The Potential of Novel Liquid PMMA Oligomer as Electrolyte in Electrochemical Devices

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Abstract: To date gel and film type polymer electrolytes have been widely synthesized due to their wide range of electrical properties. However these types of polymer electrolytes exhibit poor mechanical stability and poor electrode-electrolyte contact hence deprive the overall performance of a battery system. Therefore, in order to indulge the advantages of polymer as electrolyte, a new class of polymer electrolyte was synthesized and investigated. In this study, liquid poly (methyl methacrylate) (PMMA) electrolyte was synthesized using the simplest free radical polymerization technique using benzoyl peroxide as the initiator. It was found that this liquid PMMA oligomer has a potential as electrolyte in electrochemical devices. An ionic conductivity of ~10^{-6} S/cm at room temperature can be achieved when only small volume of hydrochloric acid (HCl) was doped in the liquid PMMA oligomer. The properties of this liquid PMMA oligomer were further investigated using Gel Permeation Chromatography (GPC) and Fourier Transform Infrared Spectroscopy (FTIR).

Keywords: Conducting polymers: PMMA: doping acid: ionic conductivity: GPC: FTIR

1 Introduction

The need of having smaller batteries with high energy and power density are becoming crucial due to the advancement in the communications and information technology such as smart phones and Tablet PCs. Polymeric materials have became the most extensively studied electrolyte host due to its flexible characteristic that make them possible to be fabricated into thin films and exhibit wide range of electrical properties. To date gel-type [1-3] and film-type [4-5] polymer electrolytes have been widely investigated. Unfortunately, these types of polymer electrolytes exhibited poor electrode-electrolyte contact or poor mechanical stability hence deprived the overall performance [6-7]. Therefore, in this study, a new type of liquid polymer electrolyte base on PMMA has been investigated. To the best of our knowledge, this liquid type polymer electrolyte has not been extensively explored. PMMA is chosen because of its unique properties that showed stability towards electrode [8]. In addition, it is a non-explosive and nonflammable material and when it leaks it will not harm the users like the common aqueous based electrolytes do. Since this liquid PMMA is not commercially available, it needs to be synthesized. Therefore, this liquid PMMA electrolyte was prepared by free radical polymerization technique because it is the easiest method that requires no stringent conditions. Note that the importance of this study is to identify the potential of this liquid polymer electrolyte as a conducting host. Therefore, at this stage meticulous polymer synthesizing technique and further purification of the polymer obtained were not implemented though a pure liquid polymer can be obtained. Although both monomer and polymer have C=O chains, polymer assist better in transportation of ion. To ensure that all electrolyte systems are in liquid condition, HCl acid was used to provide proton for the conducting ions. This study will introduce a new class of conducting material to fit the need of growing portable electronic devices. The outcome of this study will be the starting point of the development of a new liquid type polymer electrolyte.
2 Experimental

2.1 Synthesis of liquid-based PMMA oligomer electrolyte

5mL of MMA monomer (ACROS) (Mw=100.12 g/mole) was added with various amounts of benzoyl peroxide (MERCK) ranging from 10% - 50% of the monomer mass. There was no specific reasons of choosing these percentages of benzoyl peroxide as this was the initial study to obtain liquid PMMA oligomer. The test tubes were then soaked in a hot water bath for a few minutes to accelerate the polymerization process. The polymerization of PMMA was then allowed to continue at room temperature for another 24 hours. After 24 hours, only test tubes containing polymer in liquid form were doped with 1 mL of 9 M of HCl (FLUKA) acid and was characterized immediately. Thin layer chromatography (TLC) analysis was carried out on this liquid PMMA oligomer to determine the number of fractions that present in the system.

3 Results and discussion

3.1 The formation of Liquid PMMA oligomer

It was found that after 24 hours of polymerization, only test tube containing 10% of benzoyl peroxide (PL1024) remains as 100% liquid. This indicates that the rate of polymerization increased as the amount of initiator increased causing all samples containing more than 10% of benzoyl peroxide completely polymerized. Therefore, these solid polymers were discarded. Interestingly, this liquid PMMA was able to remain as liquid for another 24 hours (PL1048) and start to solidify after 72 hours of polymerization. The entire liquid was completely solidify after 168 hours. Therefore, it can be concluded that without chain stopper or inhibitor this liquid PMMA oligomer was able to sustain as liquid for 2 days.

