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Polymer chain organization in tensile-stretched poly(ethylene oxide)-based polymer electrolytes

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Abstract

Polymer chain orientation in tensile-stretched poly(ethylene oxide)-lithium trifluoromethanesulfonate polymer electrolytes are investigated with polarized infrared spectroscopy as a function of the degree of strain and salt composition (ether oxygen atom to lithium ion ratios of 20:1, 15:1, and 10:1). The 1359 and 1352 cm^{-1} bands are used to probe the crystalline PEO and $\text{P}(\text{EO})_3\text{LiCF}_3\text{SO}_3$ domains, respectively, allowing a direct comparison of chain orientation for the two phases. Two-dimensional correlation FT-IR spectroscopy indicates that the two crystalline domains align at the same rate as the polymer electrolytes are stretched. Quantitative measurements of polymer chain orientation obtained through dichroic infrared spectroscopy show that chain orientation predominantly occurs between strain values of 150% and 250%, regardless of salt composition investigated. There are few changes in chain orientation for either phase when the films are further elongated to a strain of 300%; however, the PEO domains are slightly more oriented at the high strain values. The spectroscopic data are consistent with stretching-induced melt-recrystallization of the unoriented crystalline domains in the solution-cast polymer films. Stretching the films pulls polymer chains from the crystalline domains, which subsequently recrystallize with the polymer helices parallel to the stretch direction. If lithium ion conduction in crystalline polymer electrolytes is viewed as consisting of two major components (facile intra-chain lithium ion conduction and slow helix-to-helix inter-grain hopping), then alignment of the polymer helices will affect the ion conduction pathways for these materials by reducing the number of inter-grain hops required to migrate through the polymer electrolyte.

Keywords

Polymer electrolytes; Lithium batteries; Polarized infrared spectroscopy; 2D correlation IR spectroscopy; Strain

1. Introduction

Polymer electrolytes have distinct advantages over traditional liquid electrolytes used in rechargeable lithium ion batteries. Perhaps the most important advantage is enhanced consumer safety through the elimination of the highly flammable solvents used in current lithium batteries. Only a handful of systems, however, have been commercialized despite

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over 30 years of vigorous research activity in this area. In general, the ionic conductivities of most polymer electrolyte systems are too low to sustain an operating lithium battery, especially at room temperature. Electrolyte systems that do have competitive ionic conductivities typically lack sufficient mechanical properties. Most strategies to improve polymer electrolyte performance focus on highly disordered systems, relying on a large body of experimental evidence that suggests ion conduction is higher in amorphous systems above the glass transition temperature than analogous crystalline systems. Nonetheless, there are a few striking examples of polymer electrolytes with organized polymer chains that possess higher ionic conductivities than the disordered analogs. These examples fall into two broad classes: (1) polymer chain orientation imposed through the application of an external field and (2) crystalline PEO-salt phases that exhibit relatively high ionic conductivity.

In the first class, conductivity enhancement is induced by subjecting a polymer electrolyte to an external field that orients the polymer chains. Golodnitsky and co-workers [1-3] reported substantial conductivity enhancement (6- to 40-fold increase) for PEO-based polymer electrolytes aligned through tensile stretching. The conductivity enhancement was only parallel to the stretch axis, leading the authors to propose that the increased conductivity in the mechanically-stretched materials was due to the alignment of the polymer chain helices. The authors further argued that the induced order in the polymer electrolytes increased ionic conductivity through the reduction in the number of inter-grain barriers to ionic conductivity. Golodnitsky and her collaborators [4] have also demonstrated conductivity enhancement by casting the polymer electrolytes under a magnetic field. This method produces polymer electrolytes with polymer chains oriented transverse to the film, which is appropriate for lithium battery applications. The second class of experiments consists of a group of polymer electrolytes whose crystalline phase has higher ionic conductivities than the corresponding amorphous phase. The $\text{P(EO)}_6\text{LiXF}_6$ ($X = \text{P, As, and Sb}$) reported by Gadjourova *et al.* [5,6] are the archetypal examples of these materials. In these systems, lithium ions are coordinated by ether oxygen atoms from two separate polymer chains such that the PEO chains form cylindrical tunnels around the lithium ions. The anions are not coordinated by the lithium ions and exist outside the lithium ion channels. The $\text{P(EO)}_8\text{MASF}_6$ ($M = \text{Na, K, and Rb}$) crystalline compounds reported by Zhang *et al.* [7] constitute a second example of crystalline polymer electrolytes with relatively high ionic conductivities.

