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Synthesis of New Bio-Based Solid Polymer Electrolyte Polyurethane-$LiClO_4$ via Prepolymerization Method: Effect of NCO/OH Ratio on Their Chemical, Thermal Properties and Ionic Conductivity

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***Abstract*—**Novel bio-based polymer electrolyte was synthesized with $LiClO_4$ as the main source of charge carrier. Initially, polyurethane-$LiClO_4$ polymer electrolytes were synthesized *via* prepolymerization method with different NCO/OH ratios and labelled them as PU1, PU2, PU3 and PU4. Fourier transform infrared (FTIR) analysis indicates the co-ordination between Li^+ ion and polyurethane in PU1. Differential scanning calorimetry (DSC) analysis indicates PU1 has the highest glass transition temperature (T_g) corresponds to the most abundant urethane group which is the hard segment in PU1. Scanning electron microscopy (SEM) shows the good miscibility between lithium salt and the polymer. The study found that PU1 possessed the greatest ionic conductivity and the lowest activation energy, Ea. All the polyurethanes exhibited linear Arrhenius variations indicating ion transport *via* simple lithium ion hopping in polyurethane. This research proves the NCO content in polyurethane plays an important role in affecting the ionic conductivity of this polymer electrolyte.

***Keywords*—**Ionic conductivity, Palm kernel oil-based monoester polyol, polyurethane, solid polymer electrolyte.

I. Introduction

FOR the past few years, solid polymer electrolytes (SPE) gained a lot of attention due to their wide applications in lithium ion batteries, fuel cell, chemical sensors and electrochemical devices [1]-[4]. Many attempts have been made by researchers to enhance the mechanical strength, thermal and chemical properties as well as ionic conductivity of SPE. Recently, polyurethane (PU) is one of the polymers used in SPE due to its high thermal, chemical stability, good mechanical strength, high elasticity and simple preparation process [5]-[7]. Moreover, good miscibility between lithium ion and polyurethane enhances the ion transport in the polymer electrolyte [8], [9]. Polyurethane comprised soft segment and diisocyanate based hard segment [10]-[12]. The hard-segment is important in crosslinking and intermolecular hydrogen bonding between the hard segments of urethane linkages [13]. Besides that, the hard segment (urethane group) content determines the crystallinity of polyurethane [14]. NCO/OH ratio in the hard segment affects the structure, flexibility and mechanical properties of polyurethane. Therefore, the NCO/OH ratio proves to regulate the properties of polyurethane [15] efficiently. However, the effect of varying the NCO/OH ratios in the formation of palm kernel-based polyurethane *via* prepolymerization method on the ion conductivity, thermal stability and chemical properties of polymer electrolytes are not completely investigated. Hence, bio-based polyurethanes with different NCO/OH ratios synthesized from palm kernel oil based monoester poyol were doped with lithium perchlorate salt ($LiClO_4$) to prepare SPE by using prepolymerization method [5], [25]. Subsequently, all the samples were characterized by using Fourier transform infrared spectroscopy (ATR-FTIR), 13 nuclear magnetic resonance spectroscopy (13C NMR), Soxhlet test, Differential scanning calorimetry (DSC), Scanning electron microscopy (SEM) and AC electrochemical impedance spectroscopy (EIS). The novelty of this research is the synthesis of solid polyurethane electrolyte without the use of catalyst or heating due to the presence of amide group in palm kernel oil-based monoester polyol (PKO-p) which catalyses the polymerization of PU [5]. Hence, the synthesis process is easy and simple.

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II. Materials

The palm kernel oil-based monoester polyol (PKO-p) was prepared as described elsewhere by Badri et al. [35]. 4,4-diphenylmethane diisocyanate (MDI) was obtained from Cosmopolyurethane (M) Sdn. Bhd. Acetone, polyethylene glycol (PEG, M_n=400) and Lithium perchlorate ($LiClO_4$) were supplied by Sigma Aldrich (M) Sdn. Bhd.

III. Synthesis of Polyurethane Electrolytes

PKO-p was dissolved in acetone before mixing with the MDI in a round-bottom flask under nitrogen gas atmosphere to form urethane prepolymer. Then PEG which acts as a chain extender was added into the mixture. Subsequently, 5 wt% of $LiClO_4$ was doped into the mixture and agitated at 200 rpm for an hour at ambient temperature. After that, the mixture was

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casted onto a Teflon plate and the thickness of the film was kept at 0.01cm. Then the solvent was evaporated by heating the film at 55°C for 24 hours. Four different polyurethane-$LiClO_4$ based polymer electrolytes with different diisocyanate/ PKO-p (NCO/OH) mass ratios and one polyurethane as control were synthesized as shown in Table I.

