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Characterization of High Molecular Weight Poly(vinyl chloride) – Lithium Tetraborate Electrolyte Plasticized by Propylene Carbonate

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1. Introduction

An electrolyte is a substance consisting of free ions and acts as a medium channel for transferring the charges between a pair of electrodes. Sometimes, they are also referred as "lytes" which is derived from the Greek word, "lytos", which means "it may be dissolved". Electrolyte is comprised of positively charged species which is called as cation and negatively charged species, anion. The properties of an electrolyte can be exploited via electrolysis process: separation of chemically bonded element or compounds by applying the electrical current. In the early stage, liquid electrolytes have been discovered and investigated. Liquid electrolyte is a substance that conducts the electricity in an aqueous solution by migrating both cations and anions to the opposite electrodes through an electrically conducting path as a useful electric current. However, it faces problem of leakage of hazardous liquids or gases. Other drawbacks are formation of lithium dendrite, electrolytic degradation of electrolyte and uses of flammable organic solvent (Ramesh et al., 2011a). Apart from that, it exhibits poor long–term stability due to the evaporation of the liquid phase in the cells (Yang et al., 2008). Therefore, solid polymer electrolytes (SPEs) were synthesized to prevail over the limitations of conventional liquid electrolytes.

1.1 Solid polymer electrolytes

The development on SPEs was initiated by the pioneering work of Wright et al. three decades ago (Lee and Wright, 1982). A polymer electrolyte (PE) is defined as a solvent–free system whereby the ionically conducting pathway is generated by dissolving the low lattice energy metal salts in a high molecular weight polar polymer matrix with aprotic solvent (Gray, 1997a). The fundamental of ionic conduction in the polymer electrolytes is the covalent bonding between the polymer backbones and ions. Initially, the electron donor group in the polymer would form solvation onto the cation component in the doping salt

and thus facilitate the ion separation, leading to ionic hopping mechanism. Hence, it generates the ionic conductivity. In other words, the ionic conduction of PE arises from rapid segmental motion of polymer matrix combined with strong Lewis–type acid–base interaction between the cation and donor atom (Ganesan et al., 2008). However, the well separated ions might be poor conductors if the ions are immobile and unable for the migration. Therefore, the host polymer must be sufficiently flexible to provide enough space for the migration of these two ions.

SPE serves three principal roles in a lithium rechargeable battery. Firstly, it acts as the electrode separator that insulates the anode from the cathode in the battery which removes the requirement of inclusion of inert porous membrane between the electrolytes and electrodes interface. Besides, it plays the role as medium channel to generate ionic conductivity which ions are transported between the anode and cathode during charging and discharging. This induces to enhancement of energy density in the batteries with formation of thin film. In addition, it works as binders to ensure good electrical contact with electrodes. Thus, high temperature process for conventional liquid electrolytes is eliminated as well (Gray, 1991; Kang, 2004).

1.2 Applications of solid polymer electrolytes

SPEs are of great interests in the technology field, especially the area of electrical power generation and storage systems. It is primarily due to their wider range of applications, ranging from small scale production of commercial secondary lithium ion batteries (also known as the rechargeable batteries) to advanced high energy electrochemical devices, such as chemical sensors, fuel cells, electrochromic windows (ECWs), solid state reference electrode systems, supercapacitors, thermoelectric generators, analog memory devices and solar cells (Gray, 1991; Rajendran et al., 2004). As for the commercial promises of lithium rechargeable batteries, there is a wide range of applications which ranges from portable electronic and personal communication devices such as laptop, mobile phone, MP3 player, PDA to hybrid electrical vehicle (EV) and start–light–ignition (SLI) which serves as traction power source for electricity (Gray, 1997a; Ahmad et al., 2005).