These observations challenge the conventional wisdom for designing polymer electrolytes and raise fundamental questions concerning the role of polymer chain order on ionic conductivity. Although the possibility of increasing ionic conductivity by organizing the polymer chains is an interesting and novel approach, there are a number of unanswered questions concerning the fundamental mechanism of conductivity enhancement. Specifically, in the context of field-oriented polymer electrolytes, there are few quantitative assessments of polymer chain orientation. In addition, PEO-based polymer electrolytes are often heterogeneous systems, primarily consisting of pure PEO and PEO-salt crystalline phases. The relative degree of orientation and orientation rates for the PEO and PEO-salt domains upon stretching are unknown. The lack of quantitative information concerning the degree of order among the various phases present in a polymer electrolyte, which is imposed by mechanically stretching a polymer electrolyte, frustrates attempts to fully understand the mechanism of stress-induced ionic conductivity enhancement. Polarized infrared spectroscopy provides a useful means for quantifying chain orientation for a variety of polymers. Thus, dichroic infrared spectroscopic measurements of mechanically-stretched polymer electrolytes may provide some insight into the mechanism of ionic conductivity enhancement. Such studies are reported for the $\text{PEO-LiCF}_3\text{SO}_3$ system; this class of materials has been studied over the past 30 years. Therefore, an extensive body of experimental data is available to aid in interpreting the spectroscopic data for mechanically-

stretched PEO-LiCF₃SO₃ compounds. Furthermore, the ability to spectroscopically distinguish the crystalline PEO and P(EO)₃LiCF₃SO₃ phases in the infrared spectrum will facilitate a quantitative assessment of how those individual phases respond to mechanical stretching.

2. Experimental methods

Poly(ethylene oxide), average molecular weight of 5×10^6 da., and lithium trifluoromethanesulfonate were obtained from Sigma-Aldrich and used as received. Samples of PEO-LiCF₃SO₃ were prepared by dissolving stoichiometric quantities of PEO and LiCF₃SO₃ in acetonitrile (Aldrich), and the solutions were stirred overnight at 25°C. Sample compositions were prepared such that the ether oxygen atom to lithium ion ratio was 20:1, 15:1, and 10:1. Thin films were prepared by casting the polymer electrolytes on poly(tetrafluoroethylene) plates at room temperature. To ensure film uniformity, all cast solutions were spread with the aid of a draw-down bar and then allowed to dry. Sample manipulation was performed in a dry argon atmosphere (<1 ppm H₂O). Polymer electrolyte samples were elongated up to 3-fold at room temperature.

Transmission infrared spectra were measured with a Nicolet 6700 FT-IR spectrometer (Globar source, KBr beamsplitter, and DTGS detector). Spectral resolution was set to 1 cm⁻¹. Polarized IR spectra were recorded using a holographic wire grid polarizer, and each spectrum consisted of 8 averaged scans collected under dry air purge. Integrated band intensities were measured by non-linear least squares curve fitting methods. Galactic Grams AI® was used to fit the experimental spectra with mixed Gaussian-Lorentzian peak profiles. Two-dimensional correlation FT-IR spectra were calculated with SpectraCorr® v. 1.1.0, which is available from Thermo Electron.