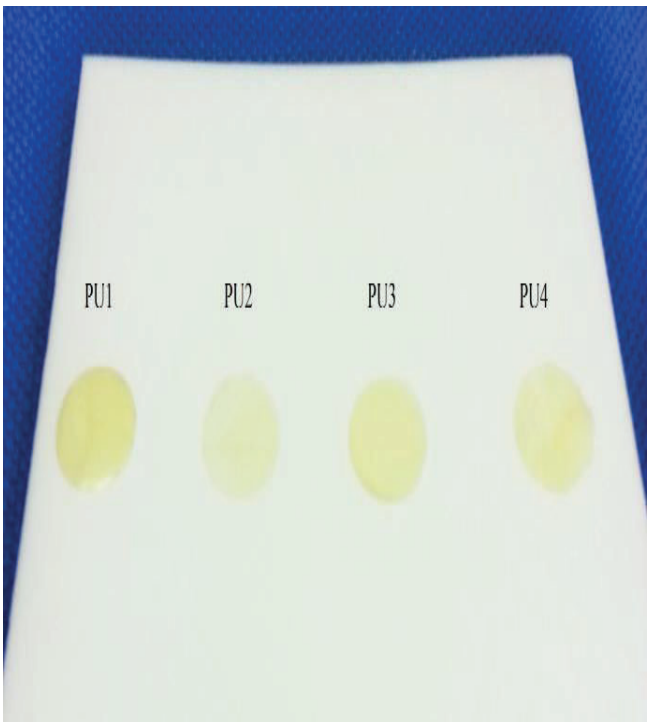


Fig. 1 Flexible Polyurethane-$LiClO_4$ polymer electrolytes with various NCO/OH ratios

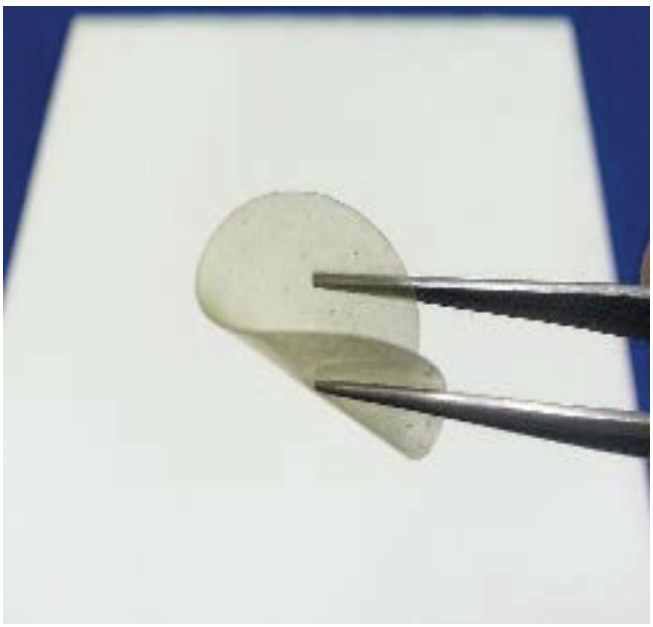


Fig. 2 Flexible PU0

TABLE I
POLYURETHANE-LICLO4 POLYMER ELECTROLYTES WITH VARIOUS NCO/OH RATIOS

Sample	NCO/OH (g/g)	$LiClO_4$ (wt %)
PU0	200/100	0
PU1	200/100	5
PU2	150/100	5
PU3	100/100	5
PU4	85/100	5

All prepared samples were yellow, translucent and void-free films as shown in Figs. 1 and 2.

The formation of bio-based polyurethane *via* uncatalyzed prepolymerization method is shown in Fig. 3.

