Dynamically disordered hopping, glass transition, and polymer electrolytes

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The central parameter of the dynamically disordered hopping (DDH) model, the renewal time, is correlated with the characteristic time constant of the glass transition relaxation in polymer–salt complexes. With this identification, the frequency-dependent permittivity of these materials can be quite adequately described. In particular, experimental evidence for a high-frequency relaxation predicted by the DDH model is presented. This relaxation corresponds to the polarization of ions in their local percolation clusters as they wait for a renewal event to occur. In light of information on the renewal time, the direct current properties of polymer–salt complexes are used to calculate the size of these local clusters. These calculations suggest that the motion of an ion in the absence of renewal (polymer segmental motion) corresponds to displacements within its local coordination "cage" rather than hopping between several available coordination sites. © *1995 American Institute of Physics.*

I. INTRODUCTION

The dynamic bond percolation (DBP) or more general dynamically disordered hopping (DDH) models were proposed as microscopic theories describing transport processes characterized by two times, one describing local carrier hopping and the second characterizing renewal or reorganization of the host. Initial application of the model was to conduction in ionic solutions of salts in polar polymers.[1–6] In these so-called polymer–salt complexes (PSC), long-range ionic diffusion only occurs in the presence of the local segmental motions of the polymer host.[7–11] As exemplified by the Vogel–Tammann–Fulcher[12–24] (VTF) form of the temperature-dependent conductivity, $\sigma(T)$,

$$\sigma(T) = \sigma_0 \exp(-B'/k_B(T-T_0)) \tag{1}$$

the faster these rearrangements, the greater the observed conductivity. Here, T_0 is an "equilibrium" glass transition temperature, B' is a pseudoactivation energy, k_B is Boltzmann's constant, and σ_0 is weakly temperature-dependent prefactor.

Equation (1) can be essentially recovered from considerations of configurational entropy[15,16] or free volume.[17,18] Although these models were originally used to describe the viscoelastic properties of polymers, their success with regard to ion transport in PSC further highlights the importance of the polymer host's mobility in controlling carrier diffusion. In both of these models, the glass transition temperature, T_g, which is the temperature above which there exists large scale segmental motion and the polymer becomes rubbery rather than glassy, plays a central role. The introduction of an "equilibrium" glass transition temperature, T_0, stems from the kinetic nature of T_g. Below T_0, the free volume or excess configurational entropy of a polymer is assumed to vanish. As the temperature rises above T_0, the motion of ions, polymer segments, or other species is facilitated by the creation of local empty space, "free volume," or from the presence of excess configurational entropy. Accordingly, the pseudoactivation energy parameter B' is related to the critical volume for displacement within the free volume model,[17,18] and to the energy barrier for the rotational motion of polymer segments in the configurational entropy model.[15,16]

Although the configurational entropy and free volume models have had some success with regard to PSC, they have many shortcomings.[8,19–22] One of their principal drawbacks is that they are not microscopic theories based on appropriate equations of motion. By contrast, the DDH model is a microscopic transport model, allowing for a broader range of observations, such as the frequency-dependent conductivity,[23–25] to be described and for microscopic mechanistic details to be ascertained.

Within the DDH framework, polymer electrolytes are viewed in terms of a generalized percolation picture in which the available percolation channels are continually redefined according to some renewal rate.[1–6] Thus, at any given instant an ion may be able to execute some local motion but be blocked from long-range diffusion. Due to the host's reorganization, however, the local environment of a charge carrier is continually changing, allowing long range mobility in a step-wise fashion. Although the DDH model contains many of the key features that are important in PSC, its application to these materials has been somewhat limited.[4,5,23–25] Druger *et al.* have used DDH to describe both the temperature and frequency dependence of the dc conductivity of PSC in various limits. They have shown that this model can describe the frequency-dependent permittivity of PSC[24] and recover the characteristic VTF form for $\sigma(T)$.[4,5] In these treatments, however, experimental knowledge, or even identification, of the characteristic average renewal time, $\bar{\tau}_R = 1/\bar{\lambda}$ (with $\bar{\lambda}$ a characteristic average renewal rate), was unavailable. The lack of a direct link between the central parameter of the DDH model and a measurable property of PSC has somewhat limited the utility of the model.

In the next section, we propose an experimental measure for the DDH renewal time, namely, the time constant for a particular polymer reorganizational mode as probed by dielectric relaxation spectroscopy. With this assignment, a

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more detailed analysis of PSC based on the DDH model is possible and richer mechanistic information can be ascertained. It is unclear, for example, the extent to which an ion can move in the absence of a renewal event; this motion may correspond to the vibrational displacement of an ion within its coordination environment or perhaps to hopping between several available coordination sites. The nature of the local displacement of an ion is discussed in Sec. IV after we revisit the frequency-dependent dielectric permittivity in Sec. III to further assess the validity of DDH to PSC in light of new knowledge about τ_R.

