

## Synthesis, Characterization and Ionic Conductivity of Supramolecular Structure of Uracil-Functionalized PEG/LiClO<sub>4</sub> Blend System

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In this paper, the synthesis and ionic conductivity behaviour of supramolecular structure based end group functionalized poly(ethylene glycol) with uracil are reported. The uracil (U) functionalized poly(ethylene glycol) (PEG), (U-PEG-U) was synthesised through Michael addition. The synthesized polymer electrolyte was characterized by Fourier-transform infrared and nuclear magnetic resonance spectral methods. Further, we described the interaction behaviour of synthesized polymer electrolyte with Li<sup>+</sup> ions. Differential scanning calorimetry and FTIR studies demonstrates that the significant ability of functionalized poly(ethylene glycol) to donate its electron to coordinate with lithium ion. It is further observed that the ionic conductivity of polymer electrolyte is not only dependent on the electron donation strength of carbonyl group, but also on the molecular structure of polyester.

**Keywords:** Supramolecular structure, Polymer electrolytes, Polyester.

### INTRODUCTION

Solid polymer electrolytes, which are complexes of solvent-free polymers and metal salts<sup>1</sup>, are prepared by dissolving salts in high-molecular-weight polar polymer hosts<sup>2</sup>. Polymer electrolytes have been studied extensively during the past two decades because of their potential applications<sup>3</sup>, which include high energy density batteries and fuel cells<sup>4,5</sup>. The motivation for this investigation is the application of polymer electrolyte in rechargeable and high energy density power sources. Ionic transport occurs in the polymer very often as a result, coupling of dissolved salt between the ions and segmental motions of the polymer chains. Poly(ethylene glycol) (PEG) based polymeric electrolytes are still among the most extensively studied polymer ionic conductors<sup>6-8</sup>, because their structures are beneficial for supporting fast ion transport. A strong electron donor within oxygen atom of carbonyl group in polyester-based polymer electrolyte would tend to complex with lithium ion. The electron donation strength of carbonyl group would affect on the solubility of Li salt and on the isolation of Li<sup>+</sup> ion within the polymer matrix<sup>9,10</sup>.

It is an important challenge to develop practical methods for preparing the solid polymer electrolytes that have higher ionic conductivity and dimensional stability<sup>11</sup>. In this regard, the preparation of polymeric electrolytes by blending them with other appropriate polymers is of interest. Polymer blend is a quick and economical alternative method for obtaining

materials that have optimized properties and for the easy control of their physical properties by compositional change<sup>12</sup>.

Supramolecular structure based polymer electrolytes is an option for fast ion transport between the acryloyl functionalized PEG and uracil<sup>13-15</sup>. The existence of strong interaction between PEG and Uracil by the presence of multiple hydrogen bonds and tends to suppress the crystallinity of PEG. Nevertheless, the addition of certain compositions such as lithium perchlorate (LiClO<sub>4</sub>) into an end functionalized uracil-PEG (U-PEG-U) system is used to design new polymeric matrices by synthetic processes or modifying existing polymer-salt complexes and thus, improve ionic conductivity. The electron donation strength and isolation of Li<sup>+</sup> ion within polymer electrolyte carbonyl group are detected by using differential scanning calorimetry, Fourier transform infrared spectroscopy and alternating current impedance investigations proves that the electron donation strength between polyester-salt complexes and its related conductivity behaviour of polymer electrolyte blend system.

### EXPERIMENTAL

Acrylic acid (Qualigens), benzoyl chloride (Alfa aser), hydroquinone (S.D. fine chem.) were purchased and used as such. The poly(ethylene glycol) (PEG) with Mw-8000 and uracil were purchased from Sigma Aldrich. Lithium perchlorate (LiClO<sub>4</sub>, Aldrich) was dried in a vacuum oven at 80 °C for 24 h and stored in a desiccator prior to use. Acetonitrile

was distilled at a suitable temperature under a nitrogen atmosphere prior to use. All other materials and solvents used were of analytical grade.

**Synthesis of acryloyl chloride:** A mixture of acrylic acid (1 mol), benzoyl chloride (2 mol) and hydroquinone (0.0025 mol) was distilled at a fairly high rate through an efficient column. The distillate was collected in a receiver containing hydroquinone (0.0025 mol). The product was obtained at a temperature between 85–100 °C. The crude product was redistilled through the same column.