3. Results and discussion

3.1. Polarized infrared spectroscopy

Figure 1 shows polarized infrared spectra of a P(EO)₁₀LiCF₃SO₃ film elongated 2.93 times its original length. The infrared spectrum of the unaligned polymer electrolyte is essentially a superposition of the infrared spectra of pure PEO and P(EO)₃LiCF₃SO₃, which is in agreement with the published P(EO)_xLiCF₃SO₃ phase diagram [8,9]. Pure PEO crystallizes in the $P2_1/a$ (C_{2h}^5) space group with four PEO chains running through each unit cell [10]. The vibrational modes of crystalline PEO are usually analyzed in terms of the helical group $D(4\pi/7)$, which presupposes negligible vibrational coupling between the four chains within the unit cell [11,12]. Crystalline P(EO)₃LiCF₃SO₃ also adopts the $P2_1/a$ space group [13], although the conformation of the polymer chains for this compound is described by the $C(2\pi/2)$ helical group [14]. Table 1 summarizes band assignments, spectral activities, and the polarization of the transition dipole moments relative to the polymer chain axis for the spectral region shown in Figure 1. The 1359 and 1343 cm⁻¹ bands are assigned to crystalline PEO domains, while the remaining bands are due to P(EO)₃LiCF₃SO₃ domains within the polymer electrolyte [15,16]. Yoshihara and co-workers [17] assigned the E_1 band at 1359 cm⁻¹ as a mixture of CH₂ wagging and CC stretching motions. The transition dipole moment of this vibrational mode is polarized perpendicular to the helical axis of the polymer. The A_2 band at 1343 cm⁻¹ is primarily due to antisymmetric CH₂ wagging motions and is polarized parallel to the helical axis [17]. The 1352 cm⁻¹ band originates from the P(EO)₃LiCF₃SO₃ phase and is probably due to molecular motions within the PEO backbone that are similar to those underlying the 1359 cm⁻¹ band [15,16]. Likewise, the low frequency shoulder at 1340 cm⁻¹ is presumably due to antisymmetric wagging motions of the PEO chains in P(EO)₃LiCF₃SO₃ [15,16]. Curve fitting analysis revealed additional bands at 1376, 1366,

and 1347 cm⁻¹; however, the specific molecular motions comprising these bands are currently unknown.

Tensile stretching produced significant changes in the polarized infrared band intensities of the P(EO)_xLiCF₃SO₃ polymer electrolytes (see Figure 1). The intensities of the vibrational modes whose transition dipole moment is parallel to the polymer chain axis increased when the polarizer was set parallel to the stretch axis. Rotating the polarizer such that the polarized infrared radiation is perpendicular to the applied stress field caused an increase in the intensities of vibrational modes with transition dipole moments perpendicular to the chain axis. A symmetry-based analysis of the vibrational modes for pure PEO has been previously published, and the changes in the infrared spectra for the PEO crystalline domains reported in Figure 1 are in agreement with those assignments [14,17]. Frech and Rhodes reported a symmetry-based analysis of the vibrational modes for the 3:1 compound [14]; however, detailed assignments are not provided for the bands presented in Figure 1. Fortunately, crystalline P(EO)₃LiCF₃SO₃ belongs to the $C(2\pi/2)$ helical group, which is isomorphous to the C_2 point group [18]. Hence, the irreducible representations of the $C(2\pi/2)$ helical group are identical to those of the C_2 point group. The irreducible representations for P(EO)₃LiCF₃SO₃ under the helical group are given as $\Gamma = 61A + 61B$ at the Brillouin zone center [19]. Vibrational modes with A symmetry have transition dipole moments parallel to the helical axis, while the transition dipole moments of modes with B symmetry are perpendicular to the helical axis. The 1376, 1366, 1352 and 1347 cm⁻¹ bands have larger intensities when the polarizer is set perpendicular to the stretch axis, similar to the pure PEO E_I mode at 1359 cm⁻¹. Thus, it is reasonable to assign those modes as having B symmetry. Similar arguments establish the 1340 cm⁻¹ band as having A symmetry.

3.2. Two-dimensional correlation FT-IR spectroscopy

Optical two-dimensional correlation spectroscopy is a powerful technique for investigating the effect of mechanical stretching on the PEO-LiCF₃SO₃ polymer films. Although this technique is becoming more familiar, it is not yet in widespread use. Noda and co-workers provide an excellent review of the technique along with several salient examples in reference [20]. A short summary of the principle equations involved is provided below.

