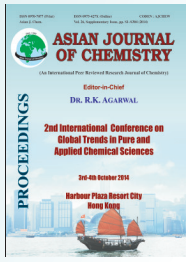
Asian Journal of Chemistry; Vol. 26, Supplementary Issue (2014), S230-S236

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.19059



Synthesis and Characterization of Polylactide-Poly(ethylene glycol) Block Copolymer as Solid Polymer Electrolyte

C.H. TAN, A. AHMAD and F.H. ANUAR*

Polymer Research Center, School of Chemical Sciences and Food Technology, Faculty of Sciences and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia

*Corresponding author: E-mail: farahhannan@ukm.edu.my

Published online: 24 December 2014; AJC-16479

A solid polymer electrolyte was developed from polylactide-poly(ethylene glycol) (PDLLA-PEG) block copolymer with lithium iodide as conducting salt. At the initial stage, the polymer host was synthesized by ring opening polymerization of DL-lactide followed by chain extension reaction using hexamethylene diisocyanate (HMDI). The poly(ether-ester-urethane) electrolyte thin films (13-18 mm) with various lithium iodide load were then prepared by solution casting technique. The formation of ester bond and urethane linkage in PDLLA-PEG-PDLLA triblock and multiblock copolymers, respectively, were confirmed using NMR spectrometer. Chemical interaction between polymer host and lithium cation from lithium iodide was confirmed by ATR-FTIR technique by observing the shift of wavenumber for the carbonyl (C=O) (1770-1730 cm^{-1}) and ether (C-O-C) (1160-1040 cm^{-1}) groups. Structural analysis carried out by XRD showed that crystallinity of the poly(ethylene glycol) soft block was reduced and became fully amorphous as the amount of lithium iodide increased up to 20 wt. %. Thermal studies by TGA indicated that poly(ester-ether-urethane) electrolyte was thermally stable up to 200 °C while DSC revealed the relation between electrolyte thermal properties and the lithium iodide content. The resulted solid polymer electrolyte with 25 wt. % lithium iodide load was found to achieve optimum ionic conductivity of 4.1670×10^{-6} S cm^{-1} at room temperature as compared to pure polymer host conductivity of 4.423×10^{-11} S cm^{-1}, which denoted an increment of five magnitudes in ionic conductivity.

Keywords: Copolymer, Polylactide, Room temperature ionic conductivity, Solid polymer electrolyte.

INTRODUCTION

An undeniable crisis regards to sustainable resources, either energy or material, has direct a good number of researchers in the development of solid polymer electrolyte (SPE) which give rise to high density electrochemical device for energy storage. A highly conductive solid polymer electrolyte can give a breakthrough in the evolution of solid state electrochemical device such as supercapasitor, lithium rechargeable batteries and even photo-electrochemical cell[1,2] which was able to convert renewable light energy into electrochemical energy. However, too much attention was paid on the conductivity value when it comes to the development of solid polymer electrolyte and resulted in common usage of non-biodegradable and/or unrenewable polymer material as electrolyte polymer host. For this purpose, an inclusion of natural biodegradable polymer in development of solid polymer electrolyte has been made in this research, as one of the effort to reduce solid waste accumulation. Among the numerous kind of biodegradable polymers, an aliphatic polyester thermoplastic called polylactide (PLA) have received much attention recently. It was due to the advantage of being not only biodegradable but also renewable, considering the monomer lactic acid is majorly produced by microbial fermentation of agricultural by-products mainly carbohydrate rich substances[3,4].

Fenton *et al.*[5] was the first group of researchers who discover the ionic conductivity properties of a non-conducting polymer matrix after introduced with lithium salt. However, a biodegradable polylactide was not yet involved in solid polymer electrolyte research, although high molecular weight polylactide was available and patented by DuPont in the year of 1954. This phenomena was due to some drawback where high modulus and low elongation at break have limited its application to rigid thermoformed packaging industry and clinical use such as drug delivery, sutures and orthopedic implant[6-9]. Major attempts made for polylactide mechanical improvement can be categorized into copolymerization, blending with other polymers/copolymers and lastly the use of plasticizer. The former was found to be the most effective way among others in accounts on the resulted products homogeneity

due to the existence of a covalent bond between the polymer chains. Works on creating polylactide multiblock with poly-(ethylene glycol) were reported where poly(ethylene glycol) form the soft segments along copolymeric backbone and rendered the copolymers with their remarkable extendibility and flexibility, while polylactide function as the hard block which formed mechanically strong domains besides afforded biodegradability to the system[10,11].

Polylactide was first to involve in solid polymer electrolyte research in the year 2013 where ethylene carbonate plasticizer and silicon dioxide ceramic filler was used respectively for mechanical and ionic conductivity improvement[12]. The stereo-forms of the polylactide used was not specified, but suggested to be semi crystalline PLLA or PDLA since there was some peaks observed in the X-ray diffractogram of the neat poly-lactide. On account of the stereo regular chain microstructure, non-optically pure PDLLA is exist in amorphous phase[3,4] and proposed to be the best candidate among polylactide stereo-isomers as polymer host for solid polymer electrolyte. The amorphous region of solid polymer electrolyte was reported to give higher ionic conductivity compared to crystalline or semi crystalline region[13-15].

