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Ion relaxation dynamics and nearly constant loss behavior in polymer electrolyte

B. Natesan, N. K. Karan, and R. S. Katiyar
Department of Physics, University of Puerto Rico, P.O. Box 23343, San Juan Puerto Rico 00931, USA

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The broadband conductive spectroscopy covering the range 10^{-2} to 10^6 Hz has been employed to examine both the ionic and the segmental motions in polymer salt complexes (PSCs), consisting of polyethylene oxide (PEO), $LiClO_4$, or $LiCF_3SO_3$. The temperature dependence of dc conductivity has been analyzed using Vogel-Tamman-Fulcher (VTF) equation and the results suggest that the temperature dependence of the dc conductivity can be well described in terms of the free volume changes with temperature. The ac conductivity at low temperatures (below 223 K) remains unchanged with the temperature, exhibiting nearly linear frequency dependence. This observation, not previously reported in polymers, indicates clearly that nearly constant loss (NCL) phenomenon, usually observed in glassy and ceramic ion conductors, is also operative in polymer electrolytes. Furthermore, a crossover from a NCL to cooperative ion hopping at higher temperatures in the frequency dependence of the conductivity has been observed. The analysis of the temperature dependence of both dc and ac conductivities demonstrates that there exists a direct correlation between the ionic conductivity and the segmental relaxation processes.

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The coupling between the polymer segmental relaxation and the ion transport in polymer electrolytes is fascinating and it is not completely understood, yet it holds the key to the development of new energy sources [1]. Although, various research groups have shown [2–4] a great deal of interest to synthesize high ion conducting polymer electrolytes over the years, the desired value of conductivity at the ambient temperature has not yet been achieved. The incomplete understanding of the conduction mechanism in polymer electrolytes is considered to be one of the main hurdles in achieving the required ambient conductivities. It is well known that the ion transport in polymer electrolytes is very much coupled to the polymer chain and the segmental motions. The concept that the ionic conductivity in polymers is related to large-scale segmental motions, characteristic of the glass transition (α relaxation), was proposed by Fuoss as early as 1941 [5]. Furthermore, many authors have suggested that the high ionic conductivity in PEO is associated with the chain mobility [6,7]. It has also been suggested that the conduction in polymer electrolytes takes place through two distinct events [8]: the first is due to the charge migration of ions between coordination sites in the host material, and the second is associated with an increase in conductivity produced by polymeric chain motions, the so-called "segmental motion." The neutron scattering, nuclear magnetic resonance, positron lifetime, x-ray diffraction and computer simulation studies carried out recently [9–13] on polymer electrolytes revealed that the segmental relaxation processes play a crucial role in determining the ion transport process.

In this paper, we have investigated the ion relaxation dynamics and the constant loss behavior of PSCs using conductive spectroscopy, in order to gain further insight into the understanding of ion transport process in polymer electrolytes. The PSCs consisting of PEO and two different lithium salts were synthesized with and without TiO_2 nanofiller. The conductivity was measured as a function of frequency from 10^{-2} to 10^6 Hz at different temperatures. The VTF analysis of the dc conductivity data indicated a strong coupling between the ionic and the polymer chain segmental motions. The temperature dependence of the ac conductivity in the above frequency domain demonstrates, for the first time, the existence of NCL behavior in polymer electrolytes.

Polymer electrolyte films based on polyethylene oxide (PEO, molecular weight $> 5 \times 10^6$) were synthesized by casting from acetronitrile solutions using $LiClO_4$ or $LiCF_3SO_3$ as dopant salts and TiO_2 as filler. The EO:Li ratio was kept at 16:1. The detailed procedure of the preparation method has been reported elsewhere [14]. The real (σ') and imaginary (σ'') parts of complex conductivity (σ^*) were measured with a Novocontrol GmbH Concept 40 broadband dielectric spectrometer as a function of frequency from 10^{-2} to 10^6 Hz at various temperatures.