From the TLC analyses, it was found that in both PL1024 and PL1048 systems, only one spot was observed with the $R_f$ value of 0.79 and 0.62 respectively. This shows that the polymerization has taken place in which the $R_f$ value for the MMA monomer was 0.87. From the $R_f$ values of the two liquid PMMA systems, it can be concluded that PL1048 system exhibit higher molecular weight than the PL1024 system.

3.2 Characterization of liquid PMMA oligomer

3.2.1 GPC

From the GPC analysis, it was proven that the molecular weight of PL1048 (3450 g/mole) was higher than the PL1024 (3000 g/mole).

3.3 The formation of Liquid PMMA oligomer electrolyte

It was found that with the addition of acid doping, PL1024 and PL1048 oligomers was able to remain as liquid for 120 hours (5 days). Therefore, it can be concluded that this acid also played the role as an inhibitor to slower down the polymerization rate.

\[
\sigma = \frac{l}{R_b A} \quad \text{Eq. (1)}
\]

where $l$ is the distance of the electrodes (cm), $A$ is the effective contact area of the electrodes and the electrolyte (cm$^2$) and $R_b$ is the bulk resistance (Ω) of the samples.
3.4 Characterization of liquid PMMA oligomer electrolyte

3.4.1 FT-IR analysis

Similar to previous study [9] the complexation in this liquid PMMA oligomer was also expected to occur between the carbonyl (C=O) group of the liquid PMMA at ~1730 cm\(^{-1}\) and H\(^+\) of the doping acid (Fig.1a-b). It was found that in both PL1024 and PL1048 systems, the C=O band dissapeared indicating that interaction had occurred between the polymer and the doping acid. In addition, it was also noted that the interaction between the C=O and the cation was slightly stronger in PL1048 than in PL1024. This probably due to higher number of available coordinating sites in PL1048. As a result, the number of free H\(^+\) ions in PL1048 were slightly lesser than in PL1024 which can be confirmed from their FTIR spectra (Fig. 1c).

3.4.2. Conductivity Studies

With the addition of only 1mL of 9M HCl into PL1024 and PL1048 systems, the ionic conductivity of ~10\(^{-6}\) S/cm can be achieved. Since the FTIR analyses of PL1048 indicated a stronger interaction between the polymer and the doping acid, therefore it exhibited slightly lower ionic conductivity than the PL1024. Furthermore, the lower ionic conductivity of PL1048 was probably due to higher viscosity of the liquid oligomer as it exhibited higher molecular weight than the PL1024. Ions were difficult to move in a more viscous medium. Similar observations were also obtained in previous study in the effect of PMMA molecular weight on the ionic conductivity [10]. The ionic conductivity values that were obtained were almost comparable to PMMA electrolyte systems that have been previously studied [11-12].

Table 1 summarized the ionic conductivity of the systems at room temperature.

<table>
<thead>
<tr>
<th>System</th>
<th>Conductivity (S/cm)</th>
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<tr>
<td>PL1024</td>
<td>1.596 x 10(^{-6})</td>
</tr>
<tr>
<td>PL1048</td>
<td>1.442 x 10(^{-6})</td>
</tr>
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</table>

4 Conclusion

This liquid PMMA oligomer has the potential as electrolyte in electrochemical devices in which the ionic conductivity achieved when only small volume of 9M acid was added into the systems was ~10\(^{-6}\) S/cm at room temperature. However, the molecular weight of the liquid oligomer was found to affect the ionic conductivity of this new liquid PMMA oligomer. The ionic conductivity of this electrolyte system can be further enhance by increasing the volume of the acid added and adding plasticizer.
Figure 1. FTIR spectra for (a) PL1024/HCl (b) PL1048/HCl and (c) H-Cl bands in both systems respectively.
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