Suppose a system is subjected to a perturbation, α , that affects the intensities of certain bands in the infrared spectrum. The perturbation is most often reported as temperature; however, the methodology is not merely restricted to temperature but may be pressure, concentration changes, strain, etc. The conventional one-dimensional spectrum, $I(\nu, \alpha)$, is measured as a function of the perturbation. A dynamic spectrum, $I_d(\nu, \alpha)$, is then defined by referencing the perturbed spectra against an appropriate reference spectrum over the perturbation range, $\alpha_{\min} < \alpha < \alpha_{\max}$.

$$I_d(\nu, \alpha) = I(\nu, \alpha) - I_{\text{ref}}(\nu, \alpha) \quad (1)$$

The reference spectrum may be chosen in a variety of ways, including the experimental spectra recorded at either $\alpha_{\min}$, $\alpha_{\max}$, or an average spectrum over the range of perturbation. The two-dimensional correlation function $X(\nu_1, \nu_2)$ is then given as

$$X(\nu_1, \nu_2) = \langle I_d(\nu_1, \alpha) \cdot I_d(\nu_2, \alpha) \rangle \quad (2)$$

Treating $X(v_1, v_2)$ as a complex number, it is possible to resolve the correlation function into two orthogonal components,

$$X(v_1, v_2) = \Phi(v_1, v_2) + i\Psi(v_1, v_2) \quad (3)$$

The real component $\Phi(v_1, v_2)$ is the synchronous 2D correlation intensity, which measures the similarity of spectral intensities at frequencies v_1 and v_2 as the perturbation is changed. The imaginary component $\Psi(v_1, v_2)$ is a measure of the degree of dissimilarity of the spectral intensities at frequencies v_1 and v_2 as a function of the perturbation. If the dynamic spectrum is Fourier transformed, i.e.,

$$I_1(\omega) = \int_0^\infty I_d(v_1, \alpha) e^{-i\omega\alpha} d\alpha \quad (4)$$

then the 2D correlation function is written as

$$X(v_1, v_2) = \frac{1}{\pi(\alpha_{\max} - \alpha_{\min})} \int_0^\infty I_1(\omega) I_2(\omega) * d\omega \quad (5)$$

Although the Fourier transformations can be calculated with fast Fourier transform algorithms, the number of computations can be large. Fortunately, practical and concise methods for computing the synchronous and asynchronous correlation spectra have been described, and most commercial software used to operate FT-IR spectrometers are capable of performing the computations. Limitations on using 2D correlation spectroscopy have been discussed by Czarnik-Matusewicz *et al.* [21] and Shashilov and Lednev [22].

There are a few instances in the literature where 2D correlation FT-IR spectroscopy is used to characterize oriented polymer systems. Unger and Siesler [23] used *in situ* rheo-optical FT-IR spectroscopy to investigate orientation effects for a blend of poly(3-hydroxybutyrate) and poly(ϵ -caprolactone). A combination of polarized FT-IR spectroscopy and 2D correlation spectroscopy was effectively used to determine that poly(ϵ -caprolactone) and poly(3-hydroxybutyrate) orient parallel and perpendicular to the stretching axis, respectively. Furthermore, poly(ϵ -caprolactone) orients prior to poly(3-hydroxybutyrate) during stretching and plays an important role in the mechanism of polymer chain alignment in this system. Nishikawa *et al.* [24] applied 2D correlation spectroscopy to elucidate the molecular changes associated with dynamic compression of uniaxially stretched poly(ethylene terephthalate). The analysis revealed that changes in the ester functional groups of the side chains occur before changes in the benzene rings composing the polymer backbone.

Two-dimensional correlation FT-IR spectra for $\text{P(EO)}_x\text{LiCF}_3\text{SO}_3$ ($x = 20, 15$, and 10) are presented in Figure 2. The 2D correlation analysis is only performed on the spectra recorded with infrared radiation polarized parallel to the stretch axis. Similar results are obtained if the perpendicular polarization is chosen. For clarity, the analysis is restricted to the 1359 and 1352 cm^{-1} bands. These two bands are effective probes of polymer chain alignment for the PEO and $\text{P(EO)}_3\text{LiCF}_3\text{SO}_3$ phases, respectively. The synchronous 2D correlation spectra consist of four positive intensity peaks, which are denoted by the correlation square in Figure 2: two autocorrelation peaks at $(1359, 1359)$ and $(1352, 1352)\text{ cm}^{-1}$ and two cross peaks appearing at $(1352, 1359)$ and $(1359, 1352)\text{ cm}^{-1}$. As expected, no autocorrelation

peaks are detected in the asynchronous 2D correlation spectra. Furthermore, cross peaks do not occur at the (1352, 1359) and (1359, 1352) cm^{-1} coordinates in the asynchronous plots. The 2D correlation spectra are in qualitative agreement for all three compositions investigated.