Figure 1 shows the temperature dependence of the dc conductivity in the form of Arrhenius plots for all the PSCs. It is evident from Fig. 1 that the room temperature dc conductivity of PEO-$LiCF_3SO_3$ polymer-salt complex is almost an order of magnitude less than that of PEO-$LiClO_4$ complex. The

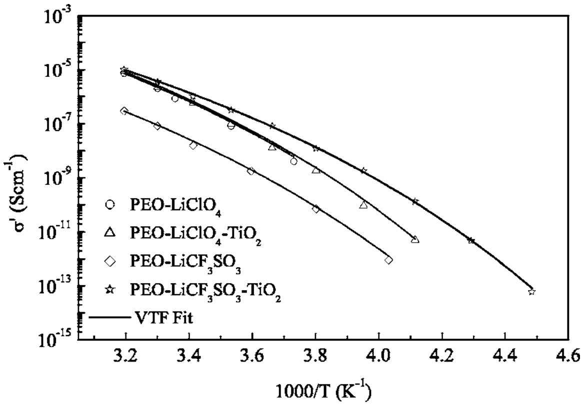

FIG. 1. Temperature dependence of dc conductivity of PSCs. The continuous lines denote the fit of experimental dc conductivity to the VTF equation, $\sigma = \sigma_0 T^{1/2} \exp[-E_v / R(T - T_0)]$

observation of low conductivity in PEO-$LiCF_3SO_3$ is due to the formation of ion pairs as seen from our Raman spectra (not shown here) which results in reducing the number of free charge carriers available for conduction. The dc conductivity increased with the addition of TiO_2 in both salts, as is apparent from Fig. 1. The observed increase in the dc conductivity is almost an order of magnitude for $LiCF_3SO_3$ complex, while for $LiClO_4$ complex it is only 2 times. This enhancement of conductivity with TiO_2 addition is due to the inhibition of PEO crystallization thereby hindering local reorganization of chains in PEO leading to a polymer electrolyte with high degree of disorder as evidenced from the broadening of disordered-longitudinal acoustic mode (D-LAM) in the Raman spectra (not shown here). Furthermore, the addition of TiO_2 suppresses the formation of ion pairs, producing more mobile ions, along with the formation of interface between PEO and TiO_2 offering a path for easier migration of ions resulting in higher conductivity.

The curvature, often seen in amorphous polymer systems, is apparent from the temperature dependence of the dc conductivity of all the PSCs (Fig. 1). This curvature in the temperature dependence of the dc conductivity is associated with the free volume changes with temperature resulting in the activation of the segmental motions, above T_g (223 K), thereby assisting the ion transport, being consistent with the report by Wang *et al.* [11], revealing such a temperature dependence of free volume changes and its relationship with both the segmental motion and conductivity using positron annihilation spectroscopy. The conductivity data were analyzed using the VTF equation [15–17]

$$\sigma = \sigma_0 T^{-1/2} \exp[-E_v/R(T-T_0)], \qquad (1)$$

where, σ_0 is the conductivity preexponent, E_v is the Vogel activation energy, T_0 is the Vogel scaling temperature, R is the gas constant, and T is the absolute temperature. A nonlinear least-squares fit of conductivity data to Eq. (1) was carried out, and the best-fitted parameters, σ_0, E_v, and T_0 were obtained. The T_0 values are between 50 to 60 K lower than the T_g determined by DSC. Such values are not unexpected since $T_g - T_0$ is usually of the order of 50 K for polymer systems [18]. The accuracy of VTF fits over a wide temperature range demonstrates the strong relation between the conductivity and the chain segmental mobility.

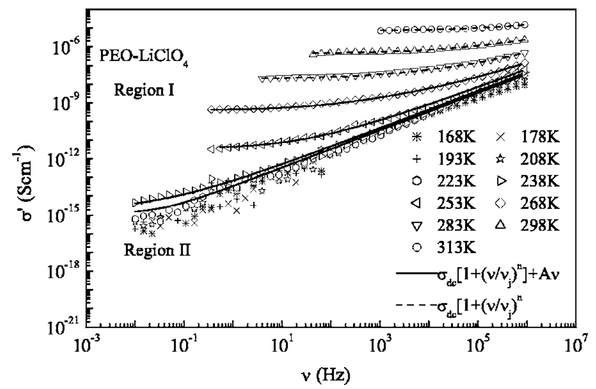

FIG. 2. Frequency dependence of conductivity at various temperatures for PEO-$LiClO_4$ complex. The dotted and continuous lines are fit of experimental ac conductivity data to $\sigma_{dc}[1+(\nu/\nu_j)^n]$ and $\sigma_{dc}[1+(\nu/\nu_j)^n]+A\nu$, respectively.