1.3 Advantages of solid polymer electrolytes

A force had been driven in the development of SPEs to replace conventional liquid electrolytes due to its attractive advantages. These features include the elimination of the problems of corrosive solvent leakage and harmful gas production, ease of processability due to elimination of liquid component, and suppression of lithium dendrite growth as well (Rajendran et al., 2004; Ramesh et al., 2010). Besides safety performance, SPE is also a promising candidate because of its intrinsic characteristics, such as ease to configure in any shape due to its high flexibility of polymer matrix, high automation potential for electrode application and no new technology requirement as well as light in weight (Xu and Ye, 2005; Gray, 1991). The other advantages of SPEs are viz., negligible vapor pressure, ease of handling and manufacturing, wide operating temperature range, low volatility, high energy density and high ionic conductivity at ambient temperature (Baskaran et al., 2007; Rajendran et al., 2004). In addition, they exhibit excellent electrochemical, structural, thermal, photochemical and chemical stabilities without the combustible reaction products at the electrode surface by

comparing with conventional liquid electrolyte (Adebahr et al., 2003; Nicotera et al., 2006; Stephan, 2006). Moreover, they produce miniaturized structures via fabrication methods and provide longer shelf–lives with no internal shorting (Gray, 1997a; Stephan, 2006).

1.4 Gel polymer electrolytes (GPEs)

SPEs possess high mechanical integrity; however they exhibit low ionic conductivity. Therefore, gel polymer electrolytes (GPEs), sometimes known as gelionic solid polymer electrolytes are yet to be developed to substitute SPEs because of its inherent characteristics (Stephan et al., 2000a). Such features are low interfacial resistance, decrease in reactivity, improved safety and exhibit better shape flexibility as well as significant increases in ionic conductivity with a small portion of plasticizers (Ahmad et al., 2008; Pandey and Hashmi, 2009). GPE is obtained by dissolving the host polymer along with a metal dopant salt in a polar organic solvent (more commonly known as plasticizer) (Osinska et al., 2009; Rajendran et al., 2008a). In other words, it is an immobilization of a liquid electrolyte in a polymer matrix (Han et al., 2002). As a unique characteristic, GPEs possess both cohesive properties of solids and the diffusive property liquids. Even though they are in a solid state, but at atomic level, the local relaxations provide liquid–like degree of freedom which is comparable to those conventional liquid electrolytes. Moreover, GPEs show better mechanical and electrochemical properties within a wide operational temperature range in comparison with that of liquid electrolytes (Ahmad et al., 2005; Stephan et al., 2000a). Other attractive advantages are leak proof construction, lighter, cheaper and easy fabrication into desired shape and size (Zhang et al., 2011). They also maintain the interfacial contacts under stresses such as the changing of volume associated with cell charging and discharging. GPEs could form good interfacial contacts with electrode materials as they are not brittle as solid crystalline or glass electrolytes (Gray, 1997a).

2. Methods to improve ionic conductivity

Ionic conductivity is the main aspect to be concerned in the solid polymer electrolytes. Ionic conductivity is defined as ionic transportation from one site to another through defects in the crystal lattice of a solid under the influence of an external electric field. Much effort has been devoted for developing highly conducting polymer electrolytes. Several ways have been done to modulate the ionic conductivity of polymer electrolytes, for instance, random and comb–like copolymer of two polymers, polymer blending, mixed salt and mixed solvent systems as well as impregnation of additives such as ceramic inorganic fillers and plasticizers.

2.1 Random copolymers

In the first study of poly(ethylene oxide) (PEO) with various inorganic lithium salts, PEO showed low conductivity at ambient temperature due to the higher degree of crystallization. To overcome this obstacle, reduced crystallinity or amorphous polyether–based host architectures have been focused. Random copolymerization is one of routes to produce amorphous host polymers. Booth and co–workers had successfully synthesized random oxyethylene–oxymethylene polymer structures in year 1990. Ethylene oxide monomers are randomly interspersed with methylene oxide groups. Thus, the methylene oxide would

break up the regular helical structure of PEO and suppress the crystalline region of polymer matrix. A similar random copolymer had been synthesized by replacing the methylene oxide with dimethyl siloxy units. This resultant polymer matrix illustrated higher flexibility which assists in ionic conduction (Gray, 1997b).