In the present work, a well-defined A-B-A block copoly-mers with outer (A) PDLLA blocks and a middle (B) Poly-(ethylene glycol) block was synthesized and their potential as novel solid polymer electrolyte using lithium iodide as conduc-ting material was reported. The synthesis of the copolymer consists of a two-step reaction where PDLLA-PEG-PDLLA triblock copolymer was first synthesized through ring opening polymerization (ROP)[9,11] followed by chain extension reaction to form PDLLA based multiblock polymer host[10,16,17]. Resulted solid polymer electrolytes after doped with various wt. % of lithium iodide conducting salt were characterized using nuclear magnetic resonance spectroscopy, Fourier transform-infrared spectroscopy, Differential scanning calorimetry, thermal thermogravimetric analysis, X-ray diffraction and AC electro-chemical impedance spectroscopy.

EXPERIMENTAL

Poly(ethylene glycol) (PEG, with two hydroxyl group, M_n = 10,000), DL-lactide (DL-LA), hexamethylene diiso-cyanate (HMDI, 98 %), stannous (II) octanoate [Sn(Oct^2), 95 %], lithium iodide were purchased from Sigma-Aldrich and used as received. Tetrahydrofuran (THF, 99 %) and diethyl ether (99.5 %) were supplied by R&M Chemicals. Dry chloro-benzene (99 %, R&M Chemicals) was prepared by extensive refluxing over calcium hydride (CaH_2, Sigma-Aldrich) and distillation. All other chemicals used were reagent grade.

Synthesis of polymer: The synthesis was conducted under dry nitrogen atmosphere. PEG/PDLLA multiblock copolymer was synthesized through two-step chemical reactions, where PDLLA-PEG-PDLLA triblock was first synthesized, followed by chain extension reaction into multiblock copolymer. PDLLA-PEG-PDLLA triblock copolymer was prepared *via* ring opening polymerization of DL-lactide using PEG-diol as initiator and stannous octanoate as catalyst. Before synthesis, poly(ethylene glycol) was dried in a three neck round bottom flask under vacuum at 105 °C for 90 min. with constant stirring. Then, DL-lactide and stannous octanoate was added into the flask. The amount of DL-lactide and poly(ethy-lene glycol) was calculated based on the monomer/initiator mol ratio of 25:1, whereas the mol ratio of DL-lactide and stannous octanoate used was 400/1 (monomer/catalyst). The reaction was carried out at 120 °C for 24 h with constant stirring. After the formation of triblock copolymers, the temperature was reduced to 82 °C and dry chlorobenzene was added to dissolve the synthesized triblock. The chain extension reaction started when HMDI was added using a 1:4 triblock/HMDI mol ratio, followed by stannous octanoate catalyst. The chain extension reaction was performed for 2 h under constant stirring. Lastly, the synthesized polymer was precipitated in the excess of diethyl ether, rinsed, dried under vacuum at 40 °C for 24 h and stored in dry box prior to use.

Preparation of solid polymer electrolyte thin films: The solid polymer electrolytes were prepared through solution casting technique. The synthesized poly(ethylene glycol)/ PDLLA poly(ether-ester-urethane) multiblock copolymer and lithium iodide were used as host polymer and the doped salt, respectively. Two grams of polymer host (per mixture) and various wt. % of salt (5, 10, 15, 20, 25 and 30 %) were dissolved separately in THF and mixed together under constant stirring at room temperature for 24 h to obtain a homogeneous solution of polymer electrolyte system. The solution obtained was then casted on a Teflon petri dish and the solvent was allowed to evaporate slowly in a fume hood. The resulting free standing film was then vacuum dried at 40 °C for 24 h to optimize solvent removal. The film samples were stored under dry nitrogen atmosphere prior to analysis.

Characterization of triblock copolymer and polymer electrolyte films: ^{1}H NMR spectra were obtained at room temperature in $CDCl_3$ solvent (deuteration degree not less than 99.8 %, Fluka) using Bruker Advance 400 NMR spectrometer working at 400 MHz for protons. The internal standard applied is tetramethylsilane.

ATR-FTIR analysis was done with a Spectrum 400 Perkin Elmer GX Spectrometer. The prepared samples were casted on NaCl window and analyzed with infrared ranged from the frequency of 4000 to 650 cm^{-1}.

A Bruker D8-Advance diffractometer with Cu anode were used to study the X-ray diffraction pattern of the prepared samples, scanned from diffraction angle, 2θ of 10° to 50°.

The samples were analyzed using a Shimadzu TGA-50 instrument for the study of thermal stability. The heating rate used was 10 °C/min and the range of measurement was started from room temperature up to 600 °C. Differential scanning calorimetry measurement was performed with a DSC822e Mettler Toledo differential scanning calorimeter with heating and cooling rates of 5 °C/min in the range of 0-100 °C, under inert nitrogen atmosphere.

HIOKI 3532-50LC HiTester impedence analyzer was used to analyze the ionic conductivity of synthesized polymer elec-trolyte. The measurement was taken from frequency range of 50 to 50000 Hz by sandwiching the prepared solid polymer electrolyte between two stainless steel electrodes with surface area of 1.7671 cm^2. The ionic conductivity, σ was calculated according to the equation $\sigma = [l/(R_b \cdot A)]$, where l represents

the film thickness (cm), R_b is the bulk resistance while A is the effective contact area between electrode and the electrolyte (cm^2).

RESULTS AND DISCUSSION

Polymer host synthesis: Poly(ethylene glycol)/PDLLA multiblock copolymer was synthesized through a two-stage reaction which involved ring opening polymerization of DL-lactide and chain extension reaction by HMDI. The reaction was shown schematically in Fig. 1. Theoretical number average molecular weight (M_n) of the synthesized PDLLA-PEG-PDLLA triblock was 13,600 g/mol, where DL-Lactide monomer was expected to form polymer (Mn = 1,800 g/mol for each polymer block) at both hydroxyl terminal groups of PEG-10,000 macroinitiator. The molecular weight of PDLLA blocks was controlled by using the appropriate mol ratio of DL-lactide to poly(ethylene glycol).