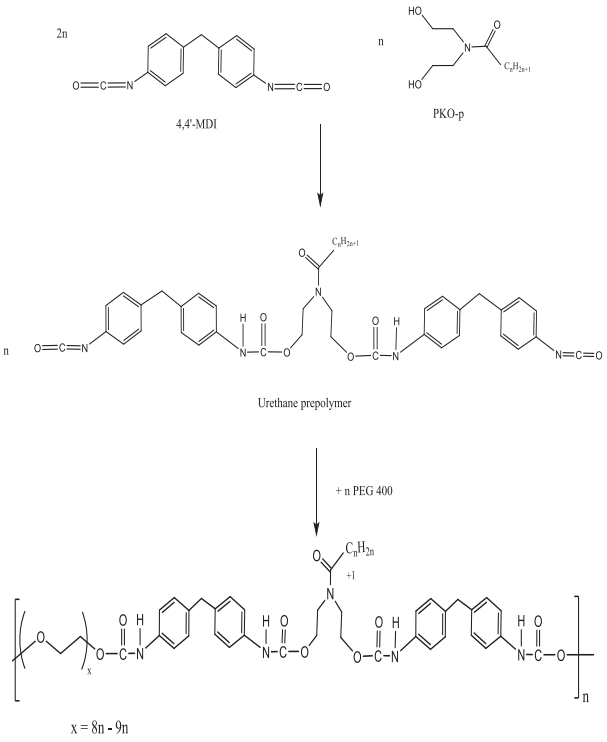


Fig. 3 Scheme of PKO-p formation based polyurethane

IV. General Characterization

The carbonyl, carbamate and amide groups of urethane in PU-$LiClO_4$ were identified by ATR-FTIR analysis using Perkin-Elmer spotlight 400 imaging system with scan resolution of 2 cm^{-1}. The structure of polyurethane-$LiClO_4$ was confirmed with using Bruker DRX 600 MHz 13C NMR spectrometer with DMSO-d6 as solvent. The percentage of solid content of PU1, PU2, PU3 and PU4 was determined by carrying out soxhlet method. The samples were placed in the soxhlet extractor tube and toluene in the round bottomed flask. Then the solvent was heated and the heating temperature was maintained at 115 °C for 24 hours [16]. The percentage of the solid content of the dry sample was calculated by referring to (1):

$$\% \text{ gel content} = \frac{\text{mass of dried sample}}{\text{mass of sample}} \times 100\% \quad (1)$$

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The surface morphology of the samples was observed using SEM model ZEISS, SUPRA 55VP at a depth of 10000x magnification from the surface at 10 kV electron beam. The average atomic percentage of main elements in PU-$LiClO_4$ was determined by conducted SEM-EDX analysis. The thermal stability of PU-$LiClO_4$ was analysed by using a DSC model Mettler Toledo 822e in nitrogen gas atmosphere. The heating temperature ranges from room temperature to 250°C. The ionic conductivity of PU-$LiClO_4$ at room temperature was measured by using EIS with the applied frequency ranged from 1 Hz to 10000000 Hz at 100 mV amplitude. A disc-shaped sample with the thickness of 0.1mm was placed between two stainless-steel block electrodes. The analysis was carried out at room temperature and also at temperature range of 303 K to 373 K. The ionic conductivity (σ) of Pu-$LiClO_4$ was calculated from the bulk resistance (R_b), the film thickness (l) and the contact area of the thin film (A=2.01cm^2) by referring to (2) :

$$\sigma = \frac{l}{(R_b \times A)} \quad (2)$$

The activation energy (Ea) of the ionic conductivity of Pu-$LiClO_4$ was obtained by different ionic conductivity at different heating temperature ranging from 303 K to 373 K. Then the activation energy was calculated by referring to (3) [17]-[19].

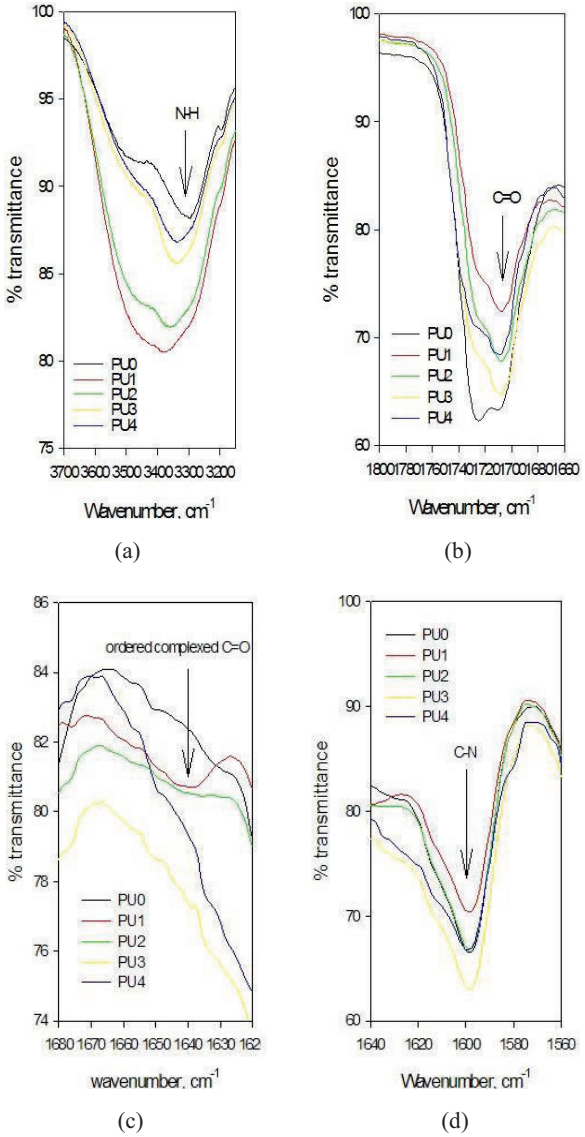
$$\sigma = \sigma_o \exp(-Ea/kT) \quad (3)$$

where σ_o, Ea and k are pre-exponential factor, activation energy and Boltzmann constant (8.617×10^{-5} eV K^{-1}), respectively. The activation energy reflects the mobility of lithium ion in the polyurethane-$LiClO_4$ polymer electrolyte.

