FTIR studies of PEMA/PVdF-HFP blend polymer electrolyte system incorporated with LiCF$_3$SO$_3$ salt

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A B S T R A C T
Poly[(ethyl methacrylate), PEMA and poly(vinylidenefluoride-co-hexafluoropropylene), PVdF-HFP have been chosen as hosts for the development of a polymer blend electrolyte system. Lithium trifluoromethanesulfonate (triflate), LiCF$_3$SO$_3$ is the lithium ion, Li$^+$ provider. The ratio of PEMA:PvDF-HFP in the blend is fixed at 70:30 in order to obtain transparent films with good mechanical stability. The polymers and LiCF$_3$SO$_3$ salt have been refluxed for 2 h at temperatures between 55 and 65 °C. The concentration of LiCF$_3$SO$_3$ salt has been varied from 0 to 40 wt.% using Fouriers transform infrared (FTIR) spectroscopy. It has been shown that blending between PEMA and PVdF-HFP has occurred from the changes in the CH$_2$ scissoring [$\delta$(CH$_2$)], asymmetrical O–C$_2$H$_5$ bending [$\gamma$(OC$_{2}$H$_5$)], CH$_2$ twisting [$\gamma$(CH$_2$)], C–O stretching of –COO– group [$\nu$(CO)], asymmetrical C–O–C stretching [$\nu$(OC–C)] and C–O stretching of –OC$_2$H$_5$ [$\nu$(C–O)] from PEMA as well as the symmetrical CF$_2$ stretching [$\nu$(CF$_2$)], $\alpha$-phase and the amorphous region of PVdF-HFP. Complexation occurs via the coordination of Li$^+$ ions with the oxygen atom in the carbonyl (–C=O) and ester (–COO–) groups of PEMA as well as with the fluorine atom in –CF$_2$ and –CF$_3$ groups in PVdF-HFP. Curve fitting of spectral bands in the symmetrical $\nu$(SO$_3^-$) stretching region in the polymer blend–salt complexes showed that free ions (1031–1032 cm$^{-1}$) and ion pairs (1040–1042 cm$^{-1}$) are present in samples incorporated with 10 wt.% LiCF$_3$SO$_3$ and above, while ion aggregates at 1049 cm$^{-1}$ are formed when 40 wt.% LiCF$_3$SO$_3$ is added into the polymer blend. The increase in the ionic conductivity at high salt contents could be explained by the greater amount of free ions as compared to ion pairs and ion aggregates.

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1. Introduction

Polymer electrolytes are potential candidates as a medium for charge transport in electrical double layer capacitors, rechargeable batteries, fuel cells and electrochromic devices. Polymer electrolytes are safe, flexible, mechanically stable and can offer higher energy density as compared to commercial liquid electrolytes. Polymer electrolytes consist of salts dissolved in solid polymers, and the polymer must contain a Lewis base which serves to coordinate the cations, thus promoting dissolution of the salt [1]. However, the cation-Lewis base bonding must be labile to allow ion mobility [2]. Poly(methyl methacrylate), PMMA and poly(ethyl methacrylate), PEMA are methacrylic ester polymers. PEMA has excellent chemical resistance, high surface resistance and offers high optical transparency [3]. PMMA electrolytes have been widely investigated by researchers due to its high ambient temperature ionic conductivity, which resembled that of liquid electrolytes. PEMA is reported [4] to exhibit higher mechanical strength than PMMA. PVC/PEMA-LiPF$_6$-EC-PC displayed higher elastic modulus and elongation as compared to PVC/PMMA-LiPF$_6$-EC-PC polymer electrolyte. High transparency, sufficient mechanical strength, elasticity and good adhesion onto substrates [3] make PEMA suitable for use as a host for ionic conduction in electrochromic devices. On the other hand, poly(vinylidenefluoride-hexafluoropropylene), PVdF-HFP consisting of crystalline VdF and amorphous HFP units allows ionic conductivity to occur with ease [5]. PVdF-HFP has high dielectric constant ($\varepsilon$ $\approx$ 8.4, and thus can accommodate high concentration of charge carriers.

PEMA contains electron pairs at the oxygen atoms of C=O and C–O–C$_2$H$_5$ groups [6] while fluorine (F) atoms in PVdF-HFP have electron pairs that can coordinate with the cation of a salt [7] to form polymer–salt complexes. From the change in the position, shape and intensity of the bands representing the polar group, complexation between an inorganic salt and polymer host can be confirmed. Lithium trifluoromethanesulfonate (LiCF$_3$SO$_3$) or lithium triflate is widely used as a doping salt to provide lithium ions (Li$^+$) for ionic conduction in polymer electrolytes. Fig. 1 shows the chemical structure of PEMA, PVdF-HFP and lithium triflate.

In this study, PEMA and PVdF-HFP were chosen so as to develop a polymer blend electrolyte system with LiCF$_3$SO$_3$ as salt. Acetone
was used as solvent. The objectives of this study are (i) to show miscibility between PEMA and PVdF-HFP, (ii) to investigate the complexation sites where Li+ ions bind to the polymers and (iii) to study the effect of ionic association on the ionic conductivity of the polymer blend−salt complexes by FTIR analyses.

To the authors’ knowledge, there are no reports on the literature about transparent blended polymer electrolytes based on PEMA/PVdF-HFP. From this investigation, the authors hope to shed some light on understanding the conduction mechanism in such electrolytes.