Nuclear magnetic resonance spectroscopy: The composition of triblock copolymer, its average molecular weight and the formation of urethane bond between triblock and HMDI at OH/NCO ratio of 1:4 were evaluated using ^{1}H NMR analysis. The ^{1}H NMR spectrum of triblock (a) and HMDI chain extended multiblock (b) were shown in Fig. 2.

The composition of PDLLA-PEG-PDLLA triblock (*e.g.* M_n of PDLLA segment) was determined by comparing the signal intensity of poly(ethylene glycol) methylene proton (H_d, 3.6 ppm) and PDLLA methyne proton (H_b, 5.2 ppm) in the ^{1}H NMR spectrum [Fig. 2(a)][10,11]. From ^{1}H NMR calculation, the combined M_n of two PDLLA blocks was 3,341 g/mol, which gives a total MW value of 13,341 g/mol for the synthesized PDLLA-PEG-PDLLA triblock copolymer, was in good agreement (98 %) with the theoretical M_n value of 13,600. A low-intensity multiplet appears at 4.25 ppm (H_c), assigned to methylene

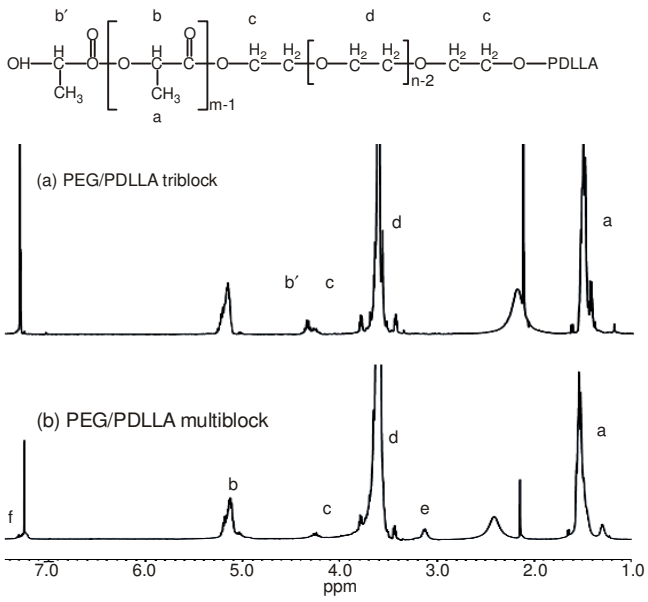


Fig. 2. 400 MHz ^{1}H NMR spectrum of PEG/PDLLA (a) triblock and (b) multiblock in $CDCl_3$ solvent

proton of poly(ethylene glycol) end unit (-CH_2-O-CO-), was an evidence for the covalent bond between PDLLA and poly-(ethylene glycol) blocks[9,11]. The signal of PDLLA methyne proton (H_b', 4.3 ppm) next to hydroxyl end group was present in triblock spectrum (a) but disappeared in the multiblock spectrum (b). This observation is in agreement with previous work[17], where chain extender HMDI was reacted with the hydroxyl end group of triblocks and formed urethane linkage. The reaction shifts the resonance of proton H_b, to 5.2 ppm. Other signals that support the formation of multiblock through urethane linkage is the appearance of peaks at 3.1 and 7.2

