Dielectric Properties of Lithium-Perchlorate-Filled Acrylonitrile–Hexyl Methacrylate Copolymer Films

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A series of poly(acrylonitrile-co-hexyl methacrylate), PAN-co-PHMA, copolymers with various hexyl methacrylate (HMA) contents were synthesized by emulsion technique. The incorporation of HMA units into the copolymers was confirmed by Fourier transform infrared and proton nuclear magnetic resonance (1H-NMR) spectroscopy. Glass transition temperatures (T_g) and thermal decomposition temperatures of copolymers were determined by differential scanning calorimetry and thermogravimetric analysis. The T_g of copolymers were lowered monotonically by increasing HMA content, while thermal stabilities of copolymers were enhanced. The frequency dependence of dielectric properties of three different amounts of LiClO_4 salt doped copolymer films was investigated. The influence of molar fraction of HMA on dielectric constant and ac conductivity of copolymer films was examined. Samples with higher HMA contents showed better stability and conductivity, as a result of increase in free volume and the mobility of the dipoles. The ac conductivity of copolymers was also improved by increasing LiClO_4 salt which was due to the existence of more charge carriers. PAN(88)-co-PHMA(12) copolymer with 1.5 mol% of lithium salt exhibited ionic conductivity of the 7.8 \times 10^{-2} S/cm at 298 K. POLYM. COMPOS., 00:000–000, 2015. © 2015 Society of Plastics Engineers

INTRODUCTION

Gel polymer electrolytes (GPEs) have been used in Li-ion batteries, solar cells, electrochromic devices, super capacitors, and sensors [1, 2]. GPEs exhibit both properties of liquid electrolyte (high ionic conductivity) and solid electrolyte (mechanical stability and safety). The selection of polymer matrix, liquid electrolyte, and dopant salt (LiClO_4, LiBF_4, LiPF_6, or LiCF_3SO_3) is so important to find the optimum combination. Poly(ethylene oxide) (PEO) [3], poly(methyl methacrylate) (PMMA) [4], poly (vinyl chloride) (PVC) [5], polyacrylonitrile (PAN) [6–8], and poly(vinylidene fluoride) (PVdF) [9, 10] have been used as polymer matrix. However, the mechanical stability of these polymer matrices is still a challenge because of the incorporation of the ionic liquids, which serve as a plasticizer for the polymer matrix [11]. Zhang et al. reported that PVdF-based polymer matrices are unstable against the negative electrode of Li-ion batteries [12]. PVdF polymers react with electrode and the stable LiF and unsaturated bonds (>C=CF–) are formed and so resulted in low battery performance.

Different approaches have been used to improve the electrochemical and mechanical properties of GPE including blending and copolymerization [13]. Poly(vinyl acetate)/poly(vinylidene fluoride-hexafluoropropylene), PVAc/P(VdF-HFP)-based blend electrolyte were prepared with LiClO_4 by solvent casting technique [14]. The maximum ionic conductivity has been obtained as 0.527 \times 10^{-2} S cm^{-1} at 303 K. PAN has been long searched as polymer matrix due to its high polarity, chemical resistance, thermal and electrochemical stability. However, due to the high crystallinity, PAN failed to adhere to the metal substrates. Hence, the physical properties of PAN were improved by copolymerization with methyl methacrylate (MMA) monomer. MMA can be easily wetted by ionic liquids [15]. It has been reported that the electrochemical stability with Li metal and thermal compatibility with liquid electrolyte can be improved by copolymerizing with MMA [16]. Zhang et al. prepared PAN–MMA-based microporous GPE matrix [17]. PAN–MMA showed an excellent miscibility with nonaqueous liquid electrolyte. It was also found that PAN–MMA-based GPE was a very stable binder between anode and cathode [12].