II. THE RENEWAL TIME

Consider a static nonrenewing system in which the mean-squared displacement of a charge carrier follows some functional form $\langle \{\mathbf{r}(t) - \mathbf{r}(0)\}^2 \rangle_0 = g(t)$. In the DDH framework, dynamic disorder is introduced into such a system via renewal events that occur at intervals of average length $\bar{\tau}_R$; to simplify notation, we will write τ_r, but it is to be remembered that this denotes an average renewal time. These events serve to reinitialize carrier motion, so that the mean-squared displacement in the renewing case, $\langle \{\mathbf{r}(t) - \mathbf{r}(0)\}^2 \rangle$, can be written as follows:

$$\langle \{\mathbf{r}(t) - \mathbf{r}(0)\}^2 \rangle = g(t - t_{N_r(t)}) + \sum_{i=1}^{N_r(t)} g(t_i - t_{i-1}), \qquad (2)$$

where $N_r(t)$ is the number of renewal events occurring before time t, t_i is the time at which the ith renewal occurs, and $t_0 = 0$. A growth law of this form serves the basis for the development of the DDH model, a central feature of which is the following relation:

$$D(\omega) = D_0(\omega - i\lambda), \qquad (3)$$

where $D(\omega)$ is the frequency-dependent tracer diffusion coefficient in the renewing system, $D_0(\omega)$ is the frequency-dependent diffusion coefficient in the corresponding static system, $i = (-1)^{1/2}$, and $\lambda = 1/\tau_R$ is the renewal rate in the case of a single time scale for renewal or the average rate in the case of a Poisson distribution of renewal rates. Application of the DDH model to polymer electrolytes depends on how well these systems obey the growth law of Eq. (2), knowledge of $g(t)$, and on a physical interpretation of the renewal time. The latter is the focus of the present section.

As stated above, the renewal time corresponds to an event that restarts carrier motion. In polymer electrolytes, the host polymer undergoes many different types of reorganization that can be probed by techniques such as dielectrical and mechanical relaxation,[26–29] and Brillouin scattering.[30,31] An unequivocal assignment of one of these reorganizational modes to the process of renewal within the DDH framework is difficult. A good deal of indirect evidence, however, suggests that the time scale for the large scale segmental motions associated with the glass transition corresponds to the DDH renewal time, τ_R.[29,32,33] In polar polymers, as are typical host materials for polymer electrolytes, this mode is dielectrically active. Since various workers use differing nomenclature with regard to this mode, we will refer to it as the "glass transition" relaxation (GTR) instead of assigning a particular greek letter as is the convention [in poly(propylene oxide), for instance, it is normally referred to as the α relaxation].

Several workers have noted the correlation between the conductivity, σ, of PPO salt complexes and the characteristic frequency of the dielectric GTR, ω_D^{GTR}, in the corresponding pure host polymer.[29,32,33] The temperature-dependent response of both of these quantities follows the empirical VTF equation:

$$f(T) = A \exp\left(- \frac{B}{(T - T_0)} \right), \qquad (4)$$

where A, B, and T_0 are fitting parameters. Empirically, it is noted that T_0 is related to the glass transition of the material by

$$T_0 = T_g - c, \qquad (5)$$

where $c = 25$–45 K. Typically, fits of the VTF equation for the conductivity of PSC and dielectric data on $\omega_D^{GTR} = (\tau_D^{GTR})^{-1}$ for the GTR of the corresponding host polymer result in similar values of the parameter B.[29,32,33] Furthermore, pressure-dependent studies of these quantities have also revealed similar pseudoactivation volumes.[32,34] Due to the strong correlation between these processes, we assume for this treatment:

$$\tau_R = \tau_D^{GTR}. \qquad (6)$$

It should be noted, however, that τ_R is likely to reflect a microscopic process whereas τ_D^{GTR} is characteristic of a bulk response. The relationship between microscopic and macroscopic orientational relaxation times has been the subject of a good deal of literature.[35–41] For simplicity, however, we shall assume Eq. (6) for this treatment. In addition, the processes giving rise to the observed GTR typically cannot be described in terms of a simple Debye model[42] characterized by single relaxation time.[26,28,43–45] τ_D^{GTR} is normally extracted using a variety of empirical expressions or from assuming a distribution of Debye relaxations in which case an average time constant is obtained.[43–45]

As mentioned above, other techniques besides dielectric spectroscopy can be used to probe polymeric motion. The strong correlation between orientational time constants as monitored by these techniques, however, has not been as clearly demonstrated as in dielectric spectroscopy. It has been suggested that Brillouin scattering, for example, monitors a process involving shorter polymer segments than dielectric relaxation and yields differing activation parameters.[30] Shear viscosity measurements are not thought to probe local segmental motions as evidenced by large molecular weight dependencies. This also accounts for the observed breakdown of Walden's rule[46,47] as recently discussed by Mendolia and Farrington.[46] Procedures to extrapolate the "local" viscosity from shear viscosity data have been proposed,[48] and the connection between bulk shear viscosity and τ_R in low molecular weight polyethers has been mentioned by Albinsson *et al.*[47] Nonetheless, in light of the well demonstrated correspondence between the dielectric and

conductivity data, we shall focus on the dielectric time constant for the GTR as probed by dielectric relaxation spectroscopy.

The above discussion focused on the relation between processes in the pure polymer and the conductivity of the corresponding salt complexes. What is needed, however, is knowledge of τ_D^{GTR} in the salt complex of interest rather than that in the pure host polymer. The presence of dissolved salt results in virtual cross linking that changes the dynamics of polymer chain motion as manifested by significant increases in T_g.[49–51] There is a reasonable amount of dielectric data on salt complexes, but the GTR relaxation is often obscured in these materials due to electrode effects and the dc conduction process.[11,25,29,32–34,48,52–61] The latter makes a significant contribution to the dielectric loss of the material that, in principle, could be subtracted. The utility of this subtraction, however, is somewhat limited.[33,61] As a result, data on τ_D for the GTR is available on only a handful of PSC.

