The Malaysian Journal of
ANALYTICAL
SCIENCES

THE EFFECT OF H_2SO_4 CONCENTRATION ON THE IONIC CONDUCTIVITY OF LIQUID PMMA OLIGOMER

(Kesan Kepekatan H_2SO_4 Ke Atas Kekonduksian Ionik Cecair PMMA Oligomer)

Norashima Kamaluddin[1,2]*, Famiza Abdul Latif[1,2], Chan Chin Han[1,2], Ruhani Ibrahim[1,2],
Sharil Fadli Mohamad Zamri[1,2]

[1]Faculty of Applied Sciences,
[2]Core Frontier Materials and Industry Application, Research Management Institute,
Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia

**Corresponding author: norashimakamaluddin@yahoo.com*

Received: 25 March 2015 ; Accepted: 11 June 2015

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. At this stage, it was found that this liquid PMMA oligomer (Mw=3000 g/mole) has a potential as electrolyte in electrochemical devices. It was found that an ionic conductivity of $\sim10^{-7}$ S/cm at room temperature can be achieved when only small volume of high molarity of sulfuric acid (H_2SO_4) was doped in the liquid PMMA oligomer. The properties of this liquid PMMA oligomer were further investigated using Fourier Transform Infrared Spectroscopy (FTIR).

Keywords: Conducting polymers, PMMA, doping acid, electrical studies, FTIR

Abstrak

Sehingga kini elektrolit polimer dalam keadaan gel dan filem telah disintesis secara meluas kerana mempunyai pelbagai sifat elektrikal. Walaubagaimanapun, elektrolit polimer ini menunjukkan kestabilan mekanikal yang lemah dan sentuhan antara elektrod dan elektrolit yang rendah sekaligus menurunkan prestasi sistem bateri. Oleh yang demikian, untuk mendapatkan faedah polimer sebagai elektrolit, satu kelas polimer elektrolit yang baru telah disintesis dan dikaji. Kajian ini melibatkan kaedah sintesis elektrolit poli(metil metakrilat) (PMMA) berasakan cecair melalui teknik pempolimeran radikal bebas menggunakan benzoil peroksida sebagai pencetus. Didapati bahawa cecair PMMA oligomer ini (Mw=3000 g/mol) mempunyai potensi sebagai elektrolit di dalam alatan elektrokimia. Kekonduksian ionik $\sim10^{-7}$ S/cm pada suhu bilik telah dicapai apabila hanya isipadu kecil asid sulfurik (H_2SO_4) yang berkepekatan tinggi terdop ke dalam cecair PMMA oligomer ini. Sifat cecair PMMA oligomer ini telah dikaji menggunakan Fourier Transform Inframerah Spektroskopi (FTIR).

Kata kunci: konduktif polimer, PMMA, asid doping, kajian elektrikal, FTIR

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. Complexes of basic polymers such as poly(vinyl alcohol) (PVA), poly(ethylene oxide) (PEO), poly(acryl amide) (PAAM) and poly(ethylene imine) (PEI) with strong acids have been shown to possess high proton conduction in the range of 10^{-4}-10^{-3} S cm^{-1} [9]. Proton conducting polymer electrolytes based on poly(vinyl acetate) (PVAc) and perchloric acid ($HClO_4$) have been prepared and exhibit maximum conductivity of 10^{-3} S/cm at room temperature [10].

To ensure that all electrolyte systems are in liquid condition, therefore, H_2SO_4 acid was used to provide proton for the conducting ions. Note that only 1 mL of the doping acid was used to study the potential of this liquid polymer electrolyte. 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.

Materials and Methods

Synthesis of Liquid-based PMMA Oligomer Electrolyte

5 mL of MMA monomer (ACROS) (Mw=100.12 g/mole) was added with 10% of benzoyl peroxide (MERCK) of the monomer mass. 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 1,3,5,7 and 9 M of H_2SO_4 acid (FLUKA) and was characterized immediately.

Fourier Transform Infrared Spectroscopy Analysis

The polymer-ion complexation was determined by PERKIN ELMER Fourier transform infrared spectrophotometer Spectrum One in the frequency range of 4000-600 cm^{-1} at a resolution of 16 cm^{-1}.

Impedance Spectroscopy

To measure the impedance of this liquid PMMA oligomer electrolyte, a Hioki 3532-50 LCR HiTester was used to perform the impedance (Z) measurement for each sample over the frequency range of 100 Hz-1 MHz. From the Cole-Cole plots obtained, the bulk resistance, R_b of each sample was determined and hence the conductivity (σ) of the samples were then calculated using Equation (1) [11].

$$\sigma = l / R_bA \tag{1}$$

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.

Results and Discussion

The Formation of Doped Liquid PMMA Oligomer Electrolyte

The molecular weight of this prepared undoped liquid PMMA oligomer was 3000 g/mole. This liquid PMMA oligomer has able to be sustained as liquid for 48 hours. Interestingly, the addition of H_2SO_4 helped to further sustain its condition in liquid form for 96 hours (4 days). It can be suggested that this acid also played the role as an inhibitor to slower down the polymerization rate.