According to Noda *et al.* [20], cross peaks develop in a synchronous spectrum whenever changes between two separate bands occur in phase during the course of the applied perturbation. Spectral features that change in phase are further characterized by a lack of spectral intensity in the asynchronous spectrum at the same coordinates. Therefore, the appearance of positive cross peaks between the 1359 and 1352 cm^{-1} bands in the synchronous 2D spectra, coupled with the absence of spectral features in the asynchronous spectrum at those coordinates, suggests that the changes in those bands occur in phase. Since, the 1359 and 1352 cm^{-1} bands correspond to the PEO and $\text{P(EO)}_3\text{LiCF}_3\text{SO}_3$ phases, respectively, the immediate interpretation of the 2D correlation spectra is that the PEO and $\text{P(EO)}_3\text{LiCF}_3\text{SO}_3$ crystalline domains align at approximately the same rate when stretched approximately 3-fold.

3.3. Assessing polymer chain orientation

A quantitative assessment of polymer chain orientation induced by tensile stretching may be calculated from the dichroic ratio, R . If an absorbance band of an oriented polymer is measured with linearly polarized infrared radiation, the dichroic ratio may be defined as

$$R = \frac{A_{\parallel}}{A_{\perp}} \quad (6)$$

where $A_{\parallel}$ is the integrated band intensity measured when the radiation is polarized parallel to the stress field direction. The quantity $A_{\perp}$ has an analogous meaning for radiation polarized perpendicular to the stretch axis.

For polymer systems that have uniaxial symmetry (or effectively uniaxial symmetry), such as those described in this paper, the average orientation can be characterized in terms of the average value of the angle between the polymer axis of the structural repeat unit and the elongation direction, θ . There is a straightforward relationship between the dichroic ratio and the average of the second Legendre polynomial, which is expressed as

$$\langle P_2(\cos\theta) \rangle = \frac{1}{2} \{ 3\langle \cos^2\theta \rangle - 1 \} = \left(\frac{R-1}{R+2} \right) \left(\frac{1}{P_2(\cos\psi)} \right) \quad (7)$$

where ψ is the angle between the chain axis and the transition dipole moment of a particular normal mode of vibration. Values of ψ are summarized for the vibrational modes occurring between 1335 and 1375 cm^{-1} in Table 1. If the chains align parallel to the stretching axis, $\langle P_2(\cos\theta) \rangle$ has a value of 1, for perpendicular alignment a value of -1/2, and for random alignment a value of 0.

Calculated values of the orientation function are presented in Figure 3 for $\text{P(EO)}_x\text{LiCF}_3\text{SO}_3$ ($x = 20, 15$, and 10) as a function of strain. Only results for the 1352 and 1359 cm^{-1} bands are discussed in detail since those bands may be deconvoluted with a relatively high degree of confidence. In all cases, the $\text{P(EO)}_3\text{LiCF}_3\text{SO}_3$ domains exhibit some degree of orientational order within the as-cast polymer electrolytes. This is most likely caused by the

use of a draw-down bar to prepare uniform thin films. However, it is interesting that the casting procedure does not orient the PEO domains in the same manner.