2.2 Comb polymers

In general, comb polymers contain pendant polymer chain and they are structurally related to grafting copolymers. The comb–branched system containing of low molecular weight of polyether chain is grafted to a polymer backbone. Thus, it lowers the glass transition temperature (T_g) and then helps to optimize the ionic conductivity by improving the flexibility of polymer chain into the system. The elastic poly[ethylene oxide–co–2–(2–methoxyethoxy)ethyl glycidyl ether] [P(EO/MEEGE)]–based polyether comb polymer electrolytes were synthesized by Nishimoto and co–workers. The degree of crystallinity was decreased with increasing the composition of MEEGE in copolymers, which in accordance with higher ionic conductivity. The introduction of the side chain of MEEGE in the copolymers enhances the flexibility of polymer matrix and hence improves the ion mobility. The highest ionic conductivity of 10^{-4} Scm^{-1} was achieved at room temperature (Nishimoto et al., 1998). Until today, this technique is still being employed in this area. Recently, many researchers have keen of interest on polyvinylidene–co–hexafluorophosphate (PVdF–co–HFP) copolymer. Composite polymer electrolytes prepared by adding SiO_2 nanowires into (PVdF–co–HFP) are described by Zhang et al. The ionic conductivity of this composite polymer electrolyte is up to 1.08×10^{-3} Scm^{-1} with the electrochemical window of 4.8 V (Zhang et al., 2011).

2.3 Polymer blending

Polymer blending is physical means to mix two or more different polymers or copolymers which are not linked by covalent bonds. This polymer blend is a new macromolecular material with special combinations of properties. For polymer blends, a first phase is adopted to absorb the electrolyte active species, whereas the second phase is tougher and sometimes substantially inert. It is a feasible way to increase the ionic conductivity because it offers the combined advantages of ease of preparation and easy control of physical properties within the definite compositional change (Rajendran et al., 2002). Polymer blending is of great interest due to their advantages in properties and processability compared to single component. In industry area, it enhances the processability of high temperature or heat–sensitive thermoplastic in order to improve the impact resistance. Besides, it can reduce the cost of an expensive engineering thermoplastic. The properties of polymer blends depend on the physical and chemical properties of the participating polymers and on the state of the phase, whether it is in homogenous or heterogeneous phase. If two different polymers able to be dissolved successfully in a common solvent, this polymer blends or intermixing of the dissolved polymers will occur due to the fast establishment of the thermodynamic equilibrium (Braun, 2005). Sivakumar et al. (2006) observed that PVA (60 wt%)–PMMA (40 wt%)–LiBF$_4$ complex exhibits the maximum conductivity of 2.8×10^{-5} Scm^{-1} at ambient temperature. It is also higher than the pure PVA system which has been reported to be 10^{-10} Scm^{-1}.

2.4 Mixed salt system

The conductivity of the mixed salts in polymer electrolyte is higher than single salt electrolyte. It is due to the addition of second salt may prevent the formation of aggregates and clusters. Therefore, it increases the mobility of ion carriers (Gray, 1997b). An approach had been done by Ramesh and Arof (2000). In this research, we synthesized poly (vinyl chloride) (PVC)–based polymer electrolytes with lithium trifluoromethanesulfonate (LiTf) and lithium tetrafluoroborate (LiBF$_4$) as doping salts. The ionic conductivity is increased by four orders of magnitude in comparison with single salt system. It is attributed to the increase in the mobility of charge carriers by avoiding the aggregation process.

2.5 Mixed solvent system

On the other hand, the increase of conductivity in binary solvent system is proven by Deepa et al. (2002). In this study, poly(methyl methacrylate) (PMMA)–based polymer electrolytes containing lithium perchlorate (LiClO$_4$), with a mixture of solvents of propylene carbonate (PC) and ethylene carbonate (EC) were prepared. The maximum ionic conductivity of 10^{-3} S cm^{-1} was obtained and it was increased by two orders of magnitude as compared to polymer electrolyte system with single solvent. Synergistic effect is the major factor to increase the ionic conductivity in this mixed solvent system. Different physicochemical properties of the individual solvents come into play and contribute to high ionic conductivity in the presence of the effect. The preparation on EC/PC/2–methyl–tetrahydrofuran (2MeTHF) ternary mixed solvent electrolyte had been done by Tobishima and co–workers. They found out that the discharge capacity of Li/amorphous V$_2$O$_5$–P$_2$O$_5$ cells with a ternary mixed solvent electrolyte are slightly better than for cells with EC/PC binary mixed solvent electrolytes.