2. Experimental

2.1. Materials

Poly(ethyl methacrylate) (PEMA, MW = 515,000, CAS = 9003-42-3, Aldrich) in powder form, poly(vinylidenefluoride-co-hexafluoropropylene) (PVdF-HFP, CAS = 9011-17-0, Aldrich) in pellet form, and acetone (J.T. Baker) were used as received. Lithium trifluoromethanesulfonate (or triflate) ([LiCF3SO3], Aldrich) was heated at 130 °C for 3 h to eliminate any moisture prior to use.

2.1.1. Preparation of PEMA/PVdF-HFP blend polymer electrolyte films

PEMA/PVdF-HFP blend polymer electrolyte films were prepared using the reflux method. The PEMA/PVdF−HFP ratio is 70:30. Different amounts (10, 20, 30 and 40 wt.%) of LiCF3SO3 salt were added to the polymer solution in acetone. The mixtures were magnetically stirred vigorously at 55–65 °C for 2 h to form PEMA/PVdF−HFP polymer blend electrolytes. The transparent resultant solutions consisting of salt and the two polymers were cast onto glass plates and dried at 45 °C in an oven for several hours to allow the complete evaporation of the acetone until solvent-free films were formed adhered onto the glass plates. Upon cooling at room temperature, the mechanically stable transparent films were carefully peeled from the glass plates and stored in the desiccator for several days for further drying before characterization. The thickness of the films is in the range from 25 to 30 μm. Table 1 shows the composition of polymer blend samples and their respective designation.

2.2. Characterization techniques

2.2.1. Fourier transform infrared (FTIR) spectroscopy

FTIR spectroscopy was carried out on all polymer electrolyte films with thickness ranging from 25 to 30 μm using the Thermo Scientific Nicolet iS5 Smart ITR in the transmission mode over the wavenumber range from 4000 to 650 cm⁻¹ at a resolution of 1 cm⁻¹.

2.2.2. Curve−fitting procedures

Several wavenumber regions of the IR spectra contained overlapping of IR bands due to several closely placed bands which are contributed by different components (i.e., PEMA, PVdF−HFP, LiCF3SO3) present in a sample. In order to resolve overlapping bands within the IR region of interest, all peaks present in PEMA, PVdF−HFP, LiCF3SO3 and PEMA/PVdF−HFP blend have been identified. This allowed us to know the number of IR bands and their respective wavenumbers within an IR region.

In our work, a series of deconvolution of IR bands were performed using OMNIC software. The deconvolution was carried out by fixing the number and line shape, and allowing band parameters such as full width at half maximum (FWHM), area, intensity and band shape to vary without constraints during the iteration [8]. The Gaussian/Lorentzian function was employed to fit the selected bands of the polymer blend and polymer blend−salt samples [9–11] and all the deconvoluted spectra were best fitted using a constant baseline. All resultant peaks created through curve−fitting match the original spectrum when added together.

If PEMA and PVdF−HFP have interacted with each other to form a blend, the infrared spectrum of PEMA/PVdF−HFP blend film will show changes in the position, intensity and shape of the IR bands from the original characteristic bands of both polymers. New bands may form and some original bands may disappear. If PEMA and PVdF−HFP are not suitable to form a blend with each other, the IR spectrum of PEMA/PVdF−HFP blend film will show the original vibrational bands of both PEMA and PVdF−HFP. Complexation between polymer blend and salt can be investigated through changes in IR bands of polar functional groups which belong to PEMA and PVdF−HFP, and also changes in the vibrational frequencies of LiCF3SO3.

2.2.3. Electrochemical impedance spectroscopy (EIS)

Impedance of the samples was determined using the Hioki 3531 Z HiTester. The measurements were done in the frequency range from 50 to 1 MHz at ambient temperature. The impedance studies were carried out by sandwiching the polymer electrolyte film between two stainless steel (SS) electrodes under spring pressure. The thickness of each sample was measured using a micrometer screw gauge. The imaginary impedance (Z") was plotted against the real impedance (Z') and the bulk resistance was obtained from the intercept with the real-axis. The ionic conductivity, σ in S cm⁻¹ of each sample was calculated using the following equation:

\[ \sigma = \frac{l}{R_b A} \]

where l is the thickness of the film, Rb is the bulk resistance and A is the area of electrolyte−electrode contact.
3. Results and discussion

3.1. Interactions between PEMA and PVdF-HFP

Some reports on infrared studies of PEMA can be obtained from the literature [12, 13]. The chemical structure of PEMA is quite similar to PMMA as the only difference between them is the chain length of alkyl group bonded to the methacrylate group. PMMA contains the methoxy group (–OCH3) bonded to the carbonyl (C=O) carbon while the ethoxy group (–OC2H5) is found in PEMA. Hence the vibrational modes of PMMA are also useful in the study of PEMA structure since the former is the most widely studied methacrylate-based polymer. The vibrational frequencies of PMMA can be found in the literature [6, 14–16].