In order to understand the ion dynamics in polymer electrolytes, the frequency dependence of conductivity at various temperatures has been analyzed and is shown in Fig. 2 for PEO-$LiClO_4$ complex. It is evident from Fig. 2 that at temperatures, below T_g (223 K), the conductivity is almost independent of temperature, whereas, above T_g, the conductivity increases with increasing temperature. This observation reveals that the ion transport is very much coupled to the segmental motion of polymer chains. Because, below, T_g the segmental motion is frozen and the ions do not contribute to long-range migration significantly. Above T_g the segmental mobility sets in thereby assisting the ions to move more freely, contributing to long-range migration. This observation indicates that the segmental motion remains to be a prerequisite for ion migration in the polymer electrolytes, providing strong, *albeit* indirect evidence that the electrical conductivity is controlled by the same mechanism as the glass transition (α relaxation). Specifically, it provides evidence that the ionic conductivity is controlled by the large-scale segmental motion characteristic of the glass-rubber transition.

The frequency dependence of conductivity is divided into two regions as shown in Fig. 2: in region I (high temperature), the frequency dependence of conductivity exhibits a plateau at lower frequencies, followed by dispersion at higher frequencies. In region II (low temperature), the conductivity is almost less sensitive to temperature and varies nearly linearly with the frequency. This is shown more clearly in Fig. 3 where $\varepsilon''(\omega)$ is plotted against temperature for PEO-$LiClO_4$ complex. At low temperatures the data at different frequencies collapse onto a single curve, revealing that $\varepsilon''(\omega)$ is independent of frequency and therefore a genuine NCL behavior. But, at higher temperatures, $\varepsilon''(\omega)$ for different frequencies seemed to diverge as seen in Fig. 3 due to the appearance of a different contribution to the ac conductivity. This ubiquitous contribution to ac conductivity consists of a nearly frequency independent dielectric loss, known as nearly constant loss (NCL). This phenomenon is usually observed in glasses and ceramics, but so far, to our knowledge, it has not been reported in the polymers. In what

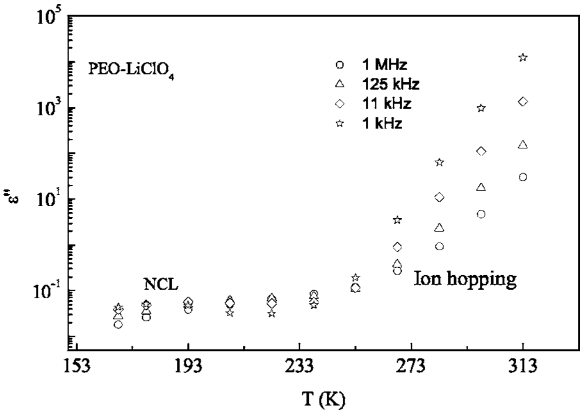

FIG. 3. Temperature dependence of dielectric loss at different frequencies for PEO-$LiClO_4$ complex.

follows, we describe the conductivity behavior in the above regions in detail.

In region I (Fig. 2), the conductivity is independent of frequency at low frequencies and it exhibits dispersion at higher frequencies. The frequency at which the crossover from frequency independent to frequency dependent conductivity occurs represents the onset of conductivity relaxation and it shifts to higher frequencies with increasing temperature. In order to understand the ac electrical response of the PSCs, the ac conductivity data was analyzed by fitting the ac conductivity data to universal power law UPL of the form [19,20]

$$\sigma'(\nu) = \sigma_{\mathrm{dc}}[1 + (\nu/\nu_j)^n], \quad 0 < n < 1, \tag{2}$$

where, σ_{dc}, is dc conductivity, ν_j is onset frequency of conductivity relaxation, and n is the power law exponent. Microscopic models such as dynamic bond percolation and dynamic disorder hopping models have been proposed [8] to describe the long-range ion transport in polymer electrolytes. According to these models, the renewal time, τ_{ren}, for the segmental reorganization arising from the changes in the local geometry due to the coordination of cations with the polymer Lewis base sites, lie within the microwave range. Moreover, these models explain the frequency dependence of conductivity satisfactorily only above 100 MHz region. Hence, we have extended the physical model (jump relaxation model) developed for structurally disordered ionic conductors [21] in order to rationalize the observed low frequency dispersion as the dynamical effects of the polymer host due to the segmental renewing rates become less significant below microwave region. According to jump relaxation model, at very low frequencies ($\nu \to 0$) an ion can jump from one site to its neighboring vacant site successfully contributing to the dc conductivity. At higher frequencies, the probability for the ion to go back again to its initial site increases due to the short time periods available. This high probability for the correlated forward-backward hopping at higher frequencies together with the relaxation of the dynamic cage potential is responsible for the observed high frequency conductivity dispersion.