**Synthesis of U-PEG-U:** The scheme for the synthesis of U-PEG-U is describe as following steps. In first step PEG, acryloyl chloride and triethylamine were taken in the 1:4:2 molar ratio and dissolved in anhydrous dichloromethane and stirred overnight under nitrogen atmosphere. Then the solution was washed in 2M K<sub>2</sub>CO<sub>3</sub> and separated into organic/aqueous phases to remove the hydrochloric acid. The organic phase was dried with magnesium sulphate, the PEG diacrylate was precipitated in cold diethyl ether, filtered and dried under vacuum.

In a second step, a solution of acryloyl chloride in THF was added through a dropping funnel into a solution of PEG acrylate, triethylamine and THF in a 500 mL flask, cooled in an ice bath and then the mixture was stirred for 24 h. The precursor collected after centrifugation, filtration and rotary evaporation of the solvent was added to a flask containing a solution of uracil and potassium *tert*-butoxide in DMSO and then the mixture was heated at 60 °C for 48 h with stirring. After distillation of the DMSO, the solid residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, filtered and concentrated to get the final product, which was dried under vacuum for 24 h to yield U-PEG-U.

**LiClO<sub>4</sub>/U-PEG-U polymer electrolyte:** The synthesized U-PEG-U is blended with LiClO<sub>4</sub> by dissolving in acetonitrile and stirred for 24 h. The solution was casted on a Teflon dish and maintained at 80 °C for 24 h to remove the solvent. The dish was then further dried under vacuum at 80 °C for an additional 48 h. To prevent contact with the air and moisture, the polymer electrolyte was transferred to a glove box under N<sub>2</sub> atmosphere. The blending molar ratios of Li<sup>+</sup> ions to the total oxygen atom contents of the ethylene oxide units in each PEG main chain were used to identify the formed Li/U-PEG-U blends.

**Characterization methods:** The synthesized polymer electrolyte was characterized by spectral methods, thermal analysis and impedance measurements.

**Fourier transform infrared spectroscopy:** IR spectra of the copolyester were recorded using a Perkin Elmer IR

spectrometer in the range of 700 to 4500 cm<sup>-1</sup>. The samples were embedded in KBr pellets.

**<sup>1</sup>H NMR spectroscopy:** <sup>1</sup>H NMR spectra were recorded on AV 3500 MHz Spectrometer by using CDCl<sub>3</sub> as solvent and chemical shift values are reported in parts per million.

**Differential scanning calorimetry:** Thermal analyses were performed using a differential scanning calorimetry instrument. The sample was weighed and sealed in an aluminum pan. The glass transition temperatures (T<sub>g</sub>) were taken as the midpoints of the heat capacity transitions between the upper and lower points of deviation from the extrapolated glass and liquid lines, at a scan rate of 20 °C min<sup>-1</sup> over a temperature range from -50 to 150 °C.

**Conductivity measurements:** Ionic conductivity measurements with alternating current were conducted on an AC impedance spectrometer designed by Eco chemie with in the frequency range from 10 MHz to 10 Hz. The electrolyte film was sandwiched between stainless steel blocking electrodes. The specimen thickness varied from 0.8 to 1.2 mm; the impedance response was gauged over the range from 20 to 120 °C. Conductivity was calculated from the bulk resistance according to the equation,

$$\sigma = l/RA$$

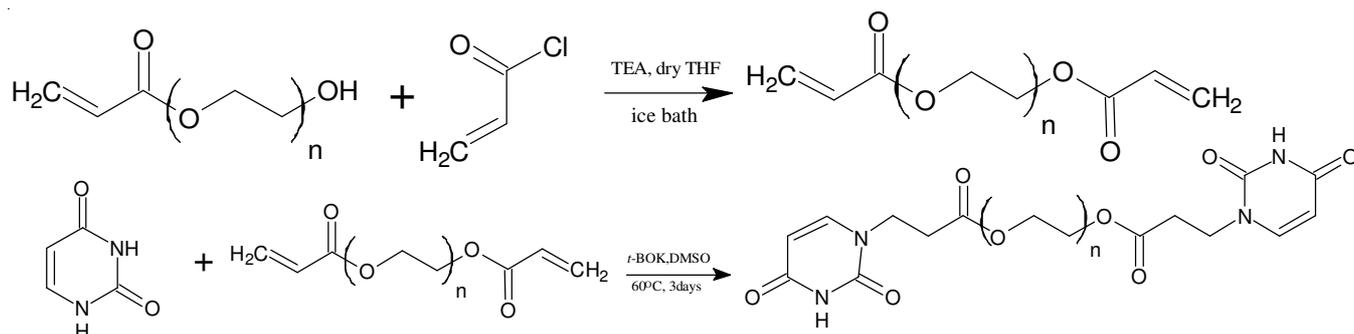
where,  $\sigma$  is the conductivity,  $l$  is thickness of the electrolyte film,  $A$  is the sectional area of the stainless steel electrode and  $R$  is the bulk resistance.