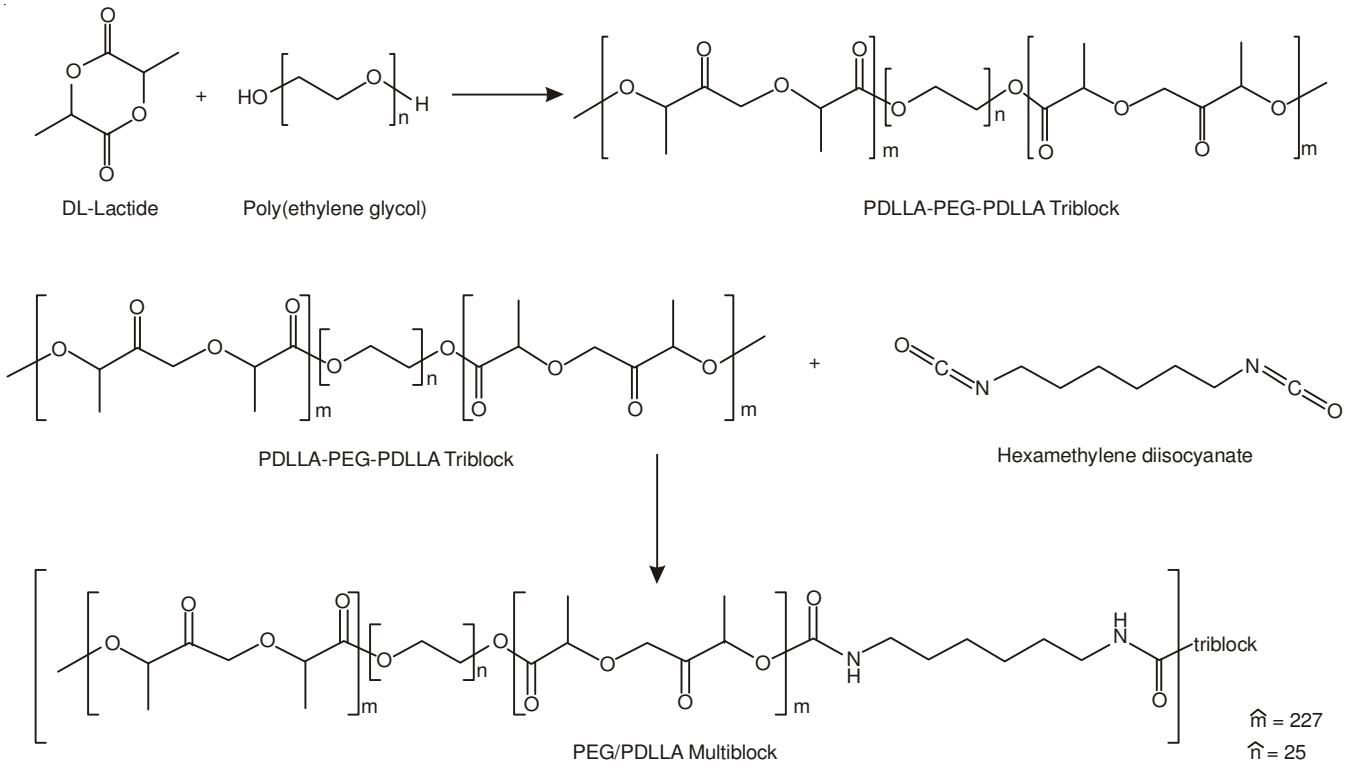


Fig. 1. Synthesis and structure of PEG/PDLLA multiblock copolymers

ppm after chain extension reaction of triblocks. These peaks were assigned to -CH_2NHCOO- (H_e) and -CH_2NHCOO- (H_f) proton of urethane linkage, respectively. However, the latter signal is partly overlapped by chloroform solvent peak.

Properties of the polymer electrolyte

Fourier transformed infrared analysis: FTIR spectroscopies of the prepared PEG/PDLLA multiblock copolymer solid polymer electrolyte were obtained to analyze the interaction between the solid polymer electrolyte polymer matrices with the doped lithium salt. Light will be shed on the oxygen atoms of the carbonyl (C=O) and ether group (C-O-C) from poly(ethylene glycol) and PDLLA, respectively. The electron-rich oxygen atoms acted as an electron donor in the solid polymer electrolyte system. Lone pair electron of oxygen atom was donated to Li^+ from the dissociated lithium iodide and formed polymer-salt complex through dative bond[18-20]. The electron density of that particular oxygen changed, as well as the bond energy of carbonyl or ether groups. Consequently, infrared absorption band of the functional groups show significant changes in radiation wavenumber and peak intensity. Fig. 3(a) and 3(b) represents the FTIR spectra of poly(ethylene glycol)/PDLLA multiblock copolymer solid polymer electrolyte with 0 to 30 % of lithium iodide loadings in the region of 1820-1700 and 1170-1000 cm^{-1}, respectively.

The symmetrical stretching of ester (COO) functional group in PDLLA gives rise to an intense and sharp peak of C=O symmetrical stretching at 1754 cm^{-1} (Fig. 3a). Upon the addition of lithium iodide in PDLLA/poly(ethylene glycol)-LiI system, the intensity of C=O symmetrical stretching peak reduced and shifted to lower wavenumber at 1751 cm^{-1}. Since the position and intensity of an absorption band corresponds to different bond energy and changes in number and dipole moment of the specific bond, addition of lithium salt apparently affect the symmetrical stretching of C=O in PDLLA blocks. Same observation on shifting of wavenumber was reported by previous studies[13,14,19,20] and was claimed as the existence of strong intermolecular interaction. This confirmed the formation of polymer-salt complex *via* dative bond resulted from the interaction between lithium ion and oxygen atom in the solid polymer electrolyte polymer host. Moreover, there was a shoulder peak appeared at the wavenumber of 1715 cm^{-1} which is similar with previous study[16], where the vibration peak was referred to -C=O of PDLLA block adjoined to -NH of HMDI.

Meanwhile, lithium cations from dissociated lithium iodide also form dative bond with oxygen atoms from poly(ethylene glycol) ether (C-O-C) functional groups. The coordination between cations and ether oxygen was expected to show changes in the ether oxygen vibration modes, as reported by Reddy and his coworkers[21]. According to previous study[13,15,22], the presence of a special triplet peak with a maximum peak at 1095 cm^{-1} and two minor peaks at 1145 and 1060 cm^{-1} can be accounted to semicrystalline phase of poly(ethylene glycol). This observation was well collaborated with poly(ethylene glycol) ether functional groups in PDLLA-PEG-PDLLA multiblock copolymer solid polymer electrolyte system as shown in Fig. 3(b). The stretching mode of the C-O-C triplet peak for the polymer host was changed in the same trend as the wt. % of lithium iodide increased, where peak intensity decreased and shifted to lower wavenumber. However, the two minor peaks of C-O-C triplet peak at 1145 and 1060 cm^{-1} were only present in infrared spectra of solid polymer electrolyte system with lithium iodide content up to 10 wt. %. This observation indicated that the ether absorption band was highly affected by cation complexation[13,22]. The peak shift of C-O-C triplet peak was referred to the interaction between lithium cation and ether oxygen atom where oxygen lone pair electrons