In this work, the characteristic peaks of PEMA due to the carbonyl stretching \( \nu(C=O) \), CH2 scissoring \( \delta(CH_2) \), asymmetrical O–C=O stretching \( \nu(CH_2) \), CH2 twisting \( \gamma(CH_2) \) and asymmetric stretching vibration of C–O–C \( \nu_a(CH_2) \) are observed at 1723, 1476, 1446, 1388 and 1142 cm\(^{-1}\), respectively. In the spectrum of pure PEMA film, bands observed at 2991, 2942 and 2927 cm\(^{-1}\), have been attributed to the overlap of C–H stretching vibrations of methylene (–CH2) and ethylene (–OCH2) groups, as reported by Venkatesh and co-workers [17]. According to Hummel [18], bands which are located between 1150 and 1260 cm\(^{-1}\) of PMMA belong to the C–O–C stretching mode of the ester group. In this work, the same bands belonging to PEMA are located in the region 1265–1142 cm\(^{-1}\). The bands attributable to \( \nu(CO) \) stretching modes of –COO– and –OCH2 groups are found at 1265 and 1175 cm\(^{-1}\) respectively, while two bands located at 1249 and 1142 cm\(^{-1}\) come from the asymmetric stretch of C–O–C \( \nu_a(CH_2) \) [19–21]. The FTIR spectra of pure PEMA, pure PVdF-HFP and pure PEMA/PVdF-HFP blend film in the region 3800–2800 cm\(^{-1}\) are shown in Fig. 2((a–i), (ii) and (iii)) and the region 1800–800 cm\(^{-1}\) are shown in Fig. 2((b–i), (ii) and (iii)). The spectra in Fig. 2(a) and (b) and numbered iv–viii are that of LiCF3SO3 salt and PEMA/PVdF-HFP (70:30) films incorporated with different concentrations of LiCF3SO3 respectively.

C–H stretching vibrations of PVdF-HFP are located at 2989 and 2911 cm\(^{-1}\). The characteristic peaks of PVdF-HFP, i.e. CH2 wagging \( \delta(CH_2) \), antisymmetric CF2 stretch \( \nu_a(CF_2) \) and CF2 out-of-plane deformation \( \gamma(CF_2) \) absorb IR radiation at 1402, 1179 and 1069 cm\(^{-1}\) [22], respectively. The bands located at 986 and 761 cm\(^{-1}\) correspond to the \( \alpha \)-phase while the band at 842 cm\(^{-1}\) is assigned to the \( \beta \)-phase of PVdF-HFP [23]. The amorphous band of PVdF-HFP is observed at 873 cm\(^{-1}\). Both \( \alpha \) and \( \beta \) phases are two of the types of crystalline phases of PVdF [24–27] while the amorphous region is believed to come from the HFP phase of PVdF-HFP.

Polymers can interact with one another to form secondary bonding, i.e. hydrogen bonding. PEMA contains oxygen (O) atoms which may bond with hydrogen (H) atoms of PVdF-HFP, while fluorine (F) atoms in PVdF-HFP may also be attracted to H atoms in PEMA. Therefore, miscibility between PEMA and PVdF-HFP can be investigated by FTIR through observing the changes of \( \nu(CH) (\sim 2900 \text{cm}^{-1}) \), \( \nu(CO) (\sim 1140–1160 \text{cm}^{-1}) \), \( \nu(C=O) (\sim 1720 \text{cm}^{-1}) \) vibrations of PEMA, and \( \nu(CH) (\sim 2900 \text{cm}^{-1}) \), \( \nu_a(CF_2) (\sim 1170 \text{cm}^{-1}) \) and \( \gamma(CF_3) \) vibrations (\sim 1060 cm\(^{-1}\)) as well as the amorphous region (\sim 880 cm\(^{-1}\)) of PVdF-HFP. Upon blending PEMA with PVdF-HFP to form the polymer blend, changes to the position, shape and intensity of peaks are observed. The changes in the IR spectra between pure PEMA and PVdF-HFP with PEMA/PVdF-HFP (70:30) blend are shown in Fig. 3.

In the blended film, the bands located at 2989 and 2924 cm\(^{-1}\) are formed through the merging and overlapping between C–H bands of both PEMA and PVdF-HFP, Fig. 3((a–i), (ii) and (iii)). This observation indicates the interaction between the C–H stretching vibrations of PEMA and PVdF-HFP. The peak due to carbonyl (C=O) group from PEMA remained at 1723 cm\(^{-1}\) but appeared with lower intensity, in proportion to the composition of PEMA (70 wt%) in the blend. Bands at 1476 and 1446 cm\(^{-1}\) assigned to the \( \delta(CH_2) \) and \( \gamma(CH_2) \) vibrations of PEMA shifted to 1485 and 1448 cm\(^{-1}\), respectively when blended with PVdF-HFP. Infrared bands located at 1388 due to \( \tau(CH_2) \) and 1365 cm\(^{-1}\) from PEMA merged with the bands at 1402 and 1385 cm\(^{-1}\) from PVdF-HFP resulting in several bands in the spectrum of the blend at 1399, 1391 and 1372 cm\(^{-1}\), which could be observed in Fig. 4((a–i), (ii), (iii)). Besides that, the different IR vibrational modes of the ester group in PEMA at 1265 due to \( \nu(CH) \) of –COO– group and 1249 cm\(^{-1}\) of \( \nu_a(CF_2) \) shifted to 1272 and 1241 cm\(^{-1}\) respectively. The \( \nu(CO) \) stretching vibration from the –OCH2 group in PEMA at 1175 cm\(^{-1}\) merged with \( \nu_a(CF_2) \) of PVdF-HFP at 1179 cm\(^{-1}\) to form a small peak at 1176 cm\(^{-1}\). The other band due to \( \nu_a(CO) \)