One of the ways to increase the room temperature ionic conductivity is to lower the glass transition temperature (T_g) of the polymer matrix. Since the T_g is a marker of the segmental motions, when decreased the T_g it is expected to increase the conductivity of the system [11]. We have previously synthesized poly(acrylonitrile-co-methyl methacrylate), PAN-co-PMMA, poly(acrylonitrile-co-ethyl methacrylate), PAN-co-PEMA, and poly (acrylonitrile-co-isobutyl methacrylate), PAN-co-PIBMA.
copolymers. There is not much work reported on the emulsion copolymerization of PAN with hexyl methacrylate (HMA) in literature. Brar and Dutta prepared acrylonitrile (AN) copolymers with HMA by photopolymerization using uranyl ions. The reactivity ratios and sequence determination of AN/HMA copolymers were determined by 2D NMR spectroscopy [18]. The copolymers of AN/HMA were obtained by the radical copolymerization in the presence of 2,2'-azobis(isobutyronitrile) (AIBN) as a free radical initiator [19]. In this study, AN/HMA copolymers with different molar ratios were prepared by emulsion technique. It is focused on increasing the room temperature ionic conductivity as well as the mechanical performance of the GPE for Li-ion batteries. Structural characterizations of the copolymers were done by Fourier transform infrared (FTIR) and 1H-NMR spectroscopy. After the determination of thermal stability of polymer matrix, various amounts of LiClO4 salt were loaded. Polymer electrolytes were prepared by solution casting and the dielectric properties were investigated.

EXPERIMENTAL

Materials

The monomers, AN (99%, Acros Organics) and HMA (98%, Aldrich) were used as received. The initiator ammonium persulfate (APS; 98%, Acros Organics), the surfactant sodium dodecyl sulfate (SDS; 98% Sigma-Aldrich), and the chain transfer agent 1-dodecanthiol (98%, Aldrich) were used without further purification. MgSO4 (97% anhydrous, Acros Organics), the dopant salt LiClO4 (99%+, Acros Organics), and N,N-Dimethyl formamide (DMF; 99.5%, Merck) were used as received.

Synthesis of PAN-co-PHMA Copolymers

A typical polymerization procedure was performed using a 250 mL four-necked flask equipped with a mechanical stirrer, condenser, nitrogen inlet, thermometer, and dropping funnel. The deionized water was charged to a four-necked flask that had been purged with nitrogen for an hour at 65°C. The surfactant, initiator (65% of total initiator), and mercaptan were added to the flask followed by the mixture of monomers (20% of total monomer). The remaining monomer mixture was added dropwise for 2 h. Then the remaining initiator was added and stirred for 30 min. The copolymerization reaction was stopped by precipitation of copolymers in 1% MgSO4 aqueous solution and washed with distilled water for several times. Further purification of the copolymers was a crucial step for removing the impurities and soxhlet extraction was applied for both homopolymers and copolymers. The products were dried in a vacuum oven at 50°C. Table 1 shows the general recipe for copolymerization.

Table 1. Recipe for the emulsion copolymerization of AN and HMA.

<table>
<thead>
<tr>
<th>Acronym</th>
<th>AN (g)</th>
<th>HMA (g)</th>
<th>Surfactant (g)</th>
<th>APS (g)</th>
<th>1-Dodecanthiol (g)</th>
<th>Water (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN</td>
<td>22.45</td>
<td>–</td>
<td>0.08</td>
<td>0.0225</td>
<td>0.4266</td>
<td>42</td>
</tr>
<tr>
<td>PAN(88)-co-PHMA(12)a</td>
<td>22.00</td>
<td>9.63</td>
<td>0.10</td>
<td>0.0316</td>
<td>0.6009</td>
<td>52</td>
</tr>
<tr>
<td>PHMA</td>
<td>–</td>
<td>22.00</td>
<td>0.07</td>
<td>0.0220</td>
<td>0.4180</td>
<td>41</td>
</tr>
</tbody>
</table>

A typical copolymer including 88 molar percent of AN and 12 molar percent HMA.

Characterization

FTIR analyses were performed with a Bruker Vertex-70 FTIR spectrometer with KBr pellets and processed with the OPUS computer program. Bruker Avance DPX 400 and Avance III Ultrashield instruments were used for 1H-NMR measurements in d6-DMSO and deuterated chloroform (CDCl3). Thermal transition temperatures of the copolymers and parent homopolymers were determined with a Perkin Elmer Diamond differential scanning calorimetry (DSC) instrument under nitrogen atmosphere. Samples were heated from 0°C to 200°C at a heating rate of 10°C min⁻¹. Thermogravimetric analysis (TGA) thermograms were taken on Perkin Elmer Pyris1 TGA instrument under nitrogen atmosphere and polymer was heated from 25°C to 800°C with a heating rate of 10°C/min.