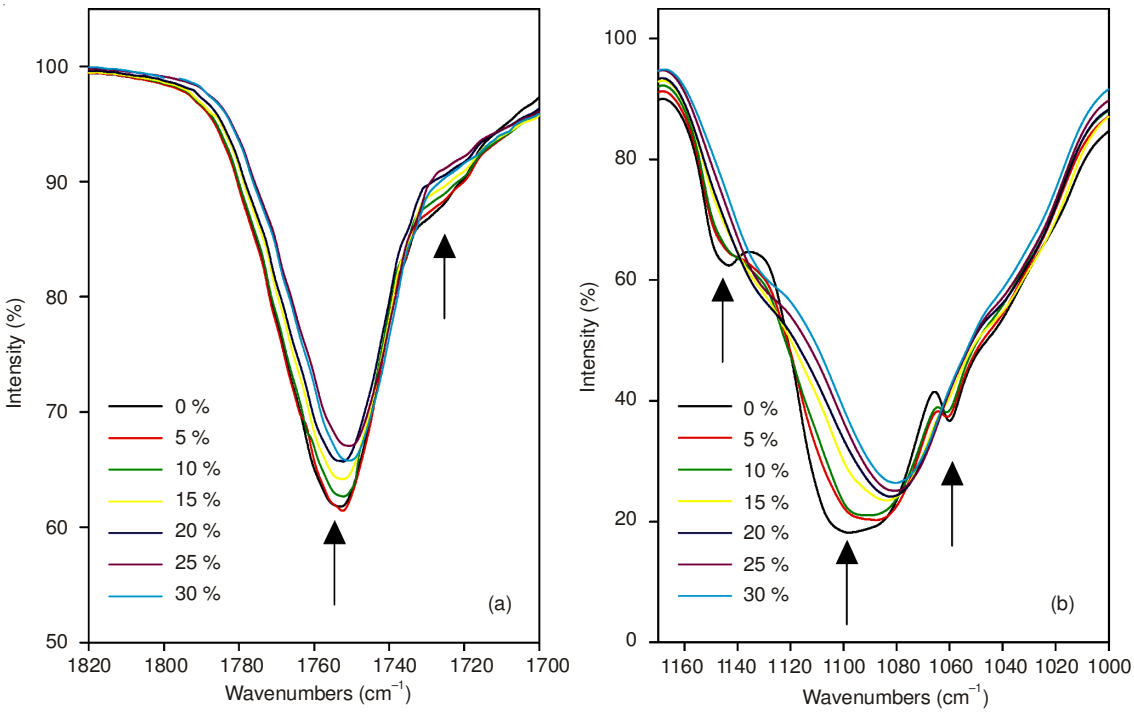


Fig. 3. FTIR spectra of poly(ethylene glycol)/PDLLA multiblock copolymer at (a) 1820-1700 cm^{-1} and (b) 1170-1000 cm^{-1}

were donated to Li^+ and complexation occurred *via* dative bond[13-15,18-20].

Differential scanning calorimetry: Differential scanning calorimetry analysis was used to measure the thermal properties, characteristic temperature and to investigate the effect of salt content on the thermal properties of the electrolyte system. Differential scanning calorimetry thermograms of the synthesized PDLLA-PEG-PDLLA multiblock copolymer and prepared solid polymer electrolyte with different wt. % of lithium iodide were shown in Fig. 4. The melting temperature (T_m) and enthalpy of fusion are derived respectively from the maximum and area under the differential scanning calorimetry endotherm peak.

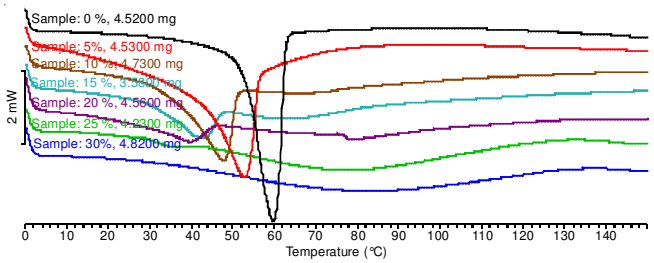


Fig. 4. Differential scanning calorimetry thermogram of PEG/PDLLA multiblock copolymer electrolyte with various LiI load

On account of PDLLA stereoisomer amorphous state, the intense and sharp endothermic peak observed in the thermogram of pure multiblock copolymer polymer host at 59 °C, corresponded to the crystalline melting temperature (T_m) of poly(ethylene glycol). However, the T_m of semicrystalline neat poly(ethylene glycol) was reported to be around 65 °C[2,11,15,19,23]. The shift in poly(ethylene glycol) T_m from 65 to 59 °C indicated that the thermal properties of poly(ethylene glycol) was modified by copolymerization with PDLLA block. This phenomena may be attributed to the increment of crystalline defect concentration, a changes in poly(ethylene glycol) crystal structure or crystal surface free energy[24], as well as the reduction of crystal size[25]. The T_m was further reduced from 59 to 35 °C as the wt. % of lithium iodide in electrolyte system increased up to 25 %. The decrement in T_m suggested that the degree of amorphous state in the solid polymer electrolyte increases with the wt. % of lithium iodide. This statement was supported by calculated degree of crystallinity (X_c) and melting enthalpy of poly(ethylene glycol) (Table-1). The degree of crystallinity (X_c) are calculated from:

$$X_c = (\Delta H_{SPE}/\Delta H^\circ_{PEG})\ 100\ \%$$

where ΔH_{SPE} is the apparent enthalpy of fusion per gram of solid polymer electrolyte while ΔH°_{PEG} is the enthalpy of fusion per gram of 100 % crystalline poly(ethylene glycol) from literature data[26,27]. The decrement of solid polymer electrolyte crystallinity was attributed in the improvement of host polymer flexibility and segmental motion which will then contribute to ionic conductivity.

Thermogravimetric analysis: The thermal stability of the synthesized PEG/PDLLA multiblock copolymer and respective solid polymer electrolyte with various loading of lithium iodide was evaluated by TGA in nitrogen gas atmosphere. The resulted TGA thermograms was shown in Fig. 5.