Due to the difficulty in obtaining this data, we propose the following scheme to predict τ_D^{GTR} in PSC based on complementary data for the host polymer and knowledge of T_0 for the salt complex. As mentioned above, the addition of salt results in the formation of virtual crosslinks that effect T_g and hence T_0 and τ_D^{GTR}.[49–51] A simple assumption that can be made is that for the same temperature above the corresponding T_0, τ_D^{GTR} is identical for the host polymer and for its salt complexes, i.e.,

$$\tau_D^{PSC}(T_0^{PSC}+d)=\tau_D^{P}(T_0^{P}+d), \tag{7}$$

or

$$\tau_D^{PSC}(T)=\tau_D^{P}(T_s), \tag{8}$$

where the shifted temperature T_s is defined by $T_s=T-T_0^{PSC}+T_0^{P}$ with the superscripts PSC and P referring to the polymer–salt complex and host polymer respectively and with d a constant. T_0^{PSC} may be approximated from fits of the temperature-dependent conductivity to Eq. (1). Correlations between VTF parameters, however, make this a bit problematic. Alternatively, if thermal analysis data is available and Eq. (5) is assumed to be valid, T_s may be rewritten as $T_s = T - T_g^{PSC} + T_g^{P}$. This relation also has complications owing to the kinetic nature of T_g.

Up to this point, we have not really rationalized Eq. (8). This result follows from the free-volume model if the thermal expansivity of a particular host polymer and PSC based on it are identical. Alternatively, a strictly empirical rationale can be given that stems from the so-called "universality" of the B parameter in Eq. (4) when T_0 is chosen as a particular reference temperature, say in relation to T_g. The roughly universal nature of the B parameter for the temperature dependence of σ_{dc} for PSC based on the same host polymer has been generally accepted.[7] The intimate connection between σ_{dc} and ω_D^{GTR} suggests that relation 8 should also be a reasonable approximation. Specifically with regard to the GTR in a particular polymer and salt complexes based on it, however, this "universality" has not been directly tested. The remainder of the present section addresses this issue.

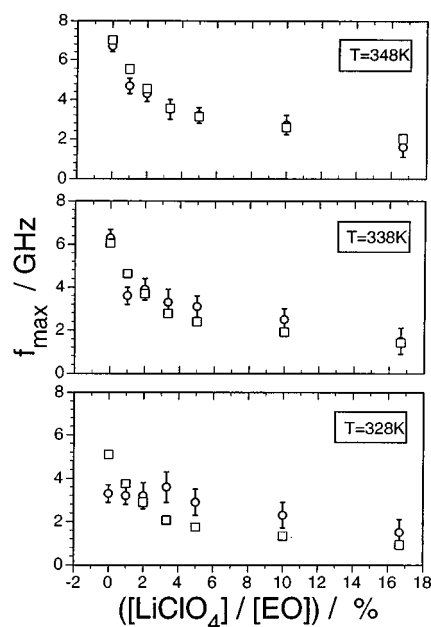Gray *et al.* have performed dielectric relaxation measurements on PEO (Polyox 301 MW$=4\times10^6$) and amor-

FIG. 1. Comparison of the position of the glass transition relaxation in PEO$_n$LiClO$_4$ reported in Ref. 60 (○) with that predicted from this work (□). The concentration is expressed as the moles of LiClO$_4$ per mole of ethylene oxide monomer unit.

phous PEO·LiClO$_4$ salt complexes using time-domain spectroscopy.[60] They were able to resolve the GTR in amorphous PEO–salt complexes over a wide range of stoichiometries. Measurements were taken at only three temperatures making extraction of the VTF parameters for the GTR of the pure PEO studied and values of T_0 for the salt complexes difficult. As a result, a test of Eq. (8) is not possible with this data alone. Other workers have measured τ_D^{GTR} in PEO, but there is some sample dependence. It has been suggested that the observed variations are due to differing molecular weights or perhaps varying degrees of crystallinity.[26,27,62–65] Studies by Porter and Boyd,[63] however, show that the position of the GTR is continuous through melting suggesting that the crystalline regions have little effect on the chain dynamics in the amorphous phase. Another possible explanation of the observed variation may be differing impurity levels. For comparison to the data of Gray *et al.*, we have chosen measurements by Connor *et al.* on Polyox FC118 (M.W. 2.8×10^6).[62] For the various samples of PEO for which $\tau_D^{GTR}(T)$ has been determined, Polyox FC118 has the closest makeup to Polyox 301. These data, however, were taken below the melting temperature of PEO. As a result, comparison of these data to the amorphous samples of Gray *et al.* assumes that the position of the GTR is unaffected by partial crystallinity.

From fits of the Connor *et al.* data on ω_D^{GTR} to the VTF equation, the VTF parameters A and B were extracted. Values of T_0 for the pure polymer and salt complexes were calculated from Eq. (5) ($c=40$ K) using values of T_g estimated from work of Ferloni *et al.*[66] on Polyox 301 complexes with LiClO$_4$. Conductivity measurements on the Ferloni *et al.* samples were in good agreement with those of Gray *et al.* Figure 1 shows the results of Gray *et al.* along

with values calculated according to Eq. (8) using the data of Connor *et al.* and Ferloni *et al.* In general, the agreement is good. This agreement may be somewhat fortuitous, however, since measurements from a variety of sources and on differing materials had to be compiled in performing the analysis. It also appears that the agreement is worse at lower temperatures. As the temperature approaches T_0, the values calculated become very sensitive to T_0 so errors in this quantity become increasingly important.

With a physical identification of the DDH renewal time in polymer electrolytes, it is now possible to use this model to develop a microscopic picture of charge transport in these materials. Beyond the renewal process itself, the principal question that remains is the nature of the local mobility of an ion dissolved in a polar polymer. By local mobility, we mean the mobility of an ion in the absence of a renewal event. This may consist of hopping between various available sites or perhaps simply vibrational motion within a particular coordination environment. The nature of these local motions is the focus of the following two sections that use the DDH model to interpret the electrical response of polymer electrolytes.