Film Preparation

A prescribed amount of LiClO4 and copolymers were dissolved in DMF with various [Li⁺]/[HMA] mole ratios of 0.1, 0.2, and 0.3. The resulting homogeneous copolymer solution was cast on a clean glass plate and films were dried under infrared (IR) lamp. Then, films were left to dry at vacuum at 50°C until the DMF was completely evaporated.

Dielectric Measurements

For dielectric measurements, the surfaces of the samples were covered with silver paste to form electrodes. The dielectric measurements were performed between 20 Hz and 1 MHz frequency range at room temperature by using Agilent 4284A LCR Meter. The real part of dielectric constant was calculated by using following equation:

\[
\varepsilon' = \frac{C_pd}{\varepsilon_0 A}
\]

where \(C_p\) is the capacitance of the sample, \(\varepsilon_0\) (dielectric permittivity in vacuum) is equal to 8.85 x 10⁻¹² F/cm, \(A\) is the effective surface area, and \(d\) is the thickness of the
samples. AC-conductivities ($\sigma_{ac}$) of the samples were calculated with the following equation:

$$\sigma_{ac} = \omega C_p d \tan \delta / A$$

(2)

where $\tan \delta$ is dielectric loss factor and $\omega$ is the angular frequency ($2\pi f$).

RESULTS AND DISCUSSION

Figure 1 presents the FTIR spectra of PAN, PHMA, and PAN-co-PHMA copolymers. PAN shows the characteristic absorption peaks at 2243 cm$^{-1}$ and 1453 cm$^{-1}$, which correspond to nitrile (–C≡N) stretching and C–H bending for –CH$_2$ and –CH groups. The strong absorption of PHMA at 1721 cm$^{-1}$ is attributed to characteristic carbonyl –C=O stretching. A very broad peak at 2928–2860 cm$^{-1}$ and the broad absorption band around 1208–1131 cm$^{-1}$ are ascribed to the C–H stretching in methyl and C–O stretching for ester groups, respectively. By comparing the FTIR spectra of the copolymers with those of parent homopolymers, it can be seen that PAN-co-PHMA copolymers keep the characteristic nitrile (–C≡N originated from PAN) and carbonyl (–C=O originated from PHMA) stretching peaks at 2243 cm$^{-1}$ and 1725 cm$^{-1}$, respectively. Both PAN and PHMA functional groups were identified in the FTIR spectra of the PAN-co-PHMA copolymers. For further random copolymer chemical composition confirmation, $^1$H-NMR analysis was performed. The $^1$H-NMR spectra of PAN-co-PHMA copolymers at various molar percent of HMA from 8% to 16% are given in Fig. 2.

The $^1$H-NMR analyses of the copolymers reveals that the composition of the copolymer formed is almost the same as the composition of the monomer feed (Table 2).
TABLE 2. Copolymer compositions obtained from 1H-NMR data.

<table>
<thead>
<tr>
<th>Comonomers in feed (molar percent)</th>
<th>Comonomers in polymer (molar percent)</th>
<th>AN/HMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN(92)-co-PHMA(8)</td>
<td>88.2/11.8</td>
<td></td>
</tr>
<tr>
<td>PAN(88)-co-PHMA(12)</td>
<td>84.9/15.1</td>
<td></td>
</tr>
<tr>
<td>PAN(84)-co-PHMA(16)</td>
<td>84.1/15.9</td>
<td></td>
</tr>
</tbody>
</table>

*a*By weight.  
*b*By proton NMR.

From the copolymer compositions, it was also found that the HMA units increase in the polymer chain as the concentration of HMA increases in the monomer feed.

DSC thermograms of PAN-co-PHMA copolymers show one \( T_g \) and the \( T_g \) of the copolymers was between those of the homopolymers of PAN (\( T_g = 88.2^\circ C \)) and PHMA (\( T_g = -13.7^\circ C \)) (Fig. 3). There is a drop in \( T_g \) of copolymers with increasing content of HMA, which points out the incorporation of HMA can weaken the polar interactions among PAN chains and partly restrict the crystallinity of PAN. Therefore, the lowering the \( T_g \) of PAN by copolymerization with HMA resulted in a ductile film formation and it is also essential to lower \( T_g \) to increase the conductivity of the system.