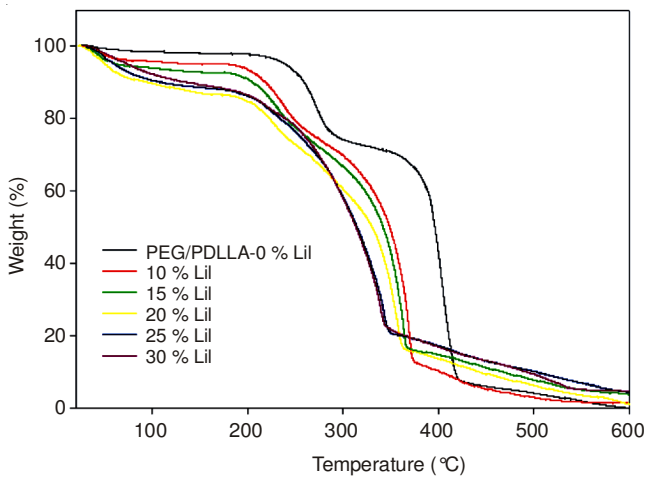


Fig. 5. Thermogravimetric analysis thermogram of PEG/PDLLA multiblock copolymer electrolyte with various weight percentage of LiI load

As a consequence of the hygroscopic nature of lithium iodide, synthesized thin film solid polymer electrolyte were expected to absorb moisture during the process of sample loading. This phenomena was contributed to the initial 3 to 10 % weight loss in 20 to 100 °C temperature range. The initial weight loss increased accordingly as the lithium iodide content in solid polymer electrolyte system increased. Excess solvent trapped in polymer matrix might also be one of the contributors in the initial weight loss. There is no major weight loss for all the polymer electrolytes until 200 °C and this suggested that prepared solid polymer electrolyte were thermally stable up to 200 °C.

TABLE-1
DEGREE OF CRYSTALLINITY OF PEG/PDLLA MULTIBLOCK COPOLYMER ELECTROLYTE AT VARIOUS LOADING PERCENTAGE OF LiI (wt. %)

LiI (wt %) to PEG/PDLLA multiblock	T_m of Poly(ethylene glycol)	Melting enthalpy (J g^{-1})	Relative percentage of crystalline (%)
Pure PEG	68		78.5
Pure PDLLA	-	-	-
0 %	59.5	102.83	48.1
5 %	52.6	93.03	43.5
10 %	47.6	48.79	22.8
15 %	42.2	29.38	13.7
20 %	39.6	18.54	8.68
25 %	35.0	2.65	1.24
30 %	-	-	-

Thermogravimetric analysis curves shown in Fig. 5 clearly indicated that PEG/PDLLA multiblock copolymer undergoes a two-step thermal degradation. The first step of the degradation corresponded to PDLLA which started at 250 °C with maximum degradation rate (T_{max}) at 270 °C. Whereas the second degradation was accounted for poly(ethylene glycol) block, with 390 and 404 °C as the value for onset temperature and T_{max}, respectively. As the lithium iodide content in the electrolyte system associated to polymer-salt complex increases, the amount of residue after 600 °C also changed in an ascending trend.

X-Ray diffraction analysis: X-Ray diffraction analysis was performed to study the structure and crystallization behaviour of the polymer-salt complexes. Fig. 6 shows the X-ray diffraction pattern of the lithium iodide (b), pure poly(ethylene glycol) (c) and, PEG/PDLLA multiblock and their complex with different weight ratio of lithium iodide (a) in the range of $2\theta = 2°$ to 80°. On account of optically inactive PDLLA amorphous phase[3], it reveals that the prominent peaks appear at 2θ values of 19.0° and 23.1° for pure polymer host are representatives of poly(ethylene glycol) crystalline phase. Concomitantly, there is no major change in the diffraction pattern of poly(ethylene glycol) after copolimerization reaction with PDLLA blocks. Most of the poly(ethylene glycol) crystalline peak remained exist though decreased in intensity and thus resulted in increased amorphous phase by introducing hard segment into the backbone of polymer chain. The amorphous nature facilitates the polymer chain mobility and gives rise to ionic conductivity enhancement which will be further discussed in electron impedance spectroscopy (EIS).

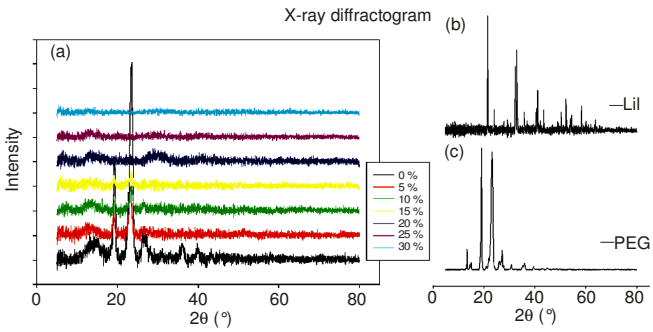


Fig. 6. X-ray diffraction pattern of the LiI salt (b), pure poly(ethylene glycol) (c), PEG/PDLLA multiblock and their complex with different weight ratio of LiI salts (a) in diffraction range of $2\theta = 2°$ to 80°

Intensity of the mentioned poly(ethylene glycol) crystalline peaks decreased gradually as the increment of lithium iodide content in multiblock polymer host up to 15 wt. % and disappeared in the PEG/PDLLA multiblock with higher LiI salt content. Accordingly, the amorphous phase of PEG/PDLLA multiblock-LiI solid polymer electrolytes increased with addition of lithium iodide. This observation was supported by differential scanning calorimetry analysis where solid polymer electrolyte relative percentage of crystallinity was decreased up on increment of LiI loading as stated in Table-1. Meanwhile, the absence of diffraction peaks corresponding to lithium iodide in LiI loaded solid polymer electrolyte indicates that LiI solvates well in the PEG/PDLLA multiblock matrix. These finding were fully corroborated with result obtained in DSC according to the absence of new endotherm peak when lithium iodide was added into the electrolyte system even up to 30 wt. %.

