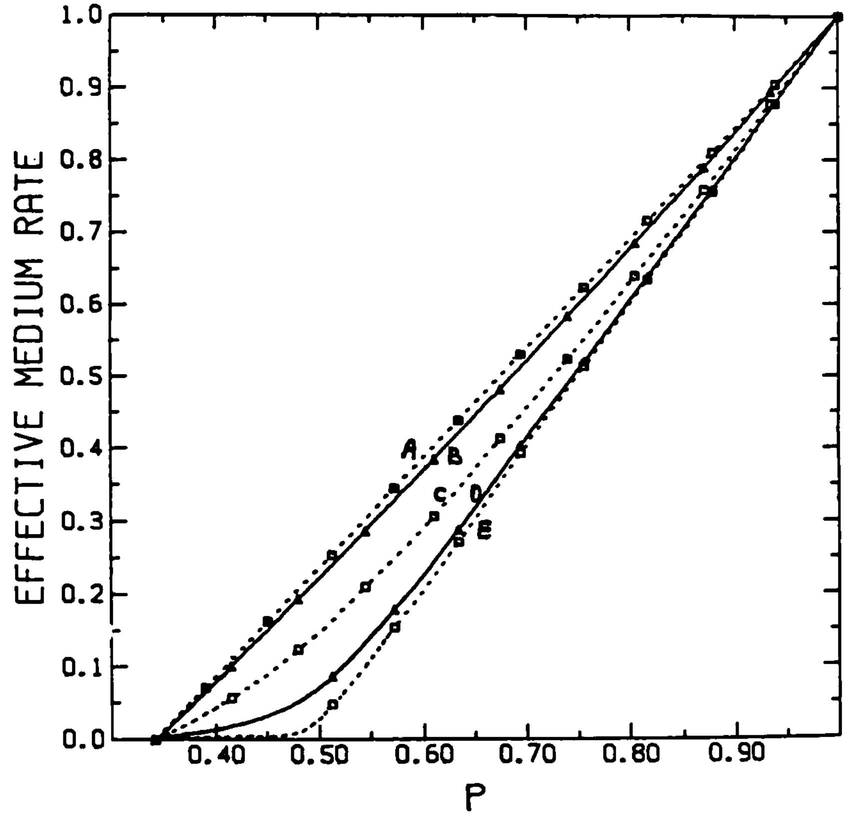


FIGURE 3 Effective-medium carrier hopping rate in a percolation model when host renewal occurs by pairwise interchange of allowed and forbidden bonds both connected to the same site, calculated for different rates of bond interchange. From Reference 30.

holds, where $D(\omega, \lambda)$ is the diffusion coefficient at frequency ω for mean renewal rate λ, and $D(0, \omega - i\lambda)$ indicates the diffusion coefficient in a static percolating lattice computed at the complex frequency $\omega - i\lambda$. This analytic continuation rule, which can also be proved to hold in more general renewal problems,[12,33,34] permits calculation for situations with dynamic renewal from known analytical results for hopping in the static percolating lattice.

The important issue about the mobility in polymer electrolytes is that it is almost entirely determined by motions of the host polymer segments: lower glass transition temperatures facilitate such motions, thus accelerating the rate of ion transport and increasing the conductivity. Quasimacroscopically, this can be thought of as arising because the largest free volume is associated with hosts of the lowest glass transition temperature. From the point of view of renewal theory, the renewal time corresponds to a mean structural relaxation time of the polymer; the faster structural relaxation occurs, the more rapidly ions can move from site to site.

An interesting comparison can be drawn with electronic dynamics in polymeric materials; there the concept of renewal is not a simple one, but an analogous temporal concept, corresponding in some senses to a scattering time, is of physical importance and under certain circumstances determines the conduction behavior.

III. RENEWAL DYNAMICS, GROWTH LAWS, AND TRANSPORT MECHANISMS FOR CHARGE MOBILITY IN POLYMERS

The two most striking results of the dynamic percolation model, based on the master equations (7) and (8), with a random renewal, or reassignment of bond probabilities, are given by Equations (9) and (11). Using general formulation of linear response theory, it can more generally be shown[12] that Equations (9) and (11) will hold for any process that obeys the growth law schematically shown in Figures 4 and 5. The requirement is simply that, on the average, after each random reinitialization event, the dynamics recommences, with mean-square carrier displacement in the new interval growing in the same way as in the previous interval. Under the general conditions of the growth laws illustrated in Figures 4 and 5, Equations (9) and (11) remain applicable.