![Fig. 2. FTIR spectra in the wavenumber region (a) 3800–2800 cm\(^{-1}\) and (b) 1800–800 cm\(^{-1}\) of (i) PEMA, (ii) PVdF-HFP, (iii) S0, (iv) S10, (v) S20, (vi) S30, (vii) S40 and (viii) LiCF3SO3.](image-url)
mode of PEMA which is located at 1142 cm\(^{-1}\) shifted to 1145 cm\(^{-1}\) as can be observed in the spectrum of the blend. \textbf{Fig. 4}.(b-i), (ii), (iii)). Vibrational bands of PVdF-HFP at 1179, 1069 and 842 cm\(^{-1}\) (\(\beta\)-phase of PVdF-HFP) as well as the band at 1071, 969 and 953 cm\(^{-1}\) belonging to the spectrum of PEMA disappeared in the polymer blend. The bands attributed to \(\alpha\)-phase and the amorphous region of PVdF-HFP at 986 and 873 cm\(^{-1}\) shifted to 984 and 885 cm\(^{-1}\), respectively. Other characteristic bands of PEMA and PVdF-HFP were also observed to shift from its original wavenumbers when blended together. These include bands at 1103 and 862 cm\(^{-1}\) of PEMA that shifted to 1106 and 860 cm\(^{-1}\). Assignments of IR vibrational wavenumber for PEMA, PVdF-HFP and PEMA/PVdF-HFP (70:30) or 50 are shown in Table 2.

The occurrence of band shifts in the polymer blend due to PEMA and PVdF-HFP from their original wavenumbers indicated that interaction had occurred between the two polymers, and that both PEMA and PVdF-HFP are compatible to form a polymer blend.

### 3.2. Interactions between PEMA/PVdF-HFP blend and LiCF\(_3\)SO\(_3\)

In order to investigate the sites where coordination of lithium ions had taken place in the blend polymer electrolytes, changes in the infrared spectra of PEMA and PVdF-HFP respectively are observed after being incorporated with 30 wt.% of lithium triflate salt. The IR spectra of 70 wt.% PEMA–30 wt.% LiCF\(_3\)SO\(_3\) and 70 wt.% PVdF-HFP–30 wt.% LiCF\(_3\)SO\(_3\) films were used as references and compared with the spectrum of 70 wt.% PEMA/PVdF-HFP–30 wt.% LiCF\(_3\)SO\(_3\) or S30. Table 3 shows the IR vibrational frequencies of PEMA/PVdF-HFP blend polymer electrolyte films incorporated with different amounts of LiCF\(_3\)SO\(_3\) salt.

The triflate ion is very sensitive to its state of coordination. Changes to its environment can be detected by different IR vibrational bands [28]. In our work, lithium triflate exhibits fundamental vibrational modes at 1252, 1231, 1195 and 1044 cm\(^{-1}\) due to asymmetrical SO\(_3\) stretching [\(\nu_1(SO_3)\)], symmetrical CF\(_3\) stretching...
[\nu_2(CF_3)], asymmetrical CF\_3 stretching [\nu_\alpha(CF_3)] and symmetrical \( \text{SO}_2 \) stretching [\nu_\beta(\text{SO}_2)] vibrational modes, respectively [15,29]. Other characteristic bands of the salt are observed around 3530, 1293 and 1649 cm\(^{-1}\). These characteristic peaks were also reported in [6]. Fig. 5 shows the main IR vibrational bands present in lithium triflate in the wavenumber range between 950 and 1350 cm\(^{-1}\).

Upon the introduction of lithium triflate salt into the PEMA/PVdF-HFP blend, several characteristic bands due to triflate anion were introduced into the IR spectra of the polymer electrolytes with shifted wavenumbers. The band of \( \nu_2(\text{SO}_3) \) of pure LiCF\_3SO\_3 was observed at 1044 cm\(^{-1}\) and appeared as peaks at wavenumbers at 1031–1032 cm\(^{-1}\) with increased intensities at higher salt contents in the polymer blend–salt complexes. According to Alia et al. [30], the \( \nu_2(\text{SO}_3) \) band of LiCF\_3SO\_3 when dissolved in acetone is located at 1034 cm\(^{-1}\). This is in agreement with our work. The \( \nu_2(CF_3) \) band originally located at 1231 cm\(^{-1}\) appeared in S20, S30 and S40 at 1229 cm\(^{-1}\). The band due to in-plane deformation of CF\_3 [\( \delta(CF_3) \)] of lithium triflate was observed from 773 cm\(^{-1}\) to lower wavenumbers at 763 cm\(^{-1}\) in S20, and 762 cm\(^{-1}\) in both S30 and S40 samples with increased intensities at higher salt contents. The appearance of characteristic bands due to triflate anion in polymer blend–salt complexes indicates that the incorporation of the lithium salt into the polymer blend has been achieved.

Fig. 6 depicts the IR spectra of (a) S0, (b) S10, (c) S20, (d) S30, (e) S40, (f) 70 wt.% PEMA–30 wt.% LiCF\_3SO\_3, (g) 70 wt.% PVdF-HFP–30 wt.% LiCF\_3SO\_3 and (h) pure lithium triflate in the region 1800–1600 cm\(^{-1}\).

The peak at 1721–1723 cm\(^{-1}\) is attributed to the \( \nu(C=O) \) band in PEMA. The fact that this peak did not show much change from its original position in pure PEMA and in pure PEMA/PVdF-HFP blend implies that complexation must have mainly occurred at the oxygen atom in the –OC\_2H\_5 ethylene group and/or the oxygen in the –COO– group. In the PEMA/PVdF-HFP–LiCF\_3SO\_3 complexes, the peak due to LiCF\_3SO\_3 salt which is located at 1649 cm\(^{-1}\) was found to appear at 1663, 1666, 1663 and 1665 cm\(^{-1}\) in S10, S20, S30 and S40, respectively. The intensity of the band became more prominent when the amount of salt was increased.

### Table 2

Assignment of IR vibrational modes in PEMA, PVdF-HFP and PEMA/PVdF-HFP (70:30) blend films.