Small values of strain (degree of elongation equal to 1.5 times the original length) produces essentially no changes in the orientation of the PEO and $\text{P}(\text{EO})_3\text{LiCF}_3\text{SO}_3$ phases for the O:Li = 20:1 sample. The $\text{P}(\text{EO})_3\text{LiCF}_3\text{SO}_3$ domains attain the same degree of orientation as the PEO domains in the O:Li = 15:1 material, while the values of the orientation function increases slightly for both phases in the 10:1 film. The orientation values for the PEO and $\text{P}(\text{EO})_3\text{LiCF}_3\text{SO}_3$ phases gradually approach 1.0 for all three polymer electrolyte compositions as the strain value is increased from 1.5 to 2.5, indicating that the polymer chains in the two phases become aligned along the stretch axis with increasing amount of strain. The relative rates of alignment for the pure PEO and the 3:1 compound within each polymer electrolyte composition are very similar, which is in agreement with the results from the 2D correlation FT-IR spectra. Elongation beyond 2.5 times the original length produces few changes in the average orientation of the polymer chains for either phase, irrespective of the sample composition. Nonetheless, the average orientation of the polymer chains in the PEO domains is higher than that of the $\text{P}(\text{EO})_3\text{LiCF}_3\text{SO}_3$ in all three compositions. Thus, the polymer chains within the PEO domains are slightly more oriented along the stretch axis than the polymer chains composing the $\text{P}(\text{EO})_3\text{LiCF}_3\text{SO}_3$ phase at strain values near 3.0.

There is no evidence from the 2D correlation spectra presented in Figure 2 that one phase orients before the other phase. Rather, the 2D correlation results and the calculated values of polymer chain orientation are consistent with both phases aligning to approximately the same degree as a function of strain, especially for strain values higher than 1.50. For a number of polymer systems, tensile stretching orients the polymer chains through a process of stress-induced melting followed by recrystallization of the newly aligned chains. In this mechanism, polymer chains are pulled from randomly oriented crystallites during stretching and then new crystalline domains form with the polymer chains directed along the stretch axis. This phenomenon is more likely to occur when a polymer is stretched at temperatures close to its melting point. In these experiments, the polymer electrolytes are stretched at room temperature, which is reasonably close to the melting point of PEO (ca. 65°C). The 2D correlation FT-IR spectra and quantitative measurements of polymer chain orientation presented in Figures 2 and 3 are consistent with a stretching-induced melt-recrystallization model. At intermediate values of strain (1.50 to 2.50 times the original length), polymer chains are pulled from both the PEO and $\text{P}(\text{EO})_3\text{LiCF}_3\text{SO}_3$ crystallites and aligned with the polymer helices parallel to the stretching direction. The polymer chains then crystallize into newly formed PEO and $\text{P}(\text{EO})_3\text{LiCF}_3\text{SO}_3$ crystalline domains.

Ionic conductivity is anisotropic in oriented polymer electrolytes, with higher values of ionic conductivity parallel to the stretch axis. At least two models for stress-induced conductivity enhancement exist in the literature. An early model of Dürr and co-workers [25] views the polymer electrolyte as being composed by two phases—highly conducting domains surrounded by poorly conducting boundaries. Conductivity enhancement is then explained through changes in the structure of these two phases as a function of stretching. Later work by Gitelman and co-workers [26-28] focused on a stochastic model of lithium ion conduction, in which barriers to lithium transport is modeled as loops in the helical structure of the polymer chains. The loops serve to impede lithium conduction under the influence of an external electric field by changing the course of lithium ion motion against the electric field. In this model, stretching is envisaged as reducing the number of PEO loops, thereby increasing conductivity through a reduction in the number of barriers to ion transport. The common feature to both models is that ion conduction is reasonably high within an individual crystalline domain, but the random arrangement of the crystalline domains in

solution-cast films produces a large number of barriers that impedes ion motion through the film.

Quantitative measurements of polymer chain orientation for both PEO and $\text{P(EO)}_3\text{LiCF}_3\text{SO}_3$ phases provide some support for the hypothesis that ionic conductivity enhancement is due to the alignment of the polymer chain helices. As discussed above, the PEO and $\text{P(EO)}_3\text{LiCF}_3\text{SO}_3$ domains become oriented through a process of stress-induced melt-recrystallization. If lithium ion conduction in crystalline polymer electrolytes is viewed as consisting of two major components (facile intra-chain lithium ion conduction and slow helix-to-helix inter-grain hopping), then alignment of the polymer helices will profoundly affect on the ion conduction pathways for these polymer electrolytes by reducing the number of inter-grain hops between $\text{P(EO)}_3\text{LiCF}_3\text{SO}_3$ domains required to migrate through the polymer electrolyte. In a stretched polymer electrolyte, a significant number of the PEO and $\text{P(EO)}_3\text{LiCF}_3\text{SO}_3$ domains recrystallize with the polymer helices oriented along the direction of the stress field. Thus, ions within the $\text{P(EO)}_3\text{LiCF}_3\text{SO}_3$ domains encounter fewer barriers to ion motion when an external electric field is applied parallel to the stretch direction compared to an electrolyte with a random distribution of chain orientations. Consequently, ionic conductivity is enhanced in the stretched samples along the stretch direction. In contrast, ionic conductivity measured perpendicular to the stretch axis is not increased because there are a relatively large number of inter-grain boundaries in the stretched materials perpendicular to the stretch direction. These boundaries impede lithium ion motion in a way that is similar to as-cast polymer films.