Electron impedance spectroscopy: The conductivity behaviour of electrolytes at room temperature with various loadings of lithium iodide ranged from 0 to 30 wt. % was reported in Fig. 7. The ionic conductivity of the polymer-salt complex increased with wt. % of lithium iodide and reached an optimum value, 4.167 e^{-6} S cm^{-1}, at 25 wt. % of lithium iodide. This optimum value signifies the maximum of effective interaction between oxygen atoms and lithium cation in electrolyte system. The presence of 25 wt. % of lithium iodide increased the conductivity up to five magnitudes in comparison to pure PEG/PDLLA multiblock copolymer polymer host with conductivity value of 4.423 e^{-11} S cm^{-1}. Lithium salt loaded in the polymer system was dissociated into conducting species due to the presence of ether and ester oxygen atom in poly(ethylene glycol) and PDLLA, respectively. The increment of the conducting species was found to be the major factor which contributes in initial conductivity increment[14,18,23]. As a consequence of the polymer-salt complex formation through dative bond between lithium cation and polymer oxygen atom as discussed in IR spectroscopy, the effective interaction then reduces the crystalline phase of the electrolyte, as proved by differential scanning calorimetry and X-ray diffraction. The amorphous nature of the electrolyte promotes segmental motion and results in better ion mobility[2]. This observation is in agreement with previous reports[28,29], where the conductivity was inversely proportional to electrolyte crystallinity. However, the conductivity of electrolyte decreased after the optimum value at 25 wt. % of lithium iodide. The excessive of salt loading will contribute to decrement of polymer chain mobility caused by formation of transient cross-links in the electrolyte system due to ion association[2,30].

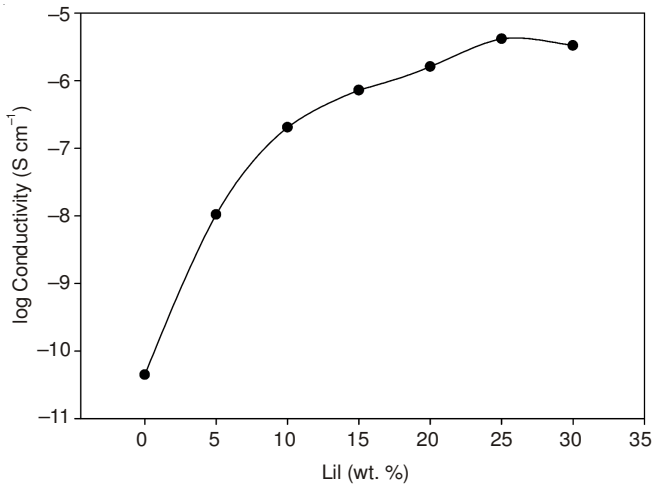


Fig. 7. Variation of ionic conductivity of PEG/PDLLA multiblock copolymer electrolyte with LiI salt concentration at room temperature

The temperature dependence of conductivity for PEG/PDLLA multiblock copolymer solid polymer electrolyte with 25 wt. % lithium iodide was shown in Fig. 8 by Arrhenius plot in temperature range of 303 to 363 K. The bulk resistant of

the electrolyte was decreased with temperature and found to be unmeasurable after 363 K due to low stability at temperature higher than 363 K. The linear correlation between temperature and conductivity of electrolyte indicated that the electrolyte system exhibited Arrhenius-like behaviour given by Arrhenius equation, $\sigma = \sigma_o \cdot e^{(-Ea/kT)}$ where σ_o, E_a and k are pre-exponential factor, activation energy and Boltzmann constant (8.6×10^{-5} eV K^{-1}), respectively. By fitting logarithm of Arrhenius equation into linear equation of graph shown in Fig. 8, the value of σ_o and $-E_a/kT$ is represented by y-axis intercept and graph slope, m. From the Arrhenius plot, E_a value is 0.99 eV and the pre exponential factor σ_o is 4.23×10^{11} S cm^{-1}.

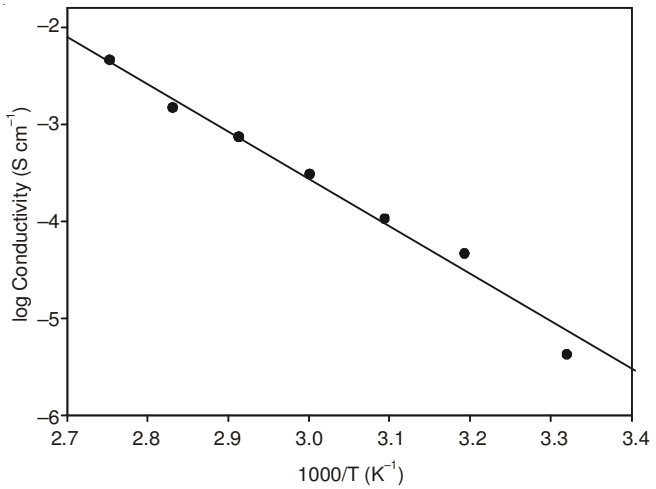


Fig. 8. Arhenius plot of PEG/PDLLA multiblock copolymer electrolyte with 25 wt. % of LiI

Conclusion

Polyether-ester-urethane copolymer from environmentally sustainable polylactide has been successfully synthesized and can function as a solid polymer electrolyte with the inclusion of lithium iodide salt through solution casting technique. An optimum conductivity value of 4.167×10^{-6} S cm^{-1} was obtained under room temperature with 25 wt. % of lithium iodide conducting salt, resulted from maximum effective interaction between conducting species and polymer matrix. The increment of temperature further boost up the conductivity with three magnitude of increment up to 4.5979×10^{-3} S cm^{-1}. ^{1}H NMR demonstrated the occurrence of ester bonded triblock and urethane bonded multiblock, whereas infrared analysis showed the evidence for polymer-salt complex formation. Prepared electrolyte was further characterized *via* TGA, DSC and XRD for thermal and structural studies.