<table>
<thead>
<tr>
<th>Assignment of bands</th>
<th>Wavenumber (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PEMA</td>
</tr>
<tr>
<td>( \nu(CH) )</td>
<td>2991, 2942, 2927</td>
</tr>
<tr>
<td>( \nu(C=O) ) of PEMA</td>
<td>1723</td>
</tr>
<tr>
<td>( \delta(CH_2) ) of PEMA</td>
<td>1476</td>
</tr>
<tr>
<td>( \gamma(OC=CH) ) of PEMA</td>
<td>1446</td>
</tr>
<tr>
<td>( \omega(CH_2) ) of PVdF-HFP</td>
<td>–</td>
</tr>
<tr>
<td>( \tau(CH_2) ) of PEMA</td>
<td>1388</td>
</tr>
<tr>
<td>Characteristic band of PVdF-HFP</td>
<td>–</td>
</tr>
<tr>
<td>( \nu(COO) ) of –COO– group of PEMA</td>
<td>1265</td>
</tr>
<tr>
<td>( \nu(COC) ) of PEMA</td>
<td>1249</td>
</tr>
<tr>
<td>( \nu(CF_2) ) of PVdF-HFP</td>
<td>–</td>
</tr>
<tr>
<td>Assignement of –OC_2H_5 group of PEMA</td>
<td>1175</td>
</tr>
<tr>
<td>( \nu(COC) ) of PEMA</td>
<td>1142</td>
</tr>
<tr>
<td>Characteristic band of PEMA</td>
<td>1025</td>
</tr>
<tr>
<td>( \alpha ) phase of PVdF-HFP</td>
<td>–</td>
</tr>
<tr>
<td>( \beta ) phase of PVdF-HFP</td>
<td>–</td>
</tr>
<tr>
<td>Amorphous region of PVdF-HFP</td>
<td>–</td>
</tr>
</tbody>
</table>

### Table 3

FTIR vibrational modes of PEMA/PVdF-HFP blend polymer electrolytes incorporated with different wt.% of LiCF\_3SO\_3.

<table>
<thead>
<tr>
<th>Assignment of bands</th>
<th>Wavenumber (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S0</td>
</tr>
<tr>
<td>( \nu(CH) )</td>
<td>2989, 2924</td>
</tr>
<tr>
<td>( \nu(C=O) ) of PEMA</td>
<td>1723</td>
</tr>
<tr>
<td>( \delta(CH_2) ) of PEMA</td>
<td>1485</td>
</tr>
<tr>
<td>( \gamma(OC=CH) ) of PEMA</td>
<td>1448</td>
</tr>
<tr>
<td>( \omega(CH_2) ) of PVdF-HFP + ( \tau(CH_2) ) of PEMA</td>
<td>1389</td>
</tr>
<tr>
<td>Characteristic band of LiCF_3SO_3</td>
<td>–</td>
</tr>
<tr>
<td>( \nu(COO) ) of –COO– group of PEMA</td>
<td>1272</td>
</tr>
<tr>
<td>( \nu(SO_2) ) of LiCF_3SO_3</td>
<td>–</td>
</tr>
<tr>
<td>( \nu(COC) ) of PEMA</td>
<td>1241</td>
</tr>
<tr>
<td>( \nu(CF_2) ) of LiCF_3SO_3</td>
<td>–</td>
</tr>
<tr>
<td>( \nu(CF_2) ) of PVdF-HFP + ( \nu(COO) ) of –OC_2H_5 group of PEMA</td>
<td>1176</td>
</tr>
<tr>
<td>( \nu(COC) ) of PEMA</td>
<td>1145</td>
</tr>
<tr>
<td>Characteristic band of PEMA</td>
<td>1106</td>
</tr>
<tr>
<td>( \nu(SO_3) ) ion aggregates of LiCF_3SO_3</td>
<td>–</td>
</tr>
<tr>
<td>( \nu(SO_3) ) ion pairs of LiCF_3SO_3</td>
<td>–</td>
</tr>
<tr>
<td>( \nu(SO_3) ) free ions of LiCF_3SO_3</td>
<td>–</td>
</tr>
<tr>
<td>( \alpha ) phase of PVdF-HFP</td>
<td>984</td>
</tr>
<tr>
<td>Amorphous region of PVdF-HFP</td>
<td>885</td>
</tr>
<tr>
<td>( \delta(CF_3) ) of LiCF_3SO_3</td>
<td>773</td>
</tr>
</tbody>
</table>
order to prove that the band existed in S10, the IR spectrum was
deconvoluted as shown in the inset of Fig. 6(b).

The increase in intensity of the vibrational bands due to triflate
anion with increasing amount of salt indicated the increase in the
number of free ions with addition of salt [31]. This peak is absent
in both pure PEMA and PVdF-HFP films. In 70 wt.% PEMA-30 wt.%
LiCF3SO3 and 70 wt.% PVdF-HFP-30 wt.% LiCF3SO3 films, this band
shifted to 1671 and 1647 cm\(^{-1}\) respectively. Li\(^{+}\) ions are more
labile and therefore are more free to move in the PVdF-HFP system
than in the PEMA system. This is because the conductivity of 70 wt.%
PVdF-HFP-30 wt.% LiCF3SO3 at 5.65 \times 10^{-6} S cm\(^{-1}\) is higher
than that obtained at 9.18 \times 10^{-6} S cm\(^{-1}\) in 70 wt.% PEMA-30 wt.%
LiCF3SO3 sample. The higher conductivity exhibited by the PVdF-
HFP system implies that the complexed Li\(^{+}\) ions are less strongly
bonded to the polymer as compared to that in the PEMA system.
This is possibly the reason why the band originally located at
1649 cm\(^{-1}\) was upshifted in the PEMA system and downshifted in
the PVdF-HFP system.