2.6 Addition of inorganic fillers

Utilization of common additives such as inorganic fillers and plasticizers is the effective and efficient approach to enhance the ionic conductivity. Fillers (also known as reinforcing fillers) are divided into two types: inorganic and organic. Variety types of inorganic fillers have been used, including mica, clay, titania (TiO$_2$), fumed silica (SiO$_2$) and alumina (Al$_2$O$_3$). On the other hand, graphite fibre and aromatic polyamide are some examples of organic fillers. The main objectives of dispersion of inorganic filler are to alter the properties of the polymer, enhance processability and improve the mechanical stability in the polymer electrolyte system. Dispersion of inorganic fillers can also improve the ionic conductivity in the polymer electrolyte. Besides improving the lithium transport properties, the inclusion of ceramic filler has been found to enhance the interfacial stability of polymer electrolytes (Osinska et al., 2009).

2.7 Plasticization

A number of attempts have been made on plasticized–polymer electrolytes in order to rise up the ionic conductivity greatly. Plasticization is generally recognized as one of the effective and efficient methods available for decreasing the crystalline region of polymer electrolytes (Suthanthiraraj et al., 2009). Plasticizer is a non–volatile and low molecular weight aprotic organic solvent which has a T_g in the vicinity of –50 °C. Carbonate ester such as propylene carbonate (PC), ethylene carbonate (EC), dimethyl carbonate (DMC) and

diethyl carbonate (DEC), and high dielectric constant solvent such as N,N–dimethylformamide (DMF), N,N–dimethylacetamide (DMAc) and γ–butyrolactone are widely used as main components of GPE (Pradhan et al., 2005; Suthanthiraraj et al., 2009; Ning et al., 2009). Other examples of common plasticizers are dibuthyl phthalate (DBP), diocthyl adipate (DOA) and polyethylene glycol (PEG) (Suthanthiraraj et al., 2009).

2.7.1 Advantages of plasticizers

The effect of plasticizers on the polymer electrolytes entirely depends on the specific characteristics of the plasticizer, for example, viscosity, dielectric constant, the interaction between polymer and plasticizer, and the coordinative bond between ion and plasticizer (Rajendran and Sivakumar, 2008b). The incorporation of plasticizer not only enhances the salt solvating power, but it also provides sufficient mobility of ions with a better contact between polymer electrolytes and electrodes (Ramesh and Arof, 2001; Rajendran et al., 2004). Apart from that, plasticizer is an attractive additive due to its superior miscibility with polymer, high dielectric constant and low viscosity (Ramesh and Chao, 2011b). Inclusion of plasticizer is the most successful skill to enhance the ionic conductivity without compromising the thermal, electrochemical and dimensional stabilities (Ganesan et al., 2008). Plasticizer are expected to improve the ionic conductivity through some important intrinsic modifications such as significant changes in local structure, enhancement of amorphous fraction and changes in local electric field distribution in the polymer matrix.

2.7.2 Roles of plasticizers

The principal function of a plasticizer is to reduce the modulus of polymer at the desired temperature by lowering its T_g. In this theory, the increase in concentration of plasticizer causes the transition from the glassy state to rubbery region at progressively lower temperature. Moreover, it reduces the viscosity of polymer system and then facilitates the ionic migration within the polymer matrix. Besides, it weakens the interactions within the polymer chains and thus improves the flexibility of polymer chains in the polymer matrix (Ganesan et al., 2008). As a result, it increases the free volume of polymer and enhances the long–range segmental motion of the polymer molecules in the system. In an approach, the polymer matrix is swollen in a plasticiser, the latter being an aprotic solvent with a high dielectric constant. A new mobile pathway for ion migration is being introduced upon addition of plasticizer by dissociating the charge carriers. Hence, it increases the amount of mobile charge carriers and promotes the ionic transportation, enhancing the ionic conductivity. The polymer component would, on the other hand, render necessary stability to the lithium anode electrolyte interface, which thereby reduces the chance of dendrite growth on the lithium anode (Rajendran et al., 2000a). In general, plasticizers are having conjugated double bond which initializes the delocalization of electrons. Therefore, it improves the donor capacity of oxygen atom which facilitates the binding of cations.