III. FREQUENCY-DEPENDENT RESPONSE

For an ionically conducting system, the measured frequency-dependent dielectric permittivity $\Sigma(\omega) = \Sigma'(\omega) - i\Sigma''(\omega)$, may be written in terms of the complex frequency-dependent dielectric constant, $\epsilon(\omega)$, and conductivity $\sigma(\omega)$ as follows:

$$\epsilon_0 \Sigma(\omega) = \epsilon(\omega) - \epsilon(\infty) + i\frac{\sigma(\omega)}{\omega}, \tag{9}$$

where ϵ_0 is the permittivity of free space (real).

According to Caillol *et al.*,[67] $\epsilon(\omega)$ and $\sigma(\omega)$ may be expressed in terms of appropriate time correlation functions:

$$\epsilon(\omega) - \epsilon(\infty) = \frac{\beta}{3V}[\langle \mathbf{M}^2 \rangle + i\omega\mathscr{L}\{\langle \mathbf{M}(t)\cdot\mathbf{M}(0)\rangle\} + \mathscr{L}\{\langle \mathbf{M}(t)\cdot\mathbf{J}(0)\rangle\}], \tag{10}$$

$$\sigma(\omega) = \frac{\beta}{3V}[\mathscr{L}\{\langle \mathbf{J}(t)\cdot\mathbf{J}(0)\rangle\} + i\omega\mathscr{L}\langle \mathbf{J}(t)\cdot\mathbf{M}(0)\rangle], \tag{11}$$

where $\mathscr{L}\{C(t)\} = \int_0^\infty e^{(-i\omega t)}C(t)dt$, $\beta = (k_B T)^{-1}$, V is the volume and

$$\mathbf{M} = \sum_i^{N_{\text{dipoles}}} \mu_i, \quad \mathbf{J} = \sum_i^{N_{\text{ions}}} q_i v_i. \tag{12}$$

Molecular dynamics simulations on aqueous electrolytes have shown the cross terms $\langle \mathbf{M}(t)\cdot\mathbf{J}(0)\rangle$ and $\langle \mathbf{J}(t)\cdot\mathbf{M}(0)\rangle$ to be small.[67] Although it is not clear how well the results of these simulations on small molecule solvents will extrapolate to polymer electrolytes, we will neglect these terms, allowing the frequency-dependent permittivity to be written as a sum of contributions from the dipoles on the polymer backbone and the dissolved ions. Hence,

$$\Sigma(\omega) = \Sigma_{\text{polymer}}(\omega) + \Sigma_{\text{ions}}(\omega), \tag{13}$$

where

$$\epsilon_0 \Sigma_{\text{polymer}}(\omega) = \frac{\beta}{3V}[\langle \mathbf{M}^2 \rangle + i\omega\mathscr{L}\{\langle \mathbf{M}(t)\cdot\mathbf{M}(0)\rangle\}], \tag{14}$$

$$\epsilon_0 \Sigma_{\text{ions}}(\omega) = i\frac{\beta}{3V\omega}\mathscr{L}\{\langle \mathbf{J}(t)\cdot\mathbf{J}(0)\rangle\}. \tag{15}$$

Σ_{polymer} for a salt complex should have features similar to those found in the dielectric relaxation spectrum of the corresponding pure polymer. As discussed above, however, the perturbation of polymer dynamics caused by virtual cross-linking results in significant shifts in the location of various relaxations. In addition, intensity and width variations may be observed due to coupling with ions.

Since we are mainly interested in the contributions from the added salt, we will focus on Σ_{ions}. Equation (15) can be rewritten in terms of a frequency-dependent diffusion coefficient, $D(\omega)$, and correlation factor, $f(\omega)$, yielding

$$\epsilon_0 \Sigma_{\text{ions}}(\omega) = \frac{i\beta}{\omega V f(\omega)}\sum_i^{N_{\text{ions}}} q_i^2 D_i(\omega), \tag{16}$$

where

$$f(\omega) = \frac{\mathscr{L}\{\Sigma_i^{N_{\text{ions}}}\langle \mathbf{v}_i(t)\mathbf{v}_i(0)\rangle\}}{\mathscr{L}\{\Sigma_i^{N_{\text{ions}}}\langle \mathbf{v}_i(t)\mathbf{v}_i(0)\rangle\} + \mathscr{L}\{\Sigma_i^{N_{\text{ions}}}\Sigma_{i\neq j}^{N_{\text{ions}}}\langle \mathbf{v}_i(t)\mathbf{v}_j(0)\rangle\}}. \tag{17}$$

In the absence of interionic correlations Eq. (17) reduces to unity. With regard to the dc limit of Eq. (17) (typically termed the Haven ratio),[68] both experiments on and simulations to model polymer and other electrolytes have shown this correlation factor to be on the order of one.[68–70] According to Eq. (3) and linear response theory, $D(\omega)$ may be written as follows:[3]

$$D(\omega) = \frac{(\lambda + i\omega)^2}{6}\int_0^\infty e^{-(\lambda+i\omega)t}g(t)dt. \tag{18}$$

Neglecting the correlations embodied in Eq. (17), and assuming $D_i(\omega) = D(\omega)$ and $q_i^2 = q^2$ for all i, Eqs. (16) and (18) result in the following form for Σ_{ions}.

$$\epsilon_0 \Sigma_{\text{ions}} = \frac{\beta N_{\text{ions}} q^2}{6\omega V}(i\omega - \lambda)^2 \int_0^\infty e^{-(\lambda+i\omega)t}g(t)dt \tag{19}$$