TGA of both homopolymers and copolymers were carried out to determine the degradation temperatures and also the weight loss behavior during heating over a period of time (Fig. 4). There were two degradation steps for pure PAN, namely, cyclization and aromatization by the release of NH\(_3\) and HCN gases [20], whereas the PHMA curve shows a single step weight loss. The copolymers were degraded at higher temperatures than their parent homopolymers and also the 10% weight loss temperatures increases with the incorporation of HMA into the structure (Table 3). PAN-co-PHMA copolymers are stable up

FIG. 3. DSC curves of PAN-co-PHMA copolymers and homopolymers.

FIG. 4. TGA thermograms of PAN-co-PHMA copolymers and homopolymers.

![TGA thermograms](image)

![DSC curves](image)

TABLE 3. TGA data for homopolymers and copolymers.

<table>
<thead>
<tr>
<th>Samples</th>
<th>( T_{10} ) (^\circ)C</th>
<th>( T_d ) (^\circ)C</th>
<th>Char yield at 600(^\circ)C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN</td>
<td>289</td>
<td>314</td>
<td>51.9</td>
</tr>
<tr>
<td>PAN(92)-co-PHMA(8)</td>
<td>349</td>
<td>367</td>
<td>27.3</td>
</tr>
<tr>
<td>PAN(88)-co-PHMA(12)</td>
<td>355</td>
<td>373</td>
<td>25.5</td>
</tr>
<tr>
<td>PAN(84)-co-PHMA(16)</td>
<td>349</td>
<td>374</td>
<td>22.7</td>
</tr>
<tr>
<td>PHMA</td>
<td>334</td>
<td>365</td>
<td>0.10</td>
</tr>
</tbody>
</table>

*a*10% Weight loss temperature.  
*b*Decomposition temperature.
to 374°C and thermal stabilities were enhanced by HMA incorporation into the copolymers.

The dielectric properties of polymers depend in general on the chemical structure, crystallinity, morphology, and type of fillers [21]. The effects of various HMA content and different LiClO₄ salt concentrations on dielectric properties of PAN-co-PHMA copolymers were investigated. Figure 5a–c shows the frequency dependency of dielectric loss factor ($\varepsilon''$) at 298 K for the copolymers. High dielectric loss factor observed at low frequencies are expected factors for the polymeric materials have dipolar structures [22]. This may have been due to the polarization of PAN dipoles more easily at low frequencies. With increase in the HMA content in the copolymers, the $T_g$ values are lowered which makes the polymer matrix more flexible. The increase in free volume around the polymer chain resulted in higher movement of dipole components and higher $D$ values. Farheen and colleagues reported that the polymer chain in the amorphous phase is more flexible with an increased segmental motion, which facilitates the mobility of ions [23, 24]. Considering the effect of LiClO₄ salt on $D$; it can be seen that $D$ values increase with increasing salt content for all copolymers. This trend can be attributed to interactions between polymer chain and the addition of LiClO₄ salt from 0.5% to 1.5% can lead to an increase in the mean free volume at room temperature. The results are in good agreement with what was found for LiClO₄-doped Poly(vinyl alcohol)/Chitosan film. The addition of salt increases the number of mobile charge carriers ($\text{Li}^+$, $\text{ClO}_4^-$) and degree of dissociation in the polymer matrix [25–27].

The frequency dependence of real part of dielectric constants ($\varepsilon'$) of the polymer electrolytes are shown in Fig. 6a–c. The dipoles are not able to follow the external electric field at high frequencies, so the $\varepsilon'$ value decreases. At low frequency, the dipoles have much more times to orient toward the external field and resulting high $\varepsilon'$ values. The same behavior was observed for the hexanoylchitosan–LiClO₄–TiO₂ composite polymer electrolytes. At high frequencies, there is no time for the buildup of the ions at the electrode–electrolyte interface leading to a decrease in the values of dielectric constant [28, 29]. Besides, the compositional changes affected the $\varepsilon'$ values of the copolymers at certain frequency. The dielectric constant increases.