2.7.3 Literature review of plasticized-gel polymer electrolytes

As reported in Michael et al. (1997), three types of ester class plasticizers, namely dioctyl phthalate (DOP), dibutyl phthalate (DBP) and dimethyl phthalate (DMP), were employed to examine its effect on ionic conductivity in the PEO–LiClO$_4$ polymer complex. Among these

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plasticizers, DOP was found to be the excellent plasticizer in term of thermal stability as proven in differential thermal analysis (DTA). The results show the reduced weight loss as increases the plasticizer concentration. Ali et al. (2007) studied the plasticized–polymer electrolytes that composed of PMMA, propylene carbonate (PC) or ethylene carbonate (EC) as plasticizer and LiTf or $LiN(CF_3SO_2)_2$ as dopant salt. According to this literature, the ionic conductivity increases with the concentration of the plasticizer. They also declare that the PC–based plasticized–polymer electrolytes exhibit higher ionic conductivity compared to the EC–based plasticized–polymer electrolytes (Ali et al., 2007).

Rajendran et al. (2004) also incorporated few types of plasticizers in the polymer electrolytes containing PVA/PMMA–$LiBF_4$. The highest ionic conductivity of 1.29 mScm[-1] had been observed for EC–based complex because of higher dielectric constant of EC (ε=85.1) (Rajendran et al., 2004). The addition of the plasticizer has been reported to reduce the crystallinity of the polymer complexes which in turns to a better ionic conductivity (Kelly et al., 1985). Kelly and co–workers assert that the presence of plasticizer exhibits downward shift in T_g due to the weaker interactions between the ions and polymer chain which in accordance with higher ion dissociation. A maximum electrical conductivity of 2.60×10^{-4} Scm^{-1} at 300 K has been observed for 30wt.% of PEG as plasticizer compared to the pure PEO–$NaClO_4$ system of 1.05×10^{-6} Scm^{-1}. This can be explained that the addition of plasticizer enhances the amorphous phase in with concomitant the reduction in the energy barrier. Eventually, it results higher segmental motion of lithium ions (Kuila *et al.*, 2007).

3. Materials

In this study, poly (vinyl chloride) (PVC), lithium tetraborate ($Li_2B_4O_7$) and propylene carbonate (PC) were employed as host polymer, dopant salt and plasticizer, respectively. In this section, we discuss about the general description of the materials and the reasons for choosing the materials.

3.1 Poly(vinyl chloride) PVC

Apart from PEO, poly(vinyl alcohol) (PVA), poly(acrylonitrile) (PAN), poly(ethyl methacrylate) (PEMA), poly(vinyl chloride) (PVC), poly(vinylidene fluoride) (PVdF) have also been used as polymer host materials. PVC is a thermoplastic polymer where its IUPAC name is poly(chloroethanediyl). It consists of numerous repeating units of monomers called vinyl chloride. It is a vinyl polymer composing of numerous repeating units of CH_2–CHCl.
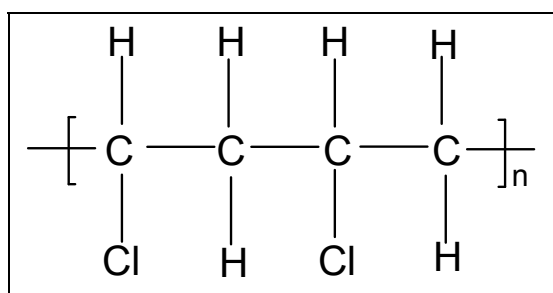

Fig. 1. Chemical structure of PVC.

PVC is mainly produced by radical polymerization (Endo K, 2002). In this polymerization, it associates the vinyl chloride molecules and thus forms the polymeric chains of macromolecules. From the scientific point of view, lone pair of electrons at the chlorine atoms is the main reason for choosing PVC as host polymer. Thus, it can form solvation onto lithium salts easily (Ramesh and Chai, 2007). PVC is chosen due to its high compatibility with the liquid electrolyte, good ability to form homogeneous hybrid film, commercially available and inexpensive (Li et al., 2006). Other unique characteristics are easy processability and well compatible with a large number of plasticizers (Ramesh and Ng, 2009). It plays an important role as mechanical stiffener because of the dipole–dipole interactions between the hydrogen and chlorine atoms (Ramesh and Chai, 2007).