## RESULTS AND DISCUSSION

**FT-IR Spectroscopy:** The synthesized polyester is characterized by FTIR spectrometer and the values are indicated below. Fig. 1a indicate the peak values from the U-PEG-U. The free C=O is 1730 cm<sup>-1</sup> and the acrylate carbon (C<sub>4</sub>=O) is 1670 cm<sup>-1</sup>. In similar phenomena Fig. 2b describe the peak values for the U-PEG-U/LiClO<sub>4</sub> blend system, the values are C=O is 1714 cm<sup>-1</sup> and the acrylate carbon (C<sub>4</sub>=O) is 1666 cm<sup>-1</sup>. The corresponding values are decreasing, because the addition of U-PEG-U, an ionically bonded to the lithium salt.

**<sup>1</sup>H NMR spectroscopy:** <sup>1</sup>H NMR spectra of U-PEG-U in CDCl<sub>3</sub>. The signal for the OH group of PEG-acrylate in the region from 5.2 to 6.3 ppm and the U rings at 10.2 ppm (amino proton), 7.2 and 5.4 ppm values are confirming the synthesis of U-PEG-U.

**Differential scanning calorimetry thermal analysis:** Thermal analysis of polymer electrolyte was studied by differential scanning calorimetry. Thermal analysis is used to identify the effect of thermal properties on the addition of



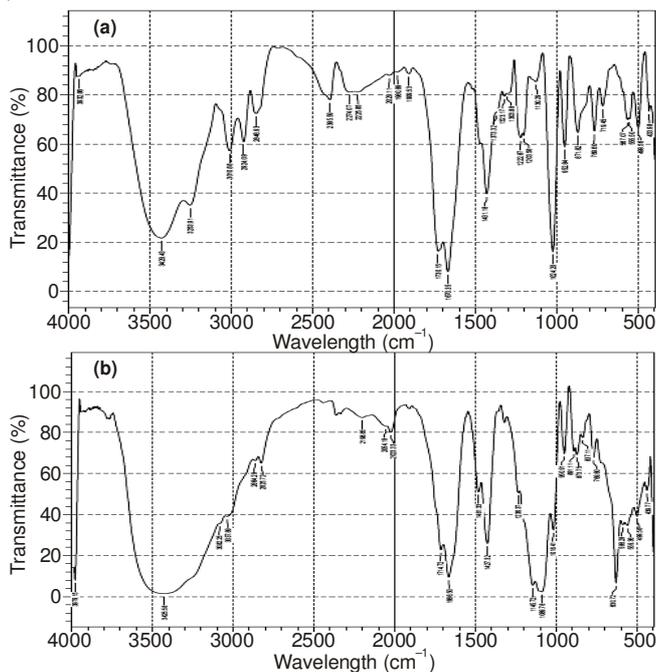


Fig. 1. (a) FTIR spectra of U-PEG-U (b) FTIR spectra of U-PEG-U/LiClO<sub>4</sub> blend system

lithium salt. Fig. 2a,b presents DSC thermogram of the U-PEG-U polymer electrolyte and the value of  $T_g$  at  $-8.8^\circ\text{C}$ . The U-PEG-U is a crystalline oligomer having values of  $T_g$  and  $T_m$  of  $-8.8$ ,  $37.3^\circ\text{C}$ , respectively. The glass transition temperature ( $T_g$ ) and melting temperature ( $T_m$ ) for polyester/LiClO<sub>4</sub> blend system observed from DSC thermograms are  $-19.6$  and  $33.6^\circ\text{C}$ , respectively. The decrease in  $T_g$  and  $T_m$  values for the blend shows the decrease in crystallinity. These data indicates that the addition of lithium salt into a noncovalently interacting functional group (U-PEG-U) that experiences self-complementary interactions to PEG disrupted in the polymer chain folding and decreased its crystalline nature of polymer electrolyte blend system.

**Ionic conductivity:** The ionic conductivity of an electrolyte is defined as the product of concentration of ionic charge carriers and their mobility,

$$\sigma = l/RA$$

where,  $\sigma$  is the conductivity,  $l$  is thickness of the electrolyte film,  $A$  is the section area of the stainless steel electrode and  $R$  is the bulk resistance. The addition of LiClO<sub>4</sub> in the blend system tends to retard or destroy the crystalline phase and results in higher ionic conductivity as a result of the strong interaction between U-PEG-U and LiClO<sub>4</sub>. In addition, the crystalline phase can be reduced and higher conductivity occurs with raising the temperature, as is expected. Notably, at  $30^\circ\text{C}$  (room temperature) the conductivity value for the U-PEG-U blend with LiClO<sub>4</sub> is  $0.96 \times 10^{-5} \text{ S cm}^{-1}$ . It would result, in an optimum environment for ionic transport and achieve the highest possible ionic conductivity.