In region II (Fig. 2), the conductivity varies nearly linearly with the frequency and it almost remains unchanged with increasing temperature, suggesting that the NCL phenomenon is also operative in the polymer electrolytes. It is further interesting to note that at low temperatures the ac conductivity becomes increasingly steeper. Similar NCL behavior has been reported in many glassy and few ceramic ion conductors [22–25]. But, to our knowledge, the present one is the first such report in polymers. Nowick *et al.* [22] have found that the power law exponent in several disordered systems became unity at low temperatures which further suggested that at these temperatures, the conductivity behave quite differently from that seen at higher temperatures approximately described by $A.\ \nu.\ T$, where the temperature dependence is very weak and the conductivity varies almost linearly with the frequency at these low temperatures. There have been reports [22–24] in crystalline and glassy ionic conductors that at low temperatures a contribution from a nearly frequency independent dielectric loss, known as "nearly constant loss" (NCL), $\varepsilon''(\nu) \approx A$, which corresponds to an almost linear frequency dependent of the form $\sigma'(\nu) = \nu\varepsilon_0\varepsilon''(\nu) \approx A\varepsilon_0\nu$ in the real part of the complex conductivity. In order to accommodate this contribution, a linear term in frequency (NCL) has been introduced to describe the ac conductivity of the disordered systems by a superposition of a Jonscher term and a NCL term of the form [22,24]

$$\sigma'(\nu) = \sigma_{\mathrm{dc}}[1 + (\nu/\nu_j)^n] + A\nu, \tag{3}$$

where, A is constant and ν in the second term of Eq. (3) varies linearly (with an exponent value nearly equal to 1.0). We extended this approach to polymer ion conducting systems to verify the universality of this approach in all forms of ionic conductors. We fitted the low temperature ac conductivity data using Eq (3). It is evident from Fig. 2 that the ac conductivity data at higher and lower temperatures were described reasonably well in terms of Eqs. (2) and (3), respectively. The dotted and continuos lines in Fig. 2 represent fitted data to Eqs. (2) and (3), respectively, whereas, the symbols correspond to the experimental data. The TiO_2 added complexes also showed similar trends. This analysis clearly indicates that there exists a crossover from nearly constant loss characterized by the linear frequency dependent ac conductivity at low temperatures to the fractional power law dependent ac conductivity (ion hopping) at higher temperatures. Thus, supporting the fact that the combination of NCL and Jonscher's power law describes well the dynamics of ions in the polymer electrolytes. However, the issue of the origin for NCL behavior is still not well understood and remains controversial. Jain *et al.* [24] proposed that the NCL arise from the motion of group of atoms in the asymmetric double well potential (ADWP) configurations. Recently, Ngai *et al.* [23,25] have pointed out that the NCL originates from the slowing down of ionic motions in the cages due to ion-ion interactions and correlations in the short time regime. Similar studies in various glassy, ceramic, and polymers with different compositions are needed in order to gain further insights about the origin of NCL phenomenon.

Ion dynamics, segmental relaxation processes, and the effect of addition of nanoparticulate TiO_2 on the ionic conductivity in PEO based polymer electrolytes have been investigated using broadband conductive spectroscopy. It is found from the dc conductivity studies that the addition of TiO_2 results in enhancing the conductivity of both PEO-$LiClO_4$ and PEO-$LiCF_3SO_3$ complexes. The temperature dependence of dc conductivity has been examined using the VTF relation and the results suggests that the changes in the free volume with increasing temperature activates the segmental motions, above T_g, and these segmental motions play a significant role in controlling the ion transport in polymer electrolytes.

The ion dynamical process in polymer electrolytes has been studied in detail in terms of the frequency dependence of the conductivity in the temperature domain. The frequency dependence of the conductivity showed two regions, namely, Region I (high temperature) and Region II (low temperature). In Region I, the conductivity exhibited a plateau at low frequencies, followed by the dispersion at higher frequencies. In Region II, the conductivity is less sensitive to temperature and exhibits nearly liner frequency dependence. This contribution to ac conductivity from nearly constant dielectric loss has been observed, for the first time, in polymer electrolytes. Furthermore, a crossover from nearly constant loss to cooperative ion hopping at higher temperatures is noticed from the frequency dependence of the conductivity.

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