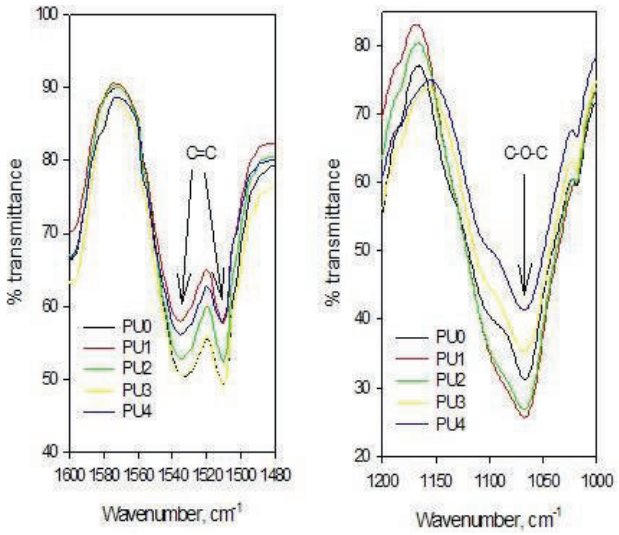
V. Results & Discussion

A. FTIR Analysis

Fig. 4 shows the FTIR spectrum of PU0, PU1, PU2, PU3 and PU4. The presence of C-N, N-H, C=C and C=O of polyurethane was identified as shown in Table II. The hydrogen bonded amine (N-H) stretching band region was detected at the range of 3296-3352 cm^{-1} [20], [21]. The carbamate peaks were detected at the range of 1597-1599 cm^{-1}. The disappearance of NCO peak at the range of 2250-2270 cm^{-1} confirms the complete prepolymerization [22]. It corresponds to the disappearance of NCO peaks in 13C NMR spectrums of the polymer electrolytes in Fig. 6. The free and hydrogen bonded C=O stretching bands of PU0 are observed at 1725 cm^{-1} and 1711 cm^{-1} as shown in Table II. However, free C=O peaks were not detected in all the polyurethane-$LiClO_4$ polymer electrolytes. Moreover, the hydrogen bonded C=O peaks in all the polymer electrolytes shifted to 1708 cm^{-1} as shown in Fig. 3 (b) due to the complex formation of Li^+ ion and carbonyl groups in PU weakens the C=O bond. Additionally, an ordered complexed C=O band appeared at 1649 cm^{-1} for PU1 in Fig. 3 (c). It may be attributed to the coordination between Li^+ ion and PU1 which has the greatest amount of urethane group. The amount of urethane group (hard segment) was proven by Soxhlet analysis as shown in Table III. So, it induces the interaction between Li^+ ions with oxygen atoms of carbonyl groups in which weakens the the C=O bond by sharing the electron density of oxygen atoms in carbonyl groups [9]. Moreover, it also indicates that the coordination between Li^+ ions and carbonyl groups does not disrupt the hydrogen bonded carbonyl groups because two lone pairs of electrons of oxygen atom in carbonyl group able to coordinate with Li^+ ion and form hydrogen bond simultaneously. The C-O-C peaks of all the PU-$LiClO_4$ remain unchanged at 1067 cm^{-1}. Hence, it implies the coordination of Li^+ ions is preferable with C=O and not with C-O-C due to the higher electron density of oxygen atom of C=O compared to the oxygen atom of C-O-C. The complex formation of Li^+ ion with carbonyl group of polyurethane is suggested as shown in Fig. 5. The C=C peaks detected in all the FTIR spectra of polyurethane-$LiClO_4$ polymer electrolytes are referred to the benzene ring of MDI used in synthesis of polyurethane-$LiClO_4$ [23].



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(e) (f)

Fig. 4 The vibration regions of (a) N-H, (b) C=O, (c) ordered complexed C=O, (d) C-N, (e) C=C and (f) C-O-C of urethane group in polyurethane-$LiClO_4$ polymer electrolytes and polyurethane

TABLE II
THE WAVENUMBERS OF FUNCTIONAL GROUPS IN POLYURETHANE /LICLO4 POLYMER ELECTROLYTES WITH VARIOUS NCO/OH RATIOS AND POLYURETHANE

Functional group	Wavenumber (cm^{-1})				
	PU0	PU1	PU2	PU3	PU4
C=O	1725, 1711	1708	1708	1708	1708
C-N	1598	1597	1598	1598	1599
N-H	3296	3352	3327	3341	3336
C=C	1533, 1510	1533,1509	1534,1509	1533,1510	1534,1510
C-O-C	1067	1067	1067	1067	1067
N=C=O	-	-	-	-	-

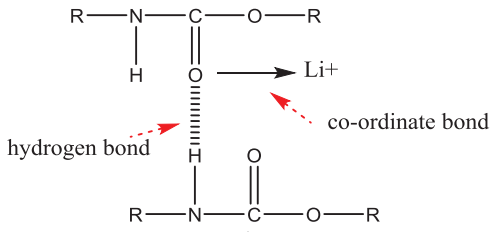


Fig. 5 The suggested complex formation between Li^+ ion and carbonyl group of polyurethane