![FIG. 6. Frequency dependency of real part of dielectric constant ($\varepsilon'$): (a) PAN(92)-co-PHMA(8), (b) PAN(88)-co-PHMA(12), and (c) PAN(84)-co-PHMA(16) with increasing LiClO₄ concentration.](image)

![FIG. 7. Frequency dependency of ac-conductivity ($\sigma_{ac}$) at 298 K: (a) PAN(92)-co-PHMA(8), (b) PAN(88)-co-PHMA(12), and (c) PAN(84)-co-PHMA(16).](image)
systematically with increasing PHMA content in the copolymer. This may be due to the dipolar side groups of PHMA, which were oriented toward the external electric field. The amount of LiClO₄ also affected the $\varepsilon'$ values of the copolymers. It can be found that the copolymers with higher salt content have higher $\varepsilon'$ values.

FIG. 8. SEM micrographs of PAN(88)-co-PHMA(12) film cross-section (a, b), surface (c, d), and PAN(84)-co-PHMA(16) film cross-section (e, f), surface (g, h). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
In general, the ionic conductivity of the polymer electrolytes depends on the concentration of conducting species and their mobility [30, 31]. For all copolymers the ac-conductivity ($\sigma_{ac}$) values increase with increasing frequency (Fig. 7(a-c)). It can be seen that the samples with higher salt content have higher ac-conductivities. At high salt concentration, there is a charge carrier formation and then resulted in an increase in ionic conductivity. The maximum ionic conductivity of 7.8 x 10^{-4} S cm^{-1} has been obtained for PAN(88)-co-PHMA(12) + LiClO$_4$(1.5) polymer composition. The conductivity was also increased by incorporation of PHMA units into the copolymers. PHMA units have longer side chain groups which create a small amount of space surrounding polymer chains and the expanded free volume. Therefore, increasing free volume causes the enhanced mobility of charge carriers in the more flexible matrix.

The effect of various HMA content in copolymers on the morphology of solvent-cast films was evaluated by scanning electron microscopy (SEM), using Quanta 400F emission SEM microscope (FEI Company, the Netherlands). The segregation or microphase separation type morphology is not expected for the copolymer matrix, since the copolymer is random (not block copolymer or polymer blend). The HMA units were added as a comonomer (not as filler) during the emulsion copolymerization to constitute copolymer matrix. The cross-section of PAN(88)-co-PHMA(12) film shows a dense structure with small number of microvoids (Fig. 8 a and b) and the surface of the film is smooth without any domain formation (Fig. 8 c and d). SEM micrographs refer to the cross-section (Fig. 8 e and f) and the surface (Fig. 8g and h) of the PAN(84)-co-PHMA(16) film, respectively. The incorporation of more HMA into copolymer structure leads to the nearly same surface morphology with smooth surface. SEM images revealed that the copolymer film morphology is not significantly affected by the HMA units in the matrix.

**CONCLUSIONS**

The PAN-co-PHMA copolymers from 92/8 to 84/16 mol% were synthesized by emulsion polymerization as a suitable membrane for Li-ion batteries. Emulsion technique provides a useful way to prepare high molecular weight copolymers with high polymerization rates. The chemical structures were analyzed by FTIR and $^1$H-NMR spectroscopy, all confirming that the random copolymers were synthesized successfully. One of the objectives was a decrease in $T_g$ values of copolymers in order to get flexible films and to improve the conductivity. A lower $T_g$ values were obtained by increasing HMA content in the copolymers. Better thermal stabilities were also observed from TGA data by incorporation of the HMA units. The copolymers are stable up to 374°C, which is higher than the operating temperature of lithium batteries. The influences of HMA content and LiClO$_4$ amounts on ac-conductivities of copolymers were also examined. The increment in number of charge carrier per unit volume contributes to increase in ac-conductivities. Hence, the conductivity of the copolymer films was significantly increased with the incorporation of the higher amount of LiClO$_4$ salt. PAN(88)-co-PHMA(12)+LiClO$_4$(1.5) composition showed the maximum conductivity (7.8 x 10^{-4}) among other compositions.

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**REFERENCES**


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