The separation of the polymeric and ionic response as well the neglect of interionic interactions that led to Eq. (19), reduces this to a problem treated by Druger *et al.*[3,23–25] They assumed simple saturation behavior for $g(t)$:

$$g(t) = [1 - e^{-\zeta t}]\langle \mathbf{r}^2(\infty)\rangle, \tag{20}$$

where ζ is a filling parameter. With this assumption, Σ_{ions} reduces to

$$\epsilon_0 \Sigma_{\text{ions}} = \frac{\sigma_{\text{dc}}\zeta\tau}{\lambda}\left(\frac{1}{1+\omega^2\tau^2} - i\frac{\omega\tau}{1+\omega^2\tau^2}\right) - i\frac{\sigma_{\text{dc}}}{\omega}, \tag{21}$$

where $\tau = 1/(\zeta + \lambda)$. Thus, this model predicts that the ionic contribution to the permittivity will consist of a dc conduction loss plus a Debye response, the ionic polarization relaxation (IPR), centered at $\omega = (\lambda + \zeta)$. Druger *et al.* showed that such an expression, when taken for a distribution of filling rates (ζ), coupled with a summation of Debye peaks for the polymer response is consistent with the observed dielectric spectra of amorphous complexes between poly(ethylene oxide) and $NH_4CF_3SO_3$ or $NaSCN$.[24,25] In light of the limited experimental data and the similarity of the predicted ion and polymer response (especially when taken for a distribution of relaxation times), however, little attempt was made to assign specific features, as is the focus of this work. In the analysis below, we suggest that the IPR and GTR occur on very different time scales, allowing their signatures to be clearly evident in the observed dielectric response.

By appealing to the nature of polymer electrolytes, Eq. (21) can be further simplified. As evidenced by the sharp drop in conductivity associated with the glass transition, long-range ionic diffusion cannot occur in the absence of renewal. In other words, conduction in polymer electrolytes is renewal limited. In a static percolation picture, this corresponds to asserting that polymer electrolytes are below their percolation threshold. The assumed form of $g(t)$ is also consistent with this picture in that it approaches a finite value at long times. The validity of this regime as applied to PSC has also been recently discussed by Druger.[5] In the renewal-limited regime, the local filling rate, ζ, of Eq. (20) is expected to be greater than the renewal rate, λ. In such a case, Eq. (21) reduces to

$$\epsilon_0 \Sigma_{\text{ion}} = \frac{\sigma_{\text{dc}}}{\lambda} \left(\frac{1}{1 + \omega^2 \tau_\zeta^2} - i \frac{\omega \tau_\zeta}{1 + \omega^2 \tau_\zeta^2} \right) - i \frac{\sigma_{\text{dc}}}{\omega}, \qquad (22)$$

where $\tau_\zeta = 1/\zeta$. As in the general case, the ionic response again consists of a dc conduction loss and a Debye response. In this case, however, the latter feature is centered about $\omega = \zeta$. It arises from the polarization of ions within the region of space accessible to them in the absence of renewal, i.e., within $\langle r^2(\infty) \rangle$. Although this motion may be subject to a restoring force and hence be better described as a resonance, we will refer it as the ionic polarization relaxation (IPR) due to the dispersive nature of the assumed $g(t)$.

With the assumptions that λ is given by the rate of the GTR and that the conduction process is renewal limited, the IPR is predicted to occur at higher frequencies than that of the GTR. Although the IPR has not been directly observed, its contribution to the high frequency dielectric constant is evident experimentally.[33] Table I compares the room temperature Σ_U to the square of the refractive index, n_D^2, for PPO and several of its complexes with NaI and one with $NH_4CF_3SO_3$.[33] Here we denote by Σ_U is the dielectric constant (real) at frequencies higher than that for all of the polymer relaxational modes including the GTR. For the PPO samples mentioned above, this corresponds to the dielectric constant at approximately 10 GHz under ambient conditions. At optical frequencies, the only contribution, besides the permittivity of free space, to Σ' is the electronic polarizability. The refractive index is a measure of this polarizability and is related to Σ' by $\Sigma' = n_D^2$. Any difference between n_D^2 and Σ_U

TABLE I. Comparison between the optical dielectric constant, n_D^2, and the high-frequency unrelaxed dielectric constant for PPO and PPO–salt complexes.

	n_D^2	Σ_U	$\Sigma_U - n_D^2$
PPO	2.11	2.10	−0.01
$PPO_{16}NaI$	2.23	3.5	1.3
$PPO_{10}NaI$	2.24	3.3	1.1
PPO_8NaI	2.15	3.3	1.2
$PPO_8NH_4CF_3SO_3$	2.10	4.0	1.9

indicates the presence of additional relaxations occurring at frequencies between the maximum frequency of the dielectric measurements and optical frequencies. For PPO, the agreement is good suggesting that the electronic polarizability is the major contributor to Σ_U. For the salt complexes, however, Σ_U is greater than n_D^2 indicating the presence of an additional relaxation process at higher frequencies, presumably the IPR. According to Eq. (22), the contribution of the IPR to Σ' is given by $\epsilon_0 \Sigma'_{\text{ions}}(0) = \sigma_{\text{dc}}/\lambda$. Using Eq. (8) and the data of Tipton *et al.* to estimate λ, the magnitude of this contribution is calculated to be 1.7 for $PPO_8NH_4CF_3SO_3$ which is in reasonable agreement with the observed difference. There are, of course, other processes that may contribute to Σ_U so the expected result is actually that $\sigma_{\text{dc}}/\epsilon_0 \lambda \leq \Sigma_U - n_D^2$. For the NaI salt complexes, the agreement is not nearly as good with the contribution of the IPR relaxation to Σ' being calculated as 0.16, 4.0, 72 for $PPO_{16}NaI$, $PPO_{10}NaI$, and PPO_8NaI respectively. As can be seen, these numbers become more unreasonable as the concentration increases. This may be due to a breakdown of the rescaling procedure used to estimate λ. In contrast with 55 K for the most concentrated $PEO \cdot LiClO_4$ sample discussed above, T_g for the most concentrated $PPO \cdot NaI$ complex was 84 K higher than that of the pure host polymer. Thus, the $PPO \cdot NaI$ salt complexes represent a more significant perturbation relative to the pure polymer. In addition, the measurements on the $PEO \cdot LiClO_4$ samples were carried out 50 K above the T_g of the most concentrated complex whereas for the $PPO \cdot NaI$ complexes, the T_g of the most concentrated complex was only 10 K below the measurement temperature. As discussed above, at temperatures close to T_g, the estimated λ is increasingly sensitive to the precise value of T_g which is difficult to determine due to its kinetic nature.