3.2 Lithium tetraborate ($Li_2B_4O_7$)

Several types of lithium salt has widely been used, such as lithium hexaflurorophosphate ($LiPF_6$), lithium hexafluoroarsenate ($LiAsF_6$), lithium bis(trifluoromethanesulfonyl) imide (LiTFSI), LiTf, $LiClO_4$ and $LiBF_4$. Lithium tetraborate (also known as boron lithium oxide or dilithium borate) (LBO or more commonly known as $Li_2B_4O_7$) was employed in this study. This compound is generally defined as one type of dopant used to provide lithium cations in the preparation of polymer electrolytes. It is constructed of lithium cations and tetraborate anions, where its stoichiometric ratio is two cations to one anion, as illustrated as below.
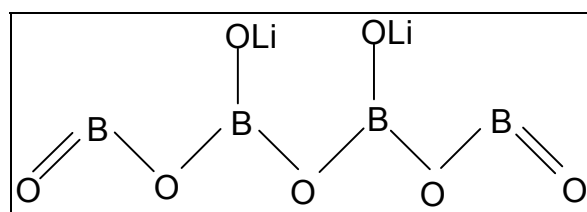

Fig. 2. Chemical structure of lithium tetraborate.

In addition, it is a new non–ferroelectric piezoelectric substrate material with a congruent melting point of 917 °C. LBO single crystal is also a superior substrate for surface acoustic wave (SAW) and bulk acoustic wave (BAW) devices as it has a specific crystallographic plane (110). Thus, it provides a zero temperature coefficient of frequency and a fairly high electromechanical coupling factor. According to Byrappa and Shekar (1992), LBO occurs naturally as diomignite, i.e. colourless crystals in fluid inclusions in the mineral spodumene. It appears as a loosely attached crystal with a very fine–grained structure. These intrinsic and unique properties make it as excellent material by comparing with other lithium salt. The fine structure of $Li_2B_4O_7$ would enhance the solubility in the polymer matrix and eventually, speed up the salt dissociation process. Other factors to choose it as doping salt are abundant availability of raw materials and no environmental pollution (Xu et al., 2004). As aforementioned, $Li_2B_4O_7$ is naturally obtained from mineral. Therefore, it is a cost effective material compared to those synthetic lithium salts, for instance $LiBF_4$, LiTFSI and LiTf. High toxicity of $LiAsF_6$ and poor chemical and thermal stabilities of $LiPF_6$ are not good choices as doping salt in polymer electrolyte. Likewise, $LiClO_4$ reacts with most organic species readily in violent ways under certain conditions such as high temperature and high current charge because of high oxidation state of chlorine (VII) in perchlorate. Moreover, the corrosion of a key component of the cell by TFSI anions restricts the possible application of LiTFSI greatly in the polymer electrolytes. Poor ionic conductivity of LiTf in non–aqueous

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solvent which caused by its low dissociation constant in low dielectric media and its moderate ion mobility, is the major shortcoming of LiTf as compared with other lithium salts (Kang, 2004). Therefore, it can be concluded that $Li_2B_4O_7$ is an indispensable electrolyte solute as it shows multiple merits than other lithium salts.

3.3 Propylene carbonate (PC)

As aforesaid, plasticizer could enhance the ionic conductivity of polymer electrolytes. Propylene carbonate (PC) is used in this study. PC is an organic, colourless and odourless organic compound. It is also well known as highly polar and aprotic solvent. Furthermore, it is a byproduct of the synthesis of polypropylene carbonate from propylene oxide and carbon dioxide. It can be obtained from the synthesis of urea and polypropylene glycol in the presence of zinc–iron double oxide catalysis. It is composed of twofold ester of propylene glycol and carbonic acid as illustrated as below.
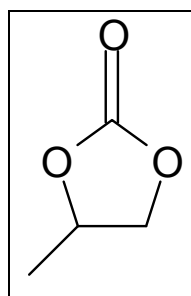

Fig. 3. Chemical structure of propylene carbonate.