B. 13C NMR Spectroscopy Analysis

The 13C NMR spectrums of polyurethane-$LiClO_4$ polymer electrolytes are shown in Fig. 6 and depicted as below:

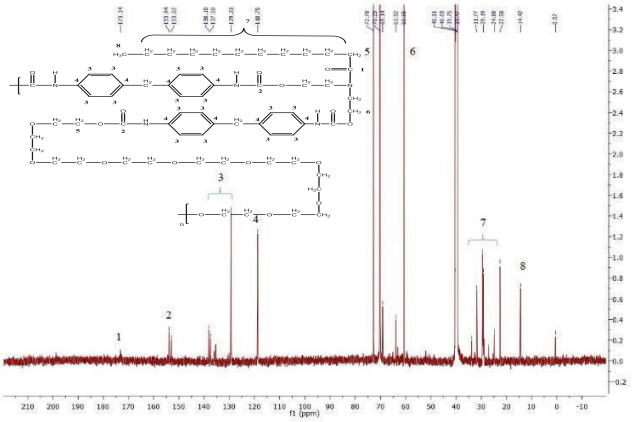
13C NMR (DMSO-d_6) for PU1: δ (ppm) = 173.2 (C(O)N), 153.8-153.9 (C(O)ONH), 129.3-138.0 (C=C), 119.0 (C=C), 70.2-72.8 (CH_2CONH), 60.6-64.0 (C(O)OCNH), 22.5-33.9 (CH_2), 14.4 (CH_3).

13C NMR (DMSO-d_6) for PU2: δ (ppm) = 173.0 (C(O)N), 153.0-153.9 (C(O)ONH), 129.3-138.1 (C=C), 119.0 (C=C), 70.2-72.8 (CH_2CONH), 60.6-64.0 (C(O)OCNH), 22.5-33.9 (CH_2), 14.4 (CH_3).

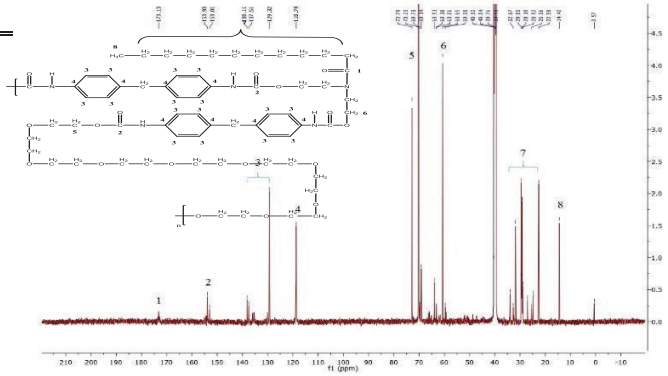
13C NMR (DMSO-d_6) for PU3: δ (ppm) = 173.2 (C(O)N), 153.2-153.9 (C(O)ONH), 129.3-137.9 (C=C), 118.9 (C=C), 70.1.2-72.7 (CH_2CONH), 60.6-63.9 (C(O)OCNH), 22.5-33.9 (CH_2), 14.4 (CH_3).

13C NMR (DMSO-d_6) for PU4: δ (ppm) = 173.2 (C(O)N), 153.0-153.5 (C(O)ONH), 129.3-137.8 (C=C), 118.7 (C=C), 70.2-72.7 (CH_2CONH), 60.6-66.0(C(O)OCNH), 22.5-33.9 (CH_2), 14.3 (CH_3).

The C=O peaks of urethane were detected at 153.0-153.9 ppm [24]. The NCO peaks were not obtained at 125 ppm where it indicates the complete polymerization has taken place [5], [26]. The methylene peaks were detected varying from 22.5 ppm to 33.9 ppm due to the various carbon chains in polyurethane-electrolytes. Lauric acid is assumed as the main carbon chain in the polyurethane because the composition of lauric acid in PKO is 50-52% [5].

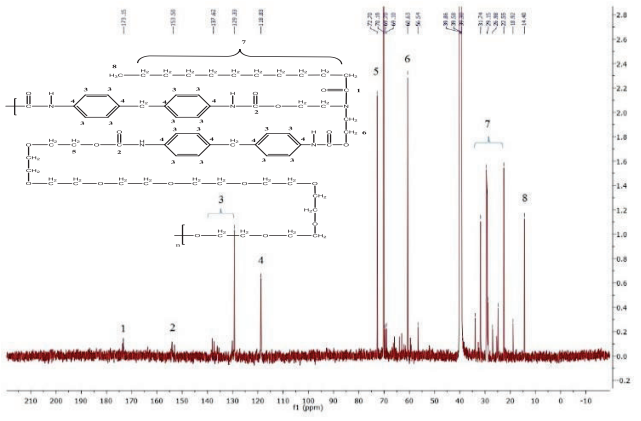


(a)