In the work of Gray *et al.*, the GTR was clearly resolved in PEO_nLiClO_4 complexes.[60] In addition, high-frequency values of Σ_U were also extracted from fits of the permittivity data. Refractive index measurements on these samples were not performed but measurements[71] on PPO_nLiClO_4 suggest that n_D for the PSC is only slightly greater than that for the pure host polymer. As a result, significant differences between the high-frequency dielectric constant of the salt complexes, Σ_U, and that of the pure polymer, Σ_U^{PEO}, can be taken as evidence for additional high-frequency processes due to the presence of ions. Again using Eq. (22), the magnitude of IPR, $\Sigma_{\text{ions}}(0)$, can be calculated. In this case, experimental quantities for both σ_{dc} and $\lambda = \omega_{\text{GTR}}$ are available. Figure 2 compares $\Sigma_U - \Sigma_U^{\text{PEO}}$ with the expected magnitude of the IPR,
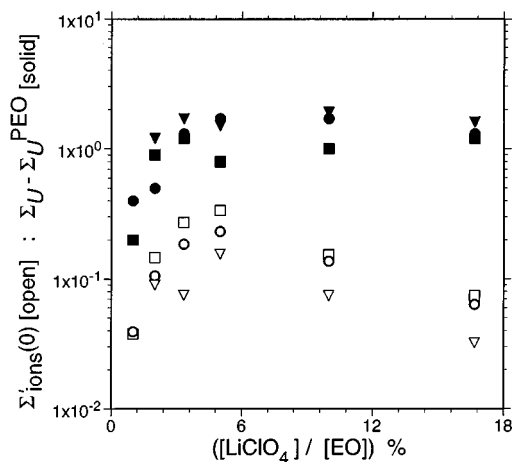
FIG. 2. Comparison of the contribution of the ionic polarization relaxation to Σ' [open symbols, $\Sigma'_{\text{ions}}(0)$], to the difference between Σ_U for PEO$_n$LiClO$_4$ and PEO (solid symbols, $\Sigma_U - \Sigma_U^{\text{PEO}}$) at $T = 328$ ($\square$), 338 ($\bigcirc$), and 348 K ($\triangledown$). The concentration is expressed in terms of the moles of LiClO$_4$ per mole of ethylene oxide monomer unit. The difference between Σ_U for the pure polymer and the salt complexes suggests the presence of additional relaxation processes at higher frequency.

$\Sigma'_{\text{ions}}(0) = \sigma_{\text{dc}}/\epsilon_0\lambda$. Again $\Sigma'_{\text{ions}}(0) < \Sigma_U - \Sigma_U^{\text{PEO}}$ consistent with this relaxation occurring at higher frequencies.

IV. dc RESPONSE

According to Eq. (18), the dc diffusion coefficient may be written as follows:

$$D(0) = \frac{1}{6}(\lambda)^2 \int_0^\infty dt \; e^{-\lambda t} g(t). \tag{23}$$

For a renewal controlled system below its percolation threshold, $g(t)$ reaches some saturation value on a time scale much faster than the renewal process. As a result, regardless of the form of $g(t)$, $D(0)$ in the renewal limited regime may be approximated as

$$\langle \mathbf{r}^2(\infty) \rangle \approx \frac{6D(0)}{\lambda}. \tag{24}$$

According to this relation, the limiting magnitude of a carrier's local displacement can be estimated from the renewal time and the diffusion coefficient. Also note that Eq. (24) implies the Walden-type product $D\eta = $ constant where the local viscosity term, η, is proportional to the renewal time τ_R. This further highlights the relevance of this limit to the discussion of polymer–salt complexes since early explanations of VTF behavior stemmed from coupling Walden's rule with appropriate expressions for the viscosity of polymers.

Very few measurements of $D(0)$ have been made in polymer electrolytes. Lindsey used pulsed field gradient-NMR techniques to measure $D_{\text{Li}}(0)$ and $D_F(0)$ in PPO ($M_w = 1.5 \times 10^6$) LiCF$_3$SO$_3$ polymer–salt complexes above 350 K.[68] Fu *et al.* have resolved the GTR in some dilute PPG·LiCF$_3$SO$_3$ complexes; however, there is not sufficient data to allow extrapolation of these results to the temperature range of the pulsed field gradient-NMR measurements.[56] In order to estimate $\langle r^2(\infty) \rangle$ in these materials, data on pure PPO
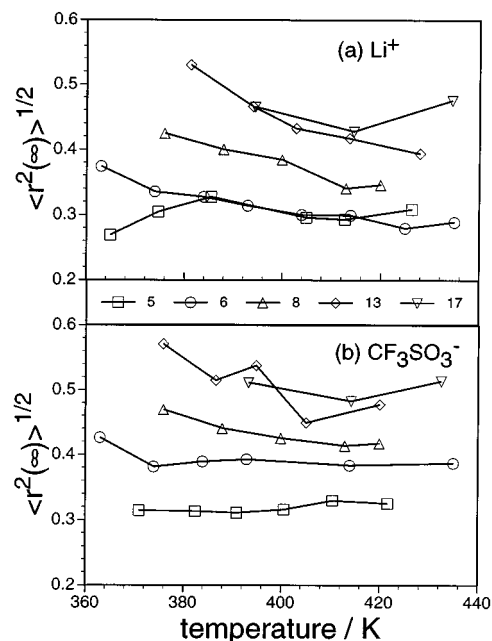

FIG. 3. The root-mean-squared displacement of (a) Li$^+$ and (b) CF$_3$SO$_3^-$ in the absence of renewal (segmental mobility) in PPO$_n$LiCF$_3$SO$_3$. The concentration is expressed in terms of moles of LiCF$_3$SO$_3$ per mole of propylene oxide monomer unit. The numbers in the legend correspond to n, and $(\langle r^2(\infty) \rangle)^{1/2}$ is given in Å.