ACKNOWLEDGEMENTS

The authors express their gratitude towards the University Kebangsaan Malaysia (UKM) for providing analytical equipment that were used in this research. This work was supported by the Ministry of Higher Education under research grant numbers ERGS/1/2013/TK07/UKM/03/1.

REFERENCES

1. M.B. Armand, J.M. Chabagno and M. Duclot, Poly-Ethers as Solid Electrolytes, Proceedings of International Conference on Fast Ion Transport in Solids, Elsevier, North-Holland (1979).
2. F.M. Gray, Polymer Electrolytes: Cambridge, The Royal Society of Chemistry, U.K., p. 17 (1997).
3. K.M. Nampoothiri, N.R. Nair and R.P. John, *Bioresour. Technol.*, **101**, 8493 (2010).
4. D. Garlotta, *J. Polym. Environ.*, **9**, 63 (2001).
5. D.E. Fenton, J.M. Parker and P.V. Wright, *Polymer*, **14**, 589 (1973).
6. C. Chen, G. Lv, C. Pan, M. Song, C. Wu, D. Guo, X. Wang, B. Chen and Z. Gu, *Biomed. Mater.*, **2**, 4 (2007).
7. X.D. Guo, L.J. Zhang, Y. Qian and J. Zhou, *Chem. Eng. J.*, **131**, 195 (2007).
8. S. Greiner, A. Kadow-Romacker, B. Wildemann, P. Schwabe and G. Schmidmaier, *Biomed. Mater. Res. A*, **83A**, 1184 (2007).
9. Y. Lemmouchi, M. Murariu, A.M.D. Santos, A.J. Amass, E. Schacht and P. Dubois, *Eur. Polym. J.*, **45**, 2839 (2009).
10. D. Cohn and A. Hotovely-Salomon, *Polymer*, **46**, 2068 (2005).
11. D. Kubies, F. Rypacek, J. Kovarova and F. Lednicky, *Biomaterials*, **21**, 529 (2000).
12. K.W. Chew, T.C. Ng and Z.H. How, *Int. J. Electrochem. Sci.*, **8**, 6354 (2013).
13. A. Ahmad, M.Y.A. Rahman and M.S. Suait, *J. Appl. Polym. Sci.*, **124**, 4222 (2012).
14. M.S. Su'ait, S.A.M. Noor, A. Ahmad, H. Hamzah and M.Y.A. Rahman, *J. Solid State Electrochem.*, **16**, 2275 (2012).
15. S.A.M. Noor, A. Ahmad, I.A. Talib and M.Y.A. Rahman, *Ionics*, **16**, 161 (2010).
16. C. Liu, Y. Jia and A. He, *Int. J. Polym. Sci.*, **Article ID 315917** (2013).
17. J. Tuominen, J. Kylma and J. Seppala, *Polymer*, **43**, 3 (2002).
18. A. Ahmad, M.Y.A. Rahman, H. Harun, M.S. Su'ait and M.A. Yarmo, *Int. J. Electrochem. Sci.*, **7**, 8309 (2012).
19. S.A.M. Noor, A. Ahmad, M.Y.A. Rahman and I.A. Talib, *Nat. Sci.*, **2**, 190 (2010).
20. M.S. Su'ait, A. Ahmad, K.H. Badri, N.S. Mohamed, M.Y.A. Rahman, C.L.A. Ricardo and P. Scardi, *Int. J. Hydrogen Energy*, **39**, 3005 (2013).
21. M.J. Reddy, P.P. Chu and U.V.S. Rao, *J. Power Sources*, **158**, 614 (2006).
22. Z. Tang, J. Wang, Q. Chen, W. He, C. Shen, X.-X. Mao and J. Zhang, *Electrochim. Acta*, **52**, 6638 (2007).
23. S.A.M. Noor, A. Ahmad, M.Y.A. Rahman and I.A. Talib, *J. Appl. Polym. Sci.*, **113**, 855 (2009).
24. C.C. Alfonso and T.P. Russell, *Macromolecules*, **19**, 1143 (1986).
25. N.K. Kalfoglou, D.D. Sotiropoulou and A.G. Margaritis, *Eur. Polym. J.*, **24**, 389 (1988).
26. T.H.J. Singh and S.V. Bhat, *Bull. Mater. Sci.*, **26**, 707 (2003).
27. X. Li and S.L. Hsu, *J. Polym. Sci. Polym. Phys*, **22**, 1331 (1984).
28. E. Zygadlo-Monikowska, Z. Florjañczyk, E. Rogalska-Joñska, A. Werbanowska, A. Tomaszewska, N. Langwald, D. Golodnitsky, E. Peled, R. Kovarsky, S.H. Chung and S.G. Greenbaum, *J. Power Sources*, **173**, 734 (2007).
29. J.-H. Ahn, G.X. Wang, H.K. Liu and S.X. Dou, *Power Sources*, **119-121**, 422 (2003).
30. A.M.M. Ali, R.H.Y. Subban, H. Bahron, T. Winie, F. Latif and M.Z.A. Yahya, *Ionics*, **14**, 491 (2008).