PC is a preferred solvent as it exhibits many unique characteristics. These properties are static stability with lithium, wide liquid range and low freezing point (Kang, 2004). Many researchers have drawn interests onto this plasticizer due to its high dielectric constant (ε= 64.9). This high dielectric constant could help in the dissociation of the charge carriers, especially the cations from the dopant salt. The electrical performance would be improved as it manifests excellent plasticizing effect (Tobishima and Yamaji, 1984). Cations are more readily to be obtained as the salt is dissolved in PC through electrolysis process, because of its high molecular dipole moment of 4.81 D (Jorné and Tobias, 1975). Moreover, high polarity of this plasticizer creates an effective solvation shell around the cations and hence forms a conductive electrolyte. PC displays the highest dielectric constant in comparison with *DEC* (ε= 2.8), *ethyl methyl carbonate (EMC)* (ε= 2.9), *DMC* (ε= 3.1), DOA (ε= 4–5), DBP (ε= 6.4), DMP (ε= 8.5) and benzyl acetate (BC) (ε= 53) (Kang, 2004; Gu et al., 2006). Despite EC illustrates higher dielectric constant than PC, however PC exhibits wider range of liquidity than EC as its melting point is up to –48.8 °C. In contrast, high melting temperature of 36.4 °C is the main shortcoming of EC. High dipole moment of PC than EC (4.61 D) with low vapor pressure also compensates the obstacle of lower dielectric constant of PC (Kang, 2004). Therefore, PC is becoming an attractive prospect as plasticizer compared to other plasticizers.

3.4 Tetrahydrofuran (THF)

Tetrahyrdofuran (THF) is a colorless, water–miscible organic liquid with low viscosity at standard temperature and pressure. It is one of the most polar ethers with a wide liquid range and is widely been used as solvent. In addition, it is an aprotic and highly volatile solvent with

dielectric constant of 7.6. Another virtue of this solvent is its good solvent properties. It can dissolve a wide range of non–polar and polar chemical substances. Therefore, it is being chosen as solvent as it shows a well–dissolution with PVC, $Li_2B_4O_7$ and PC in this study. It is also a heterocyclic compound with chemical formula of $(CH_2)_4O$, as shown in Figure 4.

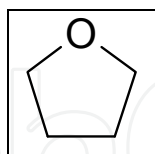Fig. 4. Chemical structure of tetrahydrofuran.

4. Experimental

These plasticized–polymer electrolytes were prepared by solution casting technique. It is the simplest and cost–effective method to produce thin films from solution by evaporating the volatile solvent. No technology is required in this technique.

4.1 Materials

High molecular weight poly (vinyl chloride) PVC was obtained from Fluka, while lithium tetraborate ($Li_2B_4O_7$) and propylene carbonate (PC) were obtained from Aldrich. Tetrahydrofuran (THF) was obtained from J.T. Baker.

4.2 Sample preparation

Prior to the preparation of the polymer electrolytes, $Li_2B_4O_7$ was dried at 100 °C for 1 hour to eliminate trace amounts of water in the material. Appropriate amount of PVC, $Li_2B_4O_7$ and PC were dissolved in anhydrous THF. The mixture was then stirred continuously for 24 hours at room temperature to achieve a homogenous solution. The resulting solution was cast on a Petri dish and was allowed to evaporate slowly in a fume hood. This procedure yields free standing films eventually. The designations of polymer film are listed in Table 1. The weight ratio of PVC (70%) to $Li_2B_4O_7$ (30%) had achieved the maximum ionic conductivity in the preliminary step which is not being shown here. As a result, the ratio of PVC to $Li_2B_4O_7$ was fixed as 70 wt% to 30 wt% in this study.

Designation	Composition of materials [PVC: $Li_2B_4O_7$: PC (wt%)]
SPC1	70.0:30.0:0.0
SPC2	66.5:28.5:5.0
SPC3	63.0:27.0:10.0
SPC4	59.5:25.5:15.0
SPC5	56.0:24.0:20.0
SPC6	52.5:22.5:25.0
SPC7	49.0:21.0:30.0
SPC8	45.5:19.5:35.0
SPC9	42.0:18.0:40.0

Table 1. The nomenclature of samples with different stoichiometric amounts of materials added into polymer electrolytes.