## Conclusion

We have investigated the synthesis of polymer electrolyte and characterized by using DSC, FTIR, <sup>1</sup>H NMR and AC impedance measurements. Further, the effect of interaction

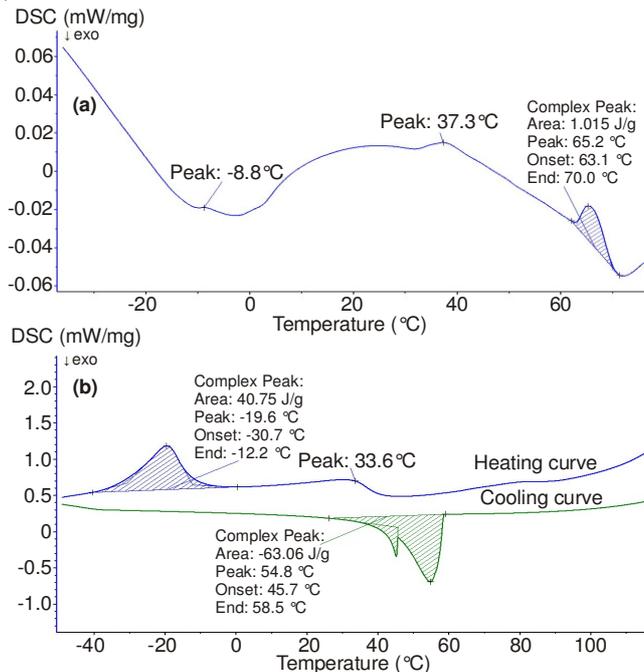


Fig. 2. (a) DSC thermogram of U-PEG-U (b) DSC thermogram of U-PEG-U/LiClO<sub>4</sub> blend system

on ionic conductivity of polyester/LiClO<sub>4</sub> blend based electrolyte system was also studied. Li ion is more preferably coordinate with the carbonyl group of U-PEG-U, it is because that the polyester C=O group of electron donate essentially to Li<sup>+</sup> is stronger one. Therefore, the ionic conductivity of polyester/LiClO<sub>4</sub> blend system is  $0.96 \times 10^{-5} \text{ S cm}^{-1}$  at room temperature. It is observed that not only the electron donation strength, but also the molecular structure affect the ionic conductivity. The synthesized polyester/LiClO<sub>4</sub> blends can be preferentially, used as solid polymer electrolytes.

## REFERENCES

- H. Cheradame and J.F. Le Nest, in eds.: J.R. MacCallum and C.A. Vincent, *Polymer Electrolyte Reviews*, Elsevier, vol. 1 and 2 (1987-1989).
- B. Scrosati, *Application of Electroactive Polymers*, New York (1993).
- M.B. Armand, *Solid State Ion.*, **9-10**, 745 (1983).
- K. Murata, S. Izuchi and Y. Yoshihisa, *Electrochim. Acta*, **45**, 1501 (2000).
- I.J. Lee, G.S. Song, W.S. Lee and D.H. Suh, *J. Power Sources*, **114**, 320 (2003).
- H. Zhang, S. Kulkarni and S.L. Wunder, *J. Electrochem. Soc.*, **153**, 239 (2006).
- C.K. Lin and I.D. Wu, *Polymer*, **52**, 4106 (2011).
- C.Y. Chiu, H.W. Chen, S.W. Kuo, C.F. Huang and F.C. Chang, *Macromolecules*, **37**, 8424 (2004).
- H.T. Kim, K.B. Kim, S.Z. Kim and J.K. Park, *Electrochim. Acta*, **45**, 4001 (2000).
- J.Y. Song, Y.Y. Wang and C.C. Wan, *J. Power Sources*, **77**, 183 (1999).
- S.V. Meille, P.J. Phillips, K. Mezghani and S. Bruckner, *Macromolecules*, **29**, 795 (1996).
- Y.W. Chen-Yang, A.Y. Hwang and A.Y. Huang, *Macromolecules*, **33**, 1237 (2000).
- J.H. Wang, O. Altukhov, C.C. Cheng, F.C. Chang and S.W. Kuo, *Soft Matter*, **9**, 5196 (2013).
- J.B. Carroll, A.J. Waddon, H. Nakade and V.M. Rotello, *Macromolecules*, **36**, 6289 (2003).
- Y.C. Lin and S.W. Kuo, *Polym. Chem.*, **3**, 882 (2012).