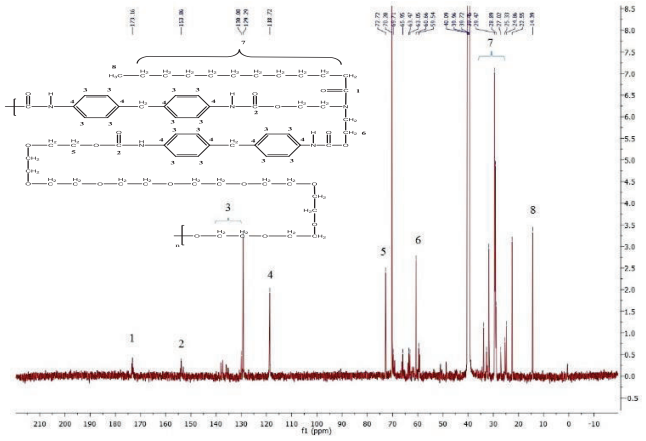


(b)

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(c)



(d)

Fig. 6 13C NMR spectrum of (a) PU1,(b) PU2,(c) PU3 and (d) PU4

C. Soxhlet Analysis

Soxhlet analysis is used to determine the amount of hard segment in polyurethane. The urethane group (hard segment) in polyurethane is polar [27]. Hence, the hard segment of polyurethane hardly dissolved in toluene. The soxhlet test proves the PU1 has the greatest amount of hard segment (urethane group). The obtained results are consistent with the DSC analysis.

TABLE III
PERCENTAGE OF GEL CONTENT FOR POLYURETHANE-LICLO4 WITH VARIOUS NCO/OH RATIOS

Sample	% Gel Content
PU1	67.9
PU2	59.5
PU3	39.8
PU4	31.8

D. Thermal Analysis

The glass transition of PU-$LiClO_4$ and endothermic temperature of PU-$LiClO_4$ were determined as shown in Fig. 7. The glass transition temperature of polyurethane-$LiClO_4$ above room temperature indicating that the glassy state of polyurethane-$LiClO_4$ at room temperature. The glass transition temperature of PU-$LiClO_4$ is decreased by lowering NCO/OH ratio. Hard segment in polyurethane restricts the polymer chain mobility [28] due to the steric hindrance of benzene ring in the hard segment. Hence, the decrease of NCO/OH ratio leads to higher flexibility of polyurethanes. Moreover, the detected endothermic peaks around 230-240°C in PU1, PU2, PU3 and PU4 are referred to the melting point of $LiClO_4$ (236°C). The solvent peaks could not be detected in DSC analysis where the boiling point of acetone is 56°C implying the acetone was removed from the polymer electrolytes during the drying process.