($M_W = 13\,000$) obtained by Tipton *et al.*[33] was used to estimated τ_D^{GTR} via Eq. (8). T_s for the salt complexes was determined from measurements of Lindsey[72] on the same materials used in the NMR measurements. The values of T_g for pure PPO measured by Lindsey[72] and Tipton *et al.*[33] were in good agreement. The results of this analysis are shown in Fig. 3. Although there are observable trends, any discussion of these would be speculation due to the approximations that are involved. We prefer instead to interpret the results in an average manner asserting simply that $(\langle r^2(\infty) \rangle_{\text{Li}})^{1/2} \approx 0.4$ Å and $(\langle r^2(\infty) \rangle_F)^{1/2} \approx 0.45$ Å at 400 K. We will return to the significance of these numbers after discussing another system.

With the exception of the slight overlap between the measurements of Fu *et al.*[56] and Lindsey[72] discussed above, diffusivity data is not available on complexes where the GTR is directly observable. Of course, the diffusion coefficient may be related to the conductivity via the Nernst–Einstein equation, allowing Eq. (25) to be rewritten as

$$\langle \mathbf{r}^2(\infty) \rangle_{\text{NE}} = \frac{6V\sigma_{\text{dc}}}{\beta N_{\text{ions}} q^2 \lambda}. \tag{25}$$

Utilizing the Nernst–Einstein equation in this fashion neglects correlations between ions and allows for only the average response of all of the charge carriers to be determined. Both simulations[69] and comparison of experimentally determined conductivities and diffusion coefficients[73,74] have shown that the Nernst–Einstein equation is not quantitatively obeyed in polymer–salt complexes. Using this relation for these materials underestimates a carrier's diffusivity, and hence, underestimates $\langle r^2(\infty) \rangle$.
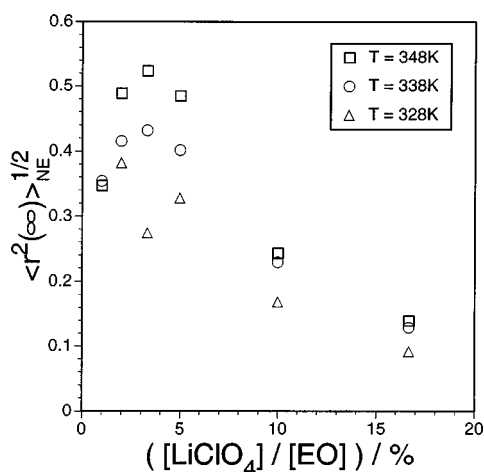
FIG. 4. The average root mean squared displacement of Li^+ and ClO_4^- ions in the absence of renewal (segmental mobility) for PEO_nLiClO_4. The concentration is expressed in terms of the moles of $LiClO_4$ per mole of ethylene oxide monomer unit, and $(\langle r^2(\infty) \rangle_{NE})^{1/2}$ is given in Å.

In the work of Gray *et al.*,[60] where the GTR was observed, dc conductivities were also reported. As a result, $\langle r^2(\infty) \rangle_{NE}$, can be calculated directly from these measurements. Density measurements, however, were not performed and are not available on these materials. Although the density is expected to vary with composition and temperature, we will assume a temperature-independent density of 1.1 g/cm^3 for all of the salt complexes. The results of this analysis are shown in Fig. 4. Again, due to the nature of the assumptions made, we prefer to interpret these results in only an average fashion asserting that $(\langle r^2(\infty) \rangle_{NE})^{1/2} \approx 0.3$ Å at 340 K. This displacement is similar to that calculated above for the $PPO \cdot LiCF_3SO_3$ complexes at slightly higher temperatures. Hence, the displacement calculated from direct measurement of the GTR and approximate knowledge of the diffusivity is in reasonable agreement with those calculated from experimental diffusivities and approximated frequencies for the GTR. This agreement suggests that the temperature rescaling to predict λ is reasonable in this case. For comparison to the NaI complexes where the rescaling of Eq. (8) seemed to fail, the $PPO \cdot LiCF_3SO_3$ measurements were taken at 100 K above the glass transition of the most concentrated sample which was in turn 65 K above that of the pure polymer.