4. Conclusions

Stress-induced polymer chain orientation was investigated for the PEO- LiCF_3SO_3 family of polymer electrolytes. Vibrational bands due to the PEO and $\text{P(EO)}_3\text{LiCF}_3\text{SO}_3$ crystalline phases are identified and used to quantitatively assess the degree of polymer chain orientation for the respective phase as a function of strain. Two-dimensional correlation FT-IR spectra demonstrate that both phases align at the same rate as the samples are stretched to a strain value of ~ 3.00 . Furthermore, the average of the second Legendre polynomial provides a quantitative assessment of polymer chain organization for both phases. The polymer chains in all three samples become significantly aligned at intermediate values of strain (1.50 to 2.50). Minor changes in polymer chain organization are detected at higher values of strain, and the relatively high values of the orientation function suggest that the polymer domains are highly aligned near a strain of 3.00.

The 2D correlation FT-IR spectra and dichroic FT-IR spectra are consistent with the polymer chains becoming oriented through a stress-induced melt-recrystallization process, wherein polymer chains are pulled from randomly-oriented PEO and $\text{P(EO)}_3\text{LiCF}_3\text{SO}_3$ domains and recrystallize with the polymer helices oriented along the stretching direction. The recrystallization process affects the ion conduction pathways of the polymer electrolyte. Thus, ionic conductivity is enhanced through the reduction in the number of inter-chain barriers to lithium ion motion parallel to the stretch direction, which result from the alignment of the polymer chains within the crystalline domains.

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Fig. 1.

FT-IR spectra of a $\text{P(EO)}_{10}\text{LiCF}_3\text{SO}_3$ polymer electrolyte. The unpolarized spectra correspond to the as-cast films prior to sample stretching. The polarized spectra were recorded at a strain of 2.93 times the original length. Perpendicular (A) and parallel (B) refer to polarizer settings relative to the stretch direction. Curve fitting results and the simulated spectra are included for spectra recorded under both polarization settings.

Fig. 2. Synchronous and asynchronous 2D correlation FT-IR spectra for $\text{P(EO)}_x\text{LiCF}_3\text{SO}_3$, where $x = 10, 15$, and 20 , that have been stretched approximately 3-fold. The dotted lines denote the correlation square between the 1359 and 1352 cm^{-1} bands.

Fig. 3. Quantitative measurements of polymer chain orientation measured as a function of strain for P(EO)_xLiCF₃SO₃, where $x = 10, 15$, and 20 . The 1359 and 1352 cm^{-1} bands originate from the PEO and P(EO)₃LiCF₃SO₃ crystalline domains, respectively.

Table 1

Band assignments for the vibrational modes depicted in Figure 1.

Frequency/cm ⁻¹	Phase	Symmetry Species	IR Spectral Activity ^(a)
1376	P(EO) ₃ LiCF ₃ SO ₃	<i>B</i>	⊥
1366	P(EO) ₃ LiCF ₃ SO ₃	<i>B</i>	⊥
1359	PEO	<i>E₁</i>	⊥
1352	P(EO) ₃ LiCF ₃ SO ₃	<i>B</i>	⊥
1347	P(EO) ₃ LiCF ₃ SO ₃	<i>B</i>	⊥
1343	PEO	<i>A₂</i>	∥
1340	P(EO) ₃ LiCF ₃ SO ₃	<i>A</i>	∥

^(a) The ⊥ and ∥ symbols refer, respectively, to vibrations whose transition dipole moments are perpendicular (90°) and parallel (0°) with respect to the helical axis.