Characterization of Liquid PMMA Oligomer Electrolyte: FT-IR Analysis

Figure 1 exhibit the FTIR spectra for H_2SO_4 doped PMMA oligomers. It was noted that a new peak was observed at 3500-3000 cm^{-1} when H_2SO_4 was added into the system. This peak can be suggested as hydrogen bond that formed between the carbonyl (C=O) group of PMMA and the H^+ ion from the acid [12]. This can be further confirmed by the decreasing of the intensity area ratio of the C=O band at ~1730 cm^{-1} as the concentration of the acid increased. It was also found that this C=O band shifted to lower frequency range suggesting that the interaction between the oligomer and the doping acid is weak.

.

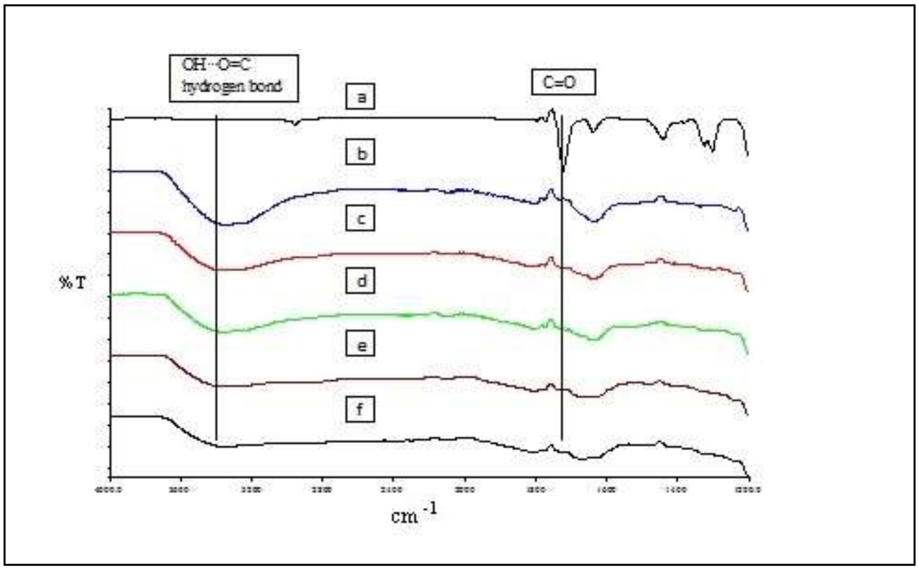

Figure 1. FTIR spectra for (a) undoped liquid PMMA oligomer and liquid PMMA oligomer doped with (b) 1 M, (c) 3 M, (d) 5 M, (e) 7 M and (f) 9 M of H_2SO_4 respectively

Electrical Studies

Since FTIR analyses indicated that the interaction between the oligomer and the doping acid was weak, therefore the H^+ ion can be easily detached from the carbonyl group and free to move. Therefore, it explains why this PMMA oligomer was able to become ionic conductor. Table 1 summarized the ionic conductivity of the PMMA oligomer electrolyte at room temperature. It was found that the ionic conductivity increased as the concentration of H_2SO_4 acid increased. As the molarity of acid increased, the number of free H^+ ion also increased which was supported by the decreased in the intensity area ratio of the C=O band at higher concentration of acid.

Table 1. Average conductivity of liquid PMMA oligomer/H_2SO_4 at room temperature

Molarity of H_2SO_4 (M)	**Conductivity (S/cm)**
1	4.167×10^{-9}
3	8.333×10^{-9}
5	2.609×10^{-8}
7	7.895×10^{-8}
9	1.744×10^{-7}

This can be further supported from the dielectric plot (Figure 2) in which PMMA oligomer doped with 9 M of acid exhibited the highest dielectric value at room temperature. Interestingly, it was noted that the dielectric constant plot of this system does not reach zero value at higher frequency like other gel or film PMMA electrolyte sytems. This may indicates that full charge dissipation does not occur at higher frequency in a liquid polymer system probably because contact area between the liquid polymer electrolyte and the electrode is better than in gel or film PMMA electrolyte systems [13-14].