In order to ascertain which oxygen atom mostly takes part in
complexation with the cation of the salt, we firstly note that the position
of the \(\nu(C=O)\) band at 1723 cm\(^{-1}\) in the blend did not shift and did not change in intensity when added with 10 wt.% of
LiCF3SO3. Complexation did occur since the 1649 cm\(^{-1}\) band shifted
to 1663 cm\(^{-1}\) as proven in Fig. 6(b). The fact that the \(\nu(C=O)\) band
did not shift implies that Li\(^{+}\) ion did not coordinate at the oxygen
atom of the carboxyl group. The \(\nu(C=O)\) band was found at 1722 cm\(^{-1}\) in both S20 and S30 samples. This band only shifted
beyond the resolution of the spectrophotometer when 40 wt.% of
lithium triflate has been added to the blend (S40) and this shift
was only 2 cm\(^{-1}\). However, it is also noted that the intensity of the
band increased with the salt content. The increase in intensity of the
\(\nu(C=O)\) band observed in S20, S30 and S40 is also an indication
that a greater amount of Li\(^{+}\) ions have complexed with the oxygen
atom in C=O upon increase in salt content. The shift of the
\(\nu(C=O)\) band to lower wavenumbers suggested that Li\(^{+}\) ions from

Kumutha and Alias [32] also observed a new band around
1643–1645 cm\(^{-1}\) which formed upon the addition of lithium
triflate salt into MG30 (polysisoprene grafted with PMMA) sample,
and tended to become more intense as the amount of salt
increased. Formation of the new band was attributed to the coordinate
of Li\(^{+}\) to C=O group of PMMA in MG30 [32]. In our
work, the band located around 1649–1665 cm\(^{-1}\) was found to form
in PEMA/PVdF-HFP-LiCF3SO3 complexes. This band is present at
1647 cm\(^{-1}\) when PVdF-HFP sample was added with 30 wt.% of
the triflate salt, Fig. 6(g). Appearance of this band in the 70 wt.% PVdF-
HFP-30 wt.% LiCF3SO3 polymer electrolyte clearly shows that the band
is attributed to the vibrational mode of the triflate ion, and
not due to the coordination of Li\(^{+}\) to carbonyl group.

Fig. 7 depicts the IR bands of polymer blend–salt complexes situ-
ated in the region 1210–1110 cm\(^{-1}\). In PEMA/PVdF-HFP blend films,
the band due to \(\nu_{a}(COC)\) band from the ester group which was origi-
nally located at 1145 cm\(^{-1}\) shifted to 1148 cm\(^{-1}\) in S10, 1153 cm\(^{-1}\)
in S20 and became a shoulder at 1155 cm\(^{-1}\) in S30, Fig. 8(a)–(d). In
S40, the band seemed to disappear as shown in Fig. 7(e). How-
ever, curve-fitting results showed that the band due to \(\nu_{a}(COC)\) band exists in S40, but is superimposed by the highly intense peak
located at 1176 cm\(^{-1}\), Fig. 7(e). The peak at 1176 cm\(^{-1}\) is formed from
the combination between \(\nu_{a}(CF_{2})\) vibration of PVdF-HFP at
1179 cm\(^{-1}\) and \(\nu(C=O)\) vibrational band due to \(-OC_{2}H_{5}\) group of
PEMA at 1175 cm\(^{-1}\).
This upshift of wavenumbers implied that coordination of lithium salt had occurred at the oxygen atom of C–O–C bond in PEMA/PVdF-HFP–LiCF$_3$SO$_3$ electrolyte films. IR spectrum of PEMA film added with 30 wt.% of LiCF$_3$SO$_3$ salt showed that the $\nu_{\text{as}}$(COC) band of PEMA shifted to higher wavenumbers from 1142 to 1150 cm$^{-1}$ as compared to pure PEMA, Fig. 7. Other vibrational modes related to the C–O bond of PEMA also manifested large shifts to higher wavenumbers when incorporated up to 40 wt.% LiCF$_3$SO$_3$ such as the other $\nu_{\text{as}}$(COC) band and $\nu$(CO) of –COC– group up to 10 and 11 cm$^{-1}$, respectively (Table 3).

This indicated that coordination of Li$^+$ ions does occur at the oxygen atom of the –OC$_2$H$_5$ group present in PEMA. Ramesh et al. [6] also reported downshift of $\nu$(C=O) band of PMMA from 1732 to 1726 cm$^{-1}$ and upshift of the $\nu_{\text{as}}$(COC) band from 1150 to 1168 cm$^{-1}$ in poly(vinyl chloride) (PVC)/poly(methyl methacrylate) (PMMA)–LiCF$_3$SO$_3$ complexes, which were attributed to the interaction between Li$^+$ and the oxygen atoms in PMMA. This shows that coordination of Li$^+$ ions to oxygen atoms at both C=O and C–O–C bonds could occur simultaneously in PEMA polymer present in our polymer blend system.

Comparedly, Li$^+$ ions coordinate at the oxygen atom located at the –COC– group rather than at the C=O group of PEMA, as shown in both PEMA/PVdF-HFP–LiCF$_3$SO$_3$ and 70 wt.% PEMA–30 wt.% LiCF$_3$SO$_3$ samples. In our work, the $\nu$(C=O) band of PEMA shifted only slightly (1–2 cm$^{-1}$) from its original position upon the addition of lithium salt while the $\nu_{\text{as}}$(COC) band demonstrated a larger shift (~10 cm$^{-1}$), as shown in S30, Fig. 7(d). Similarly, Ramesh et al. [6] also obtained larger IR wavenumber shift for C–O–C bond (18 cm$^{-1}$) as compared to the C=O group (6 cm$^{-1}$). However, inorganic salt does not necessarily interact with the C=O group of polymers due to its high polarity.