This leads to important expectations for the diffusion coefficient, and therefore the conductivity, in particular situations. 1) If transport within each interval is ballistic or free-particle-like, such that

$$<\overline{r^2}>_{\tau_{ren}} \sim \bar{\tau}^2_{ren}, \qquad (12)$$

then Equation (9) yields

$$D \sim (2d)^{-1}\bar{\tau}_{ren}. \qquad (13)$$

In this case one can associate the renewal time with the scattering time, and (13) is then reminiscent of Drude behavior: for a nearly free electron carrier, such as one finds in good crystalline molecular metals, the conductivity goes like the scat-

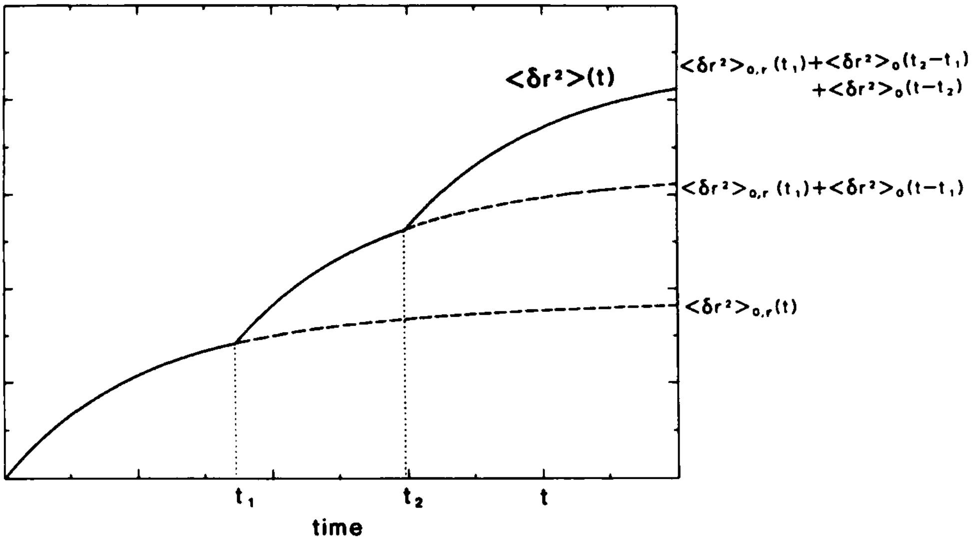


FIGURE 4 Mean-square displacement for renewal events occurring at a specified sequence of times. From Reference 12.

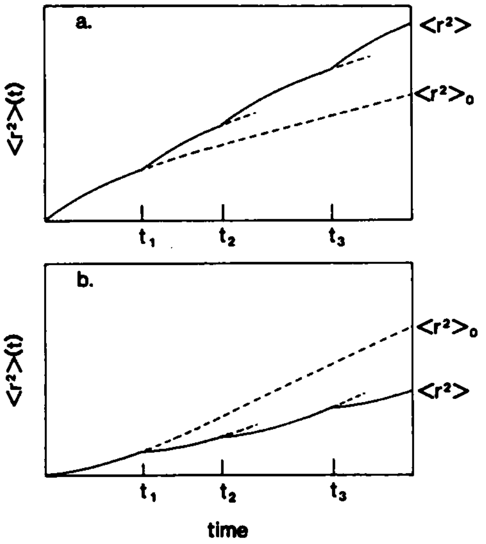


FIGURE 5 Effect of renewal at times t_1, t_2, . . . (a) on a concave-down and (b) on a concave-up $<r^2>_0(t)$ dependence, corresponding respectively to hopping-like and coherent-like transport. From References 11 and 12.

tering time, and the longer the time between scattering events the higher the conductivity will be. In this case the scattering, due to phonon interruption of the phase of the electronic carrier, replaces the renewal as the important reinitialization time.