We now turn to the significance of these displacements in terms of developing a physical picture of transport in polymer electrolytes. For this purpose, it is informative to draw comparisons with vibrational data. Infrared transmission studies on low molecular weight PPO (MW=450) complexed with alkali metal thiocyanates have identified a low-frequency vibration.[75] The position and breadth of this band is dependent on the alkali metal and concentration of the complex. For $PPO_{10}NaSCN$ and $PPO_{10}KSCN$, it is observed at 135 and 190 cm^{-1}, respectively. The band was not clearly resolved in the LiSCN case but appears to be shifted to even higher frequencies and is quite broad. If this mode is analyzed in terms of a harmonic oscillator, the average mean-squared displacement, $\langle r^2 \rangle$, of the vibration can be estimated

from the equipartition theorem. For an isotropic three-dimensional oscillator,

$$\frac{1}{2}\omega_0^2 m \langle \mathbf{r}^2 \rangle = \frac{3}{2} k_B T, \tag{26}$$

where m is the particle mass. For the $PPO_{10}MSCN$ complexes above, $(\langle r^2 \rangle)^{1/2} = 0.24$ Å for $M = Na$ and $(\langle r^2 \rangle)^{1/2} = 0.13$ Å for $M = K$. Although somewhat smaller, these displacements are on the order of $\langle r^2(\infty) \rangle$ calculated for the complexes above. Thus, $\langle r^2(\infty) \rangle$ is not much larger than the vibrational displacement of a cation within its coordination shell. The simplest interpretation of this result is that ion hopping between several different coordination environments does not occur in the absence of host renewal. Rather, ions only execute small displacements with long-range transport being facilitated by the renewal process that results in small rearrangements of their coordination environments. Within this simplistic interpretation, anionic displacements can be argued to be larger than cationic ones since anion motion is not as strongly constrained by polymer solvation.

Of course, $\langle r^2(\infty) \rangle$ represents an ensemble average. As a result, the magnitude of $\langle r^2(\infty) \rangle$ may not be characteristic of each individual ion during any given renewal period. It may be possible, for instance, that $\langle r^2(\infty) \rangle$ is dominated by a small number of ions exhibiting large displacements with the majority of ions moving very little during a renewal period. This possibility was recently discussed as a means of interpreting the effects of ionic interactions on the conductivity of polymer electrolytes, and it corresponds to taking a bi-exponential form of Eq. (20) with two time constants, ς_1 and ς_2, such that $\varsigma_1 \leq \lambda \leq \varsigma_2$.[76]

V. CONCLUSION

We have presented arguments that the DDH renewal time can be linked with the characteristic time constant for the GTR. This correlation was based on the strong correspondence between the temperature and pressure dependence of ω_D^{GTR} for host polymers and σ_{dc} for salt complexes of these polymers. Underlying the relation between τ_R and τ_D^{GTR} is the notion that the motions associated with the glass transition are those that restart carrier motion in the language of the DDH model. Even if this holds true, equating τ_R with the time constant for the glass transition relaxation as probed by dielectric relaxation spectroscopy is only a rough approximation due to the difficulty in relating microscopic time constants, as is τ_R, with macroscopic ones. Even with this limitation, equating τ_R and τ_D^{GTR} allows for an understanding of the electrical response of PSC in terms of a microscopic model.

In the renewal limited regime, as was argued to be appropriate for PSC, the DDH model predicts a dc conduction process that dominates the dielectric loss at low frequencies. Superimposed on this are the various dipolar responses of the host polymer, including the GTR, that typically occur in the microwave region under ambient conditions. At frequencies higher than these dipolar processes, the DDH model predicts the presence of an additional ionic process, the IPR. This high-frequency relaxation arises from the polarization of ions in small regions of space as they wait for a renewal event to

occur. The dc conduction loss is an obvious signature of PSC and other electrolytes. Evidence for the high-frequency relaxation was gleaned from comparison of Σ_U for various polymer–salt complexes with optical dielectric constants or with Σ_U for the corresponding host polymer.

The DDH model in this form predicts no ionic contribution, other than the dc conduction loss, at lower frequencies. With the exception of frequency shifts due to glass transition effects, the current treatment expects that the dipolar region of the spectrum will remain unchanged from that of the pure host polymer (although it may be obscured by the dc conduction loss). In polyethers, changes in the magnitude of various relaxations and some evidence for additional relaxations in the dipolar region have been noted upon ion complexation.[60] These have been suggested to arise from ion pair rotations or from the enhancement of polymer modes due to coupling with ions.[60] The failure of our treatment to account for these observations may come about from the neglect of ion–polymer coupling terms $\langle \mathbf{M}(t) \cdot \mathbf{J}(0) \rangle$ and $\langle \mathbf{J}(t) \cdot \mathbf{M}(0) \rangle$ and from the neglect of ionic interactions as embodied in the correlation factor $f(\omega)$. Nonetheless, the DDH model consistently predicts several characteristic features of the dielectric spectra of PSC.

Identification of the renewal time with the GTR also allows for the displacements that give rise to the IPR to be estimated. These displacements were calculated for a number of systems and found to be on the order of 0.4 Å at 100 °C. Although it is not clear whether $\langle r^2(\infty) \rangle$ is characteristic of each individual ion during a given renewal period, the size of $\langle r^2(\infty) \rangle$ argues that ion motion is quite restricted and that ion hopping between several different coordination sites does not occur in the absence of host segmental mobility. In fact, the displacements predicted by the DDH model are only slightly larger than those corresponding to the metal–oxygen vibration in PSC. This is in fact reasonable, since fully amorphous PSC materials are dense, liquidlike continua, in which ionic mobility is indeed limited by renewal (host segmental motions), and no large local holes are available.

With respect to the very complex and challenging[61] issue of conduction mechanisms in PSC electrolytes, the present results, combined with experimental studies,[7–11,31–34,46–48,50–61,65,66,71–81] and modeling work[82] using both Monte-Carlo[69,76,83] and molecular dynamics[85–88] methods, seems to permit a general understanding. The PSCs are normally studied at high salt concentrations (substantially exceeding 0.1 M), at which interionic interactions cause substantial[5] ion pairing and clustering; these have been well-studied experimentally. As McLin and Angell first suggested,[48] recent simulation studies[69,76,83–88] have shown that most charge transport is due to quasifree ions, and their mobility, in turn, is well described by the DDH model. This straightforward mechanism appears to be in agreement with all available evidence.[89]

ACKNOWLEDGMENTS

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