This phenomenon was reported by Sim et al. [33] whereby FTIR studies showed the addition of lithium perchlorate (LiClO$_4$) salt into polyacrylate (PAA)/poly(ethylene oxide) (PEO) blend system shifted the ester C–O band, and not the C=O band of the PAA. In this research, the band due to C–O–C bond shifted from 1145 to 1148 cm$^{-1}$ although no wavenumber shift was observable for C=O band in S10. This implies that lithium salt tends to coordinate to the oxygen atom of C–O–C bond.

The tendency of the coordination of lithium ions to occur at the ester C–O–R (where R = CH$_3$, C$_2$H$_5$, etc.) of polymer based on acrylics could be due to the freedom of rotation about a single-bond, which in this case is the C–O–C bond of PEMA, in contrast to the restricted coordination about the double bonded C=O group. Although both C=O and C–O–C bonds in PEMA contain two lone pairs of electrons to act as coordination sites to bind with Li$^+$ ions, respectively, the ability of C–O–C bond to undergo rotation provides it the flexibility to expose lone pair electrons to Li$^+$ ions and facilitate complexation to occur. Rotation about the C–O bond allows the ester group to exist as the syn- and anti-conformers. Hence, more Li$^+$ can coordinate with the oxygen atom at the C–O–C bond rather than at the C=O group. Fig. 9 shows the possible rotation about the C–O–C bond of PEMA to produce two different conformers of the ester group.

Upon the addition of lithium triflate salt, the IR spectra of PEMA/PVdF-HFP films showed that the wavenumber of the band shifted from the original location at 1176–1175 cm$^{-1}$ in S10 and 1173 cm$^{-1}$ in S20 with tremendous increase in intensity, Fig. 7(a)–(c). This band then returned to its original position at 1176 cm$^{-1}$ for S30, Fig. 7(d) and remained unaffected in S40. Fig. 8(a) and (b) shows that the band at 1175 cm$^{-1}$ which is attributed to $\nu$(CO) vibrational band of O–C$_2$H$_5$ group remained
at 1175 cm$^{-1}$ but increased in intensity when incorporated with 30 wt.% of LiCF$_3$SO$_3$. The same phenomenon was observed with PVdf-HFP sample whereby the band at 1179 cm$^{-1}$ due to the $\nu_2$(CF$_2$) vibration of PVdf-HFP appeared to be more intense but remained at the same position when incorporated with 30 wt.% of LiCF$_3$SO$_3$. \textbf{Fig. 8}(b). The changes in the wavenumbers of the band comprised of both $\nu_2$(CF$_2$) vibration of PVdf-HFP and $\nu$(CO) vibrational band of PEMA suggested that coordination could have occurred at the fluorine (F) atoms of CF$_2$ group and oxygen (O) atom of C–O group belonging to PVdf-HFP and PEMA, respectively.

In the region between 1200 and 1340 cm$^{-1}$, several vibrational bands belonging to PEMA and LiCF$_3$SO$_3$ superimposed on one another to form a broad band composed of few components which increased in intensity from low to high content of salt. In \textbf{Fig. 10}, the deconvolution of IR spectra of the wavenumber region showed that the characteristic bands of lithium triflate at 1293 cm$^{-1}$, 1252 cm$^{-1}$ of $\nu_3$(SO$_3$) and 1232 cm$^{-1}$ due to $\nu_2$(CF$_3$) of the salt were introduced into the polymer blend system when incorporated with LiCF$_3$SO$_3$ in S10, S20, S30 and S40. The band due to $\nu_2$(CF$_3$) of LiCF$_3$SO$_3$ was observed to remain at its position at 1229 cm$^{-1}$ with increased intensity as the salt content was increased from 10 to 40 wt.%. The triflate bands shifted in position and grew in intensity with increasing salt content. Two bands at 1265 cm$^{-1}$ and 1249 cm$^{-1}$ in S0 attributed to the different vibrations of the PEMA ester group were observed to shift to higher IR wavenumbers and became very intense. This could be caused by the interactions between Li$^+$ ions and the partially negative oxygen of the ester group.

\textbf{Fig. 11}(a) and (b) illustrates the vibrational frequencies between 1350 and 1450 cm$^{-1}$, and 1000 and 1100 cm$^{-1}$. Peaks at 1394 cm$^{-1}$ and 1069 cm$^{-1}$ due to $\omega$(CH$_2$) and $\gamma$(CF$_3$) vibrational bands of PVdf-HFP shifted to higher wavenumbers of 1404 and 1079 cm$^{-1}$, respectively. The peak located at 1034 cm$^{-1}$ comes from the vibrational mode of $\nu_3$(SO$_3$) of lithium triflate. At lower wavenumber region, the band due to the amorphous region of PVdf-HFP shifted slightly to lower wavenumbers from 885 to 883, 882, 881 and 882 cm$^{-1}$ in S10, S20, S30 and S40, respectively. With increasing salt content, this band was observed to become sharper and increase in intensity, which indicates that more Li$^+$ ions interact with the amorphous region of PVdf-HFP. This implies that interaction had taken place between lithium salt with the $\omega$(CH$_2$) and $\gamma$(CF$_3$) vibrational bands as well as the amorphous region of PVdf-HFP. The shift of $\omega$(CH$_2$) band could be due to the change in environment of C–H bond caused by the coordination of Li$^+$ to fluorine atoms in PVdf-HFP.
blend. is group on /ETB of 3.3. 30 tents. ions of the content in /ETB line a(COC), merely –COC– wt.%.