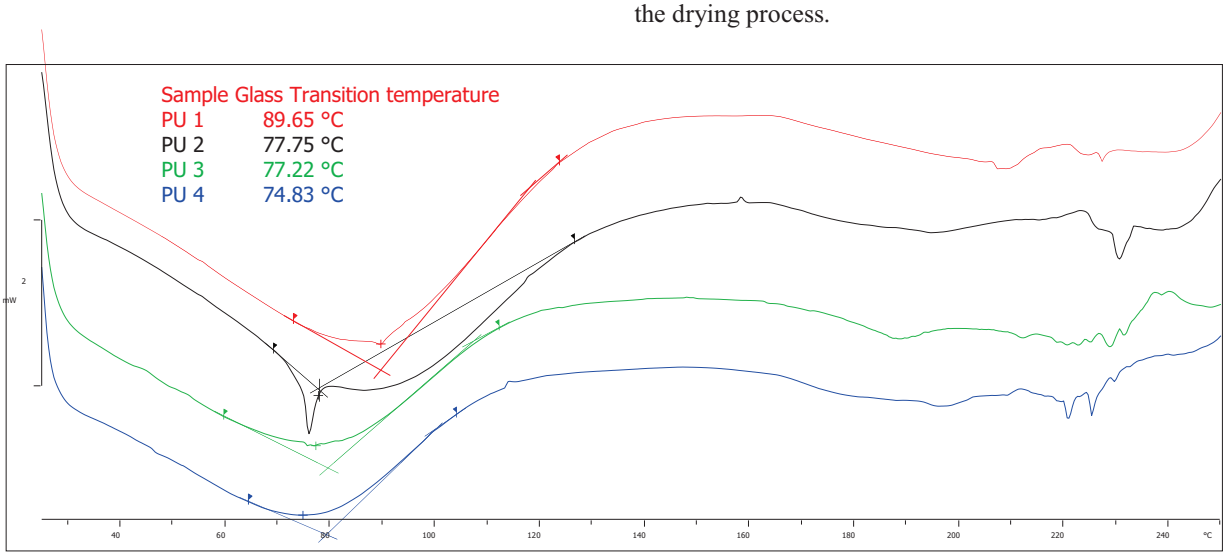


Fig. 7 DSC thermogram of PU1, PU2, PU3 and PU4

E. Morphology Studies

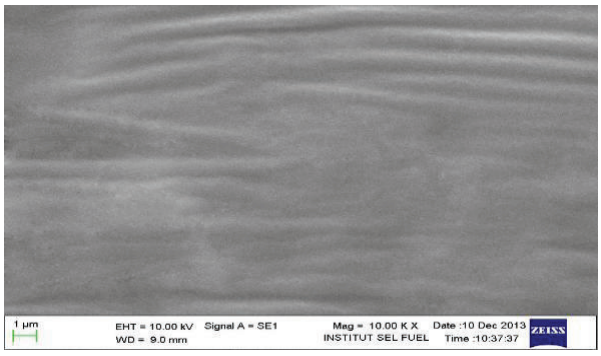
The SEM micrographs in Fig. 8 reveal the formation of homogeneous polymer *via* step-wise polymerization and the polymer films are free of void. It proves that prepolymerization method could prevent adverse reactions in the polymerization of PU-$LiClO_4$. Furthermore, no trace of phase separation in PUs was detected in the SEM micrographs

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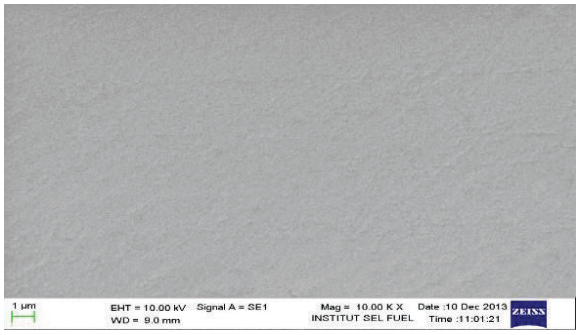
indicating a good interaction between the lithium salt and the polyurethanes [8] and was proven by FTIR analysis. EDX-SEM analysis as shown in Table IV was conducted to determine the lithium salt distribution in PUs. However, light elements such as lithium and hydrogen could not be detected in EDX-SEM analysis [29]. Hence, the detection of Cl atoms in different spots of PU-$LiClO_4$ is attributed to the lithium salts and it reveals the dispersion of lithium salt in the polyurethane-$LiClO_4$. Moreover, the agglomeration of lithium salts could not be detected in all the polyurethane electrolytes manifests the homogeneity between lithium salt and polyurethane matrix.

TABLE IV
EDX-SEM ANALYSIS OF PU FILMS WITH VARYING NCO/OH RATIOS

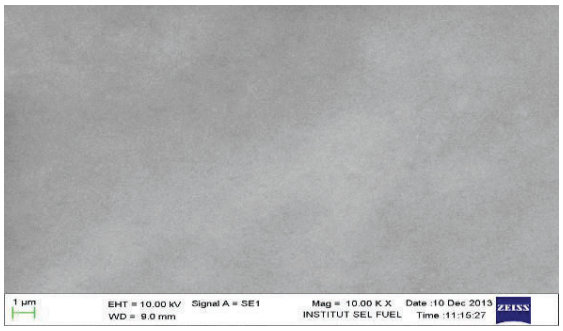
Sample	Element	Average mass %	Average atomic %
PU1	C	60.29	85.39
	N	0.71	0.89
	O	8.73	9.30
	Cl	4.45	2.17
PU2	C	57.60	79.57
	N	0.78	0.92
	O	14.75	15.29
	Cl	5.09	2.38
PU3	C	47.55	70.73
	N	3.59	4.55
	O	17.03	18.91
	Cl	6.96	3.53
PU4	C	68.56	87.82
	N	0.76	0.91
	O	9.69	9.31
	Cl	3.19	1.38



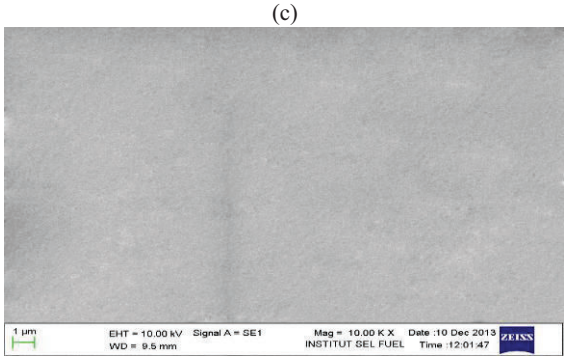
(a)



(b)



(c)



(d)