2) If within each renewal interval the carrier behaves diffusively so that

$$<\overline{r^2}>_0 \sim \bar{\tau}_{ren}, \qquad (14)$$

substitution into Equation (9) yields

$$D \sim (2d)^{-1} \cdot \text{const.} \qquad (15)$$

Under these conditions, the renewal rate does not affect the diffusion in any way. This occurs for hopping conductivity in situations above the static percolation threshold, where within a renewal interval the mean-square displacement has not yet sensed the finite bounds of an isolated cluster.[11] Hopping type conductive polymers, in which the mean free path is of the order of less than a lattice spacing, are expected to fall into this regime. Then the temperature dependence of the conductivity will be due to activation of the hopping rate itself, not to any renewal process change in the behavior of the hopping conductors.

3) Below the static percolation threshold, where

$$<x^2>_{\tau_{ren}} \sim a^2, \qquad (16)$$

substitution in the general form (9) yields

$$D \sim (2d)^{-1}a^2/\bar{\tau}_{ren}. \qquad (17)$$

In this case, within each renewal interval the carrier typically is limited to a region of characteristic dimension a (the typical size of a connected cluster of sites). Then each renewal permits the carrier to start over, and Equation (17) shows that the diffusion rate is simply proportional to the renewal rate. This is the situation for polymer electrolytes in all cases, and might also be the situation in redox electronic conductivity, if either the relative geometries of neighboring sites must change in different redox states, or if substantial excursions are necessary to lead to degenerate (coincidence event)[35,36] geometries of the two neighboring sites between which electron hopping occurs.

The temperature dependence of the conduction process follows, fairly simply, from its dependence upon renewal time. For a nearly free electron or ballistic transport, the conductivity is expected to decrease with increase in temperature, as the relaxation or renewal time or scattering time becomes shorter, and therefore D decreases according to Equation (13). For simple diffusion, the temperature dependence should probably be activated since the constant in Equation (15) includes the hopping rate w, which is itself activated. For situations in which conduction occurs below the static percolation threshold, the rate of diffusion will be proportional to the rate of renewal, and this is expected to follow (in most cases) free volume type behavior rather than simple Arrhenius activation.

The considerations suggested here a represented at greater length elsewhere.[11,12,21–28,37] It is possible to show that these results hold not only under dc conditions, but up to the frequency ω_{max} such that

$$\omega_{max}\, \bar{\tau}_{ren} \gtrsim \pi. \tag{18}$$

In particular, an $<r^2>_0(t)$ vs. t dependence having positive $d^2<r^2>_0(t)/dt^2$ (corresponding, for example, to the free-particle-like case 1) implies a real part of $D(\omega)$ that decreases with renewal rate and hence with temperature at fixed ω (provided Equation (18) is satisfied), while the opposite limit of $d^2<r^2>_0(t)/dt^2$ negative (corresponding, for example, to case 3) similarly yields a Re $D(\omega)$ that increases with temperature. Intuitively, as long as the frequency-dependent experimental probe measures the system on a time longer than the renewal time, the same behavior at the finite frequency of the probe should be seen as at zero frequency.

This paper has tried to make two points. First, ionic mobility in polymer electrolytes and polyelectrolytes can be understood in terms of a dynamic disorder model, in which the motion of the ion is controlled by the dynamics of the polymer host, and ion motion cannot occur until facilitated by segmental motion of the polymeric host. This leads to typical curved Arrhenius plots for conductivity, and to a suggestion (an important one experimentally) that decreasing a glass transition temperature as much as possible yields maximal ionic mobility. The second point is that the notions of reinitialization time, and growth-law behavior of the mean-square displacement, imply generally that ionic transport, hopping transport, nearly free electron transport, and transport on a percolation lattice both above and below threshold can be understood using the same general formalism. Applications of this formalism, including frequency and temperature dependence, and its comparison with particular experiments, can be found in the literature. Further testing of this concept, in particular in the rich new area of electroactive polymers, should substantially increase our insight into precisely what it is that facilitates or hinders charge carrier motion in electroactive polymers.

Acknowledgments

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