The extent of coordination to the oxygen atom of C=O group can be observed through the changes (i.e. wavenumber and intensity) of the ν(C=O) band, while coordination to the oxygen atom of –COC– group can be studied through changes to the νa(COC), ν(CO) of –OC2H5 group and ν(CO) of –COO– group of PEMA. The νa(CF2) band of PVdF-HFP can be observed for coordination to the fluorine atoms. All the bands mentioned above showed changes in the wavenumbers, which shows that coordination of Li⁺ ions have occurred at the oxygen atoms of C=O and –COC– groups of PEMA, and fluorine atom in CF2 group.

Fig. 12 shows the plot of intensity of the IR bands ν(C=O), νa(COC), ν(CO) of –COC– group of PEMA and ν(CO) of –OC2H5 group + νa(CF2) of PVdF-HFP with respect to lithium triflate salt content up to 40 wt.%. Intensity is influenced by the magnitude of dipole moment of an IR active group, and is proportional to the concentration of the species present according to Beer–Lambert law [34].

For ν(C=O), it can be observed that this band decreased slightly in intensity when incorporated with 10 wt.% LiCF3SO3 and then grew in intensity up to 30 wt.%. Coordination seems to saturate after 30 wt.%. As the shifted ν(C=O) band in S20, S30 and S40 represents the Li⁺ coordinated on C=O group, the increase in intensity for this band shows the increase in the coordination of C=O group up to 40 wt.%. The higher intensity of the ν(C=O) band in S0, S10 and S20 is merely due to the larger dipole moment in C=O group as compared to –COC– and CF2 groups. The νa(COC) and ν(CO) of –COO– in PEMA as well as the combined νa(CF2) of PVdF-HFP with ν(CO) of –OC2H5 grew in intensity up to 40 wt.% and the gradient of the line became steeper above 20 wt.%. This shows that coordination of Li⁺ onto –COC– and CF2 groups increase continually up to 40 wt.% of LiCF3SO3 and the increase is more significant at higher salt contents. This implies that there are still available coordination sites on C=O, –COC– and CF2 groups that can improve the conduction of ions in the polymer blend.

3.3. Interaction between Li⁺ and CF3SO3⁻ ions, and the effect on ionic conductivity

In order to study the ionic association between lithium cation and triflate anion, the symmetric SO3 stretching [ν(SO3)] of pure LiCF3SO3 was investigated in the polymer blend–salt complexes. Huang and Frech [35] reported that lithium cations, Li⁺ interact with the triflate anions, CF3SO3⁻ through the SO3⁻ end and that the non-degenerate vibrational mode of ν(SO3) can be used to distinguish between free ions (i.e. CF3SO3⁻) which do not interact directly with Li⁺, ion-pairs (i.e. Li CF3SO3, Li2 CF3SO32⁻, Li3 CF3SO32⁻) and highly aggregated ions (i.e. Li3 CF3SO3 - , Li5 CF3SO3 - ) in the region between 1030 and 1034 cm⁻¹, 1040 and 1045 cm⁻¹ and 1049 and 1053 cm⁻¹, respectively. Each type of ionic species present will contribute differently to the total ionic conductivity of a sample. In order to determine the presence of free ions, ion pairs and highly aggregated ions in the polymer blend–salt complexes, deconvolution of the IR spectra of the samples were carried out in the symmetric ν(SO3) stretching region as shown in Fig. 13.

Curve fitting of IR bands between 980 and 1100 cm⁻¹ of the polymer blend–salt complexes shows the presence of the characteristic band of PEMA around 1020 cm⁻¹ and multiple bands located in the region 1050–1030 cm⁻¹ which represent the different ionic species of the triflate anion. The ν(SO3) band at 1031–1032 cm⁻¹ attributable to free triflate anions were observed in S10, S20, S30 and S40 after the addition of lithium triflate salt. In addition to the presence of free ions, another band arising from ion pairs of lithium triflate at 1040–1042 cm⁻¹ was also observed in S10, S20, S30 and S40 samples. The intensity of the free ions, ion pairs and ion aggregates as well as the ionic conductivity with respect to the different contents of LiCF3SO3 salt are shown in Fig. 14.

Both the ν(SO3) bands corresponding to free ions and ion pairs grew in intensity with increase in the lithium triflate salt. In all the polymer electrolyte samples, the intensity of free ions is higher than that of ion pairs and ion aggregates, which explains the rise in

![Fig. 12. Intensity of ν(C=O), νa(COC), ν(CO) of –COC–, ν(CO) of –OC2H5 – and νa(CF2) vibrational modes with respect to wt.% of LiCF3SO3 in PEMA/PVdF-HFP (70:30) blend.](image1)

![Fig. 13. Deconvolution and band-fitting of IR spectra between 1100 and 960 cm⁻¹ for (a) S10, (b) S20, (c) S30 and (d) S40.](image2)
The increase in the ionic conductivity to $4.13 \times 10^{-7}$ S cm$^{-1}$ in S40 sample could be attributed to the higher amount of free ions as compared to that of ion pairs and ion aggregates. The transparent PEMA/PVdF-HFP films incorporated with lithium triflate salt with adequate conductivity can be useful in electrochromic devices.

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