Fig. 8 SEM images of (a) PU1, (b) PU2, (c) PU3, (d) PU4

F. Ionic Conductivity

Table V shows the ionic conductivity of polyurethane-$LiClO_4$ decreased from 1.19×10^{-7} to 1.10×10^{-9} $S.cm^{-1}$ from PU1 to PU4 due to the decreasing of NCO content in PU-$LiClO_4$. It indicates PU1 facilitates the interaction between urethane groups and lithium ions. Thus, it enhances the ion hopping of lithium ions. Moreover, the benzene ring in hard segment could increase the conductivity by inducing electron delocalization along the polyurethane chain [14]. The activation energies (Ea) of polyurethane-$LiClO_4$ polymer electrolytes as shown in Table V were determined by plotting graphs with Log σ vs 1/T (Fig. 9). –Ea/k denotes the graph slope. All the polyurethane-$LiClO_4$ obey Arrhenius law indicating lithium ion transport *via* a simple ion hopping in polyurethane due to the crystalline properties of polyurethane-$LiClO_4$ as proven by DSC analysis [30]. The activation energy of polyurethane-$LiClO_4$ decreased from PU4 to PU1 implying the greater amount of urethane groups in polyurethane-$LiClO_4$ conduces greater interaction with lithium ion. The low Ea values indicate the low restriction of lithium ion mobility in the polyurethane-$LiClO_4$ [9], [31]. Ion hopping could be increased by heating and produces higher conductivity [9]. It is observed that the ionic conductivity increased as the temperature increased. The highest ionic conductivity was achieved by PU1 which is 5.01×10^{-5} $S.cm^{-1}$ at 373 K. Increasing the temperature leads to the creation of free volume. Thus the ionic species can move into these free areas resulting in higher conductivity [32], [33]. As shown in Table V and Fig. 10, PU0 does not have lithium salt therefore it shows the lowest conductivity and does not obey Arhenius law 10 due to its electrical insulating properties [34]. One of the

factors that affects the ionic conductivity of the polymer electrolyte is the concentration of the charge carrier. However, this research proves that NCO content in polyurethane also plays an important role in affecting the ionic conductivity of this polymer electrolyte. It is assumed that the ionic conductivity of PU-$LiClO_4$ can be increased by increasing the concentration of lithium salt in the polymer electrolyte.

TABLE V
IONIC CONDUCTIVITIES AT 298K AND 373 K AND ACTIVATION ENERGY OF PU-LICLO4 WITH VARYING NCO/OH RATIOS

Sample	Conductivity ($S.cm^{-1}$) at 298 K	Conductivity ($S.cm^{-1}$) at 373 K	Ea (eV)
PU0	2.06×10^{-10}	1.46×10^{-7}	-
PU1	1.19×10^{-7}	5.01×10^{-5}	0.32
PU2	1.95×10^{-8}	1.74×10^{-5}	0.34
PU3	2.65×10^{-9}	1.55×10^{-6}	0.38
PU4	1.10×10^{-9}	1.55×10^{-6}	0.40

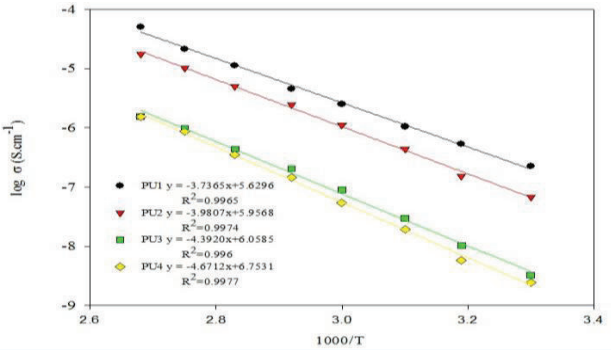


Fig. 9 Log σ vs 1000/T for PU1, PU2, PU3 and PU4

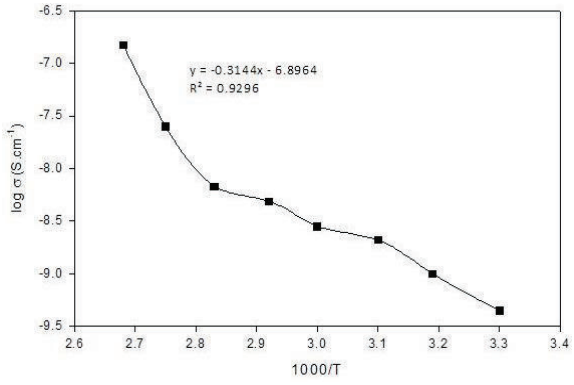


Fig. 10 Log σ vs 1000/T for PU0

VI. CONCLUSION

All the polyurethane-$LiClO_4$ was successfully prepared by casting method and all the structures of polyurethane-$LiClO_4$ were confirmed by FTIR and 13C NMR analysis. PU1 which has the greatest amount of urethane group as proven by soxhlet analysis gave the highest conductivity (1.19×10^{-7} $S.cm^{-1}$ at 298 K and 5.01×10^{-5} $S.cm^{-1}$ at 373 K). FTIR analysis proved the coordination between lithium ion and polyurethane in PU1. PU1 has the highest glass transition temperature due to the steric hindrance of benzene ring in the hard segment. Phase separation in the polymer electrolytes was not detected in SEM micrographs and it indicates that the lithium salts are uniformly distributed in the polymers. This research proves the importance of NCO content in affecting the ionic conductivity of polyurethane-$LiClO_4$

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