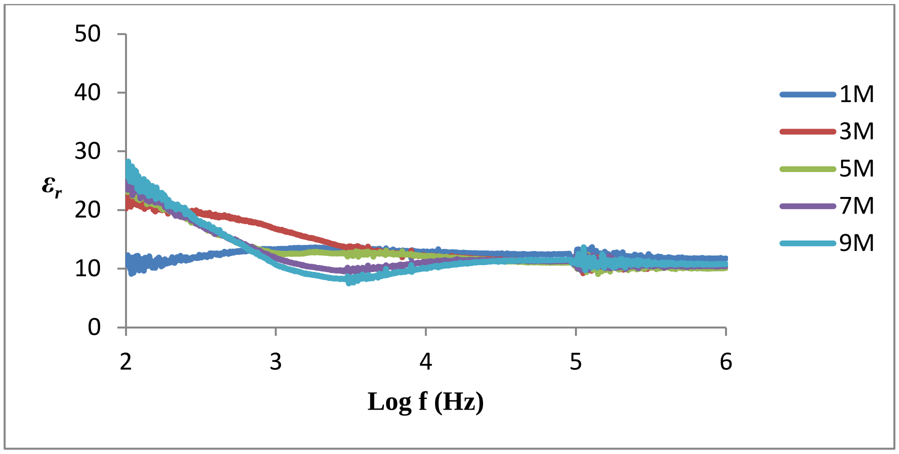

Figure 2. Variation of the dielectric constant with frequency for liquid PMMA oligomer doped with 1 M, 3 M, 5 M, 7 M and 9 M of H_2SO_4 at room temperature respectively

Conclusion

This new type of liquid PMMA oligomer can be considered as a new class of polymer electrolyte and has the potential as electrolyte in electrochemical devices in which the ionic conductivity achieved when only small volume of high molarity of H_2SO_4 was added into the systems was ~10^{-7} S/cm at room temperature.

Acknowledgement

Financial support and technical support from Malaysia Toray Science Foundation (MTSF) (Ref: CRO-CA/13.206 [File Ref: 13/G191]), The Ministry of Higher Education (FRGS grant) and UiTM are highly acknowledged.

References

1. Saikia, D. and Kumar, A. (2005). Ionic transport in P(VDF-HFP)–PMMA–$LiCF_3SO_3$–(PC + DEC)–SiO_2 composite gel polymer electrolyte. *European Polymer Journal*, 41: 563-568.
2. Kumar, R., Sharma, J. P. and Sekhon, S. S. (2005). FTIR study of ion dissociation in PMMA based gel electrolytes containing ammonium triflate: Role of dielectric constant of solvent. *European Polymer Journal*, 41: 2718-2725.
3. Rajendran, S., Bama, V. S. and Prabhu, M. R. (2010). Effect of lithium salt concentration in PVAc/PMMA-based gel polymer electrolytes. *Ionics*, 16: 27-32.
4. Idris, R., Glasse, M. D., Latham, R. J., Linford, R. G. and Schlindwein, W. S. (2001). Polymer electrolytes based on modified natural rubber for use in rechargeable lithium batteries. *Journal of Power Sources*, 94l: 206-211.
5. Idris, R., Mohd, N. H. N. and Arjan, N. M. (2007). Preparation and characterization of the polymer electrolyte system ENR50/PVC/EC/PC/$LiN(CF_3SO_2)_2$ for electrochemical device applications. *Ionics*, 13: 227-230.
6. Hou, X. and Kok, S. S. (2000). Mechanical properties and ionic conductivities of plasticized polymer electrolytes based on ABS/PMMA blends. *Polymer*, 41: 8689-8696.

7. Zhou, S. and Fang, S. (2007). High ionic conductivity of all-solid polymer electrolytes based on polyorganophosphazenes. *European Polymer Journal*, 43: 3695-3700.
8. Appetecchi, G. B., Croce, F. And Scrosati, B. (1995). Kinetics and stability of the lithium electrode in poly(methylmethacrylate)-based gel electrolytes. *Electrochimia Acta*, 40(8): 991-997.
9. Rikukawa, M. and Sanui, K. (2000). Proton-conducting polymer electrolyte membranes based on hydrocarbon polymers. *Prog. Polym. Sci.*, 25: 1463-1502.
10. Arun Kumar, D., Selvasekarapandian, S., Baskaran, R., Savitha, T. and Nithya, H. (2012). Thermal vibration and AC impedance studies on proton conducting polymer electrolytes based on poly(vinyl acetate). *Journal of Non-Crstalline Solids*, 358: 531-536.
11. Nik Aziz, N. A., Idris, N. K. And Isa, M. I. N. (2010). Proton conducting polymer electrolytes of methylcellulose doped ammonium fluoride: Conductivity and ionic transport studies. *Journal of the Physical Sciences*, 5(6): 748-753.
12. Pu, H. and Wang, D. (2006). Studies on proton conductivity of polyimide/H_3PO_4/imidazole blends. *Electrochimia Acta*, 51: 5612-5617.
13. Latif, F. , Aziz, M., Kartun, N., Ali, A. M. M. and Yahya, M. Z. (2006). The role and impact of rubber in poly(methyl methacrylate)/lithium triflate electrolyte. *Journal of Power Sources*, 159: 1401-1404.
14. Uma, T., Mahalingam, T. and Stimming, U. (2005). Conductivity studies on poly(methyl methacrylate)–Li_2SO_4 polymer electrolyte systems. *Materials Chemistry and Physics*, 90: 245-249.