4.3 Instrumentation

After the samples were prepared, the characterizations have been employed to investigate the electrical, structural and thermal properties of the samples. These analytical and evaluative methods include ac–impedance spectroscopy, Fourier Transform Infrared spectroscopy (FTIR) and thermogravimetry analysis (TGA).

4.3.1 Ac-impedance spectroscopy

Impedance spectroscopy (IS) is a powerful analytical tool to characterize the electrical properties of materials and their interfaces with electronically conducting electrodes. It is also widely been used to envisage the dynamics of bound or mobile charge in the bulk or interfacial regions of any kind of solid or liquid material: ionic, semiconducting, mixed electronic–ionic and even insulator (dielectric) (Barsoukov & Macdonald, 2005). The principle of the impedance spectroscopy is based on the ability of a medium to pass an alternating electrical or frequency current. It is well functioned by conducting current and measuring the potential difference created by the circulation of this current. When an electric field is applied across the sample, the polar group might be activated as dipoles which always interact with the corresponding ions due to the Coulombic electric force. Thus, these dipole moments will rearrange themselves under the influence of the external electric field, depending on the mobility of backbone. So, lithium cations can travel faster along these activated or polarizing areas to reach opposite of the electrode and generate current (Selvasekarapandian et al., 2006).

The prepared samples were subjected to ac–impedance spectroscopy. The thickness of the samples was measured by using micrometer screw gauge. The ionic conductivities of the samples were determined, by using HIOKI 3532–50 LCR HiTESTER, over a frequency range between 50 Hz and 1 MHz. The ionic conductivity was measured from ambient temperature to 100 °C. Samples were mounted on the holder with stainless steel (SS) blocking electrodes under spring pressure with the configuration SS/SPE/SS.

4.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

The main fundamental of FTIR is to determine structural information about a molecule. The main principle of FTIR is related to the interferometry which is an optic study. It separates infrared beam of light which serves as light source radiation into two ray beams. Once the beam of infrared is passed through the sample, the molecules would absorb the infrared radiation and then excite to a higher energy state. Thus, the energies associated with these vibrations are quantized; within a molecule, only specific vibrational energy levels are allowed. The amount of energy absorbed at each wavelength was recorded. The frequencies which have been absorbed by the sample are determined by detector and the signal is amplified. Hence, IR spectrum was obtained. FTIR spectroscopy is not only applied in the crystalline region of complexation, whereas the complexation in amorphous phase can also be determined.

FTIR analysis was performed by using Perkin–Elmer FTIR spectroscopy RX 1 in the wave region between 4000 and 400 cm^{-1}. The resolution of the spectra was 4 cm^{-1} and recorded in the transmittance mode.

4.3.3 Thermogravimetry Analysis (TGA)

TGA is a versatile thermal study in polymer field. It is primarily used to determine thermal stability and thermal degradation of the samples as a function of change in temperature under inert conditions. The main principle of TGA is to monitor the weight of the samples on a sensitive balance (also known as thermobalance) continuously as the sample temperature is increased, under an inert atmosphere or air at a controlled uniform rate. The data were recorded as a thermogram of weight which is in y–axis against sample temperature which is in x–axis.

The thermal stability of polymer films was performed by Mettler Toledo Thermal Gravimetric Analyser which comprised of TGA/SDTA851@ as main unit and STARe software. Sample weighing 2–3 mg placed into 150 µl of silica crucible. The samples were then heated from 30 °C to 400 °C at a heating rate of 10 °C min^{-1} under nitrogen flow rate of 10 ml min^{-1}.

5. Results and discussion

5.1 Ac-impedance spectroscopy

The bulk ionic conductivity of polymer electrolytes is determined by using the equation as shown below.

$$\sigma = \frac{l}{R_b\, A}$$

where l is the thickness (cm), R_b is bulk resistance (Ω) and A is the known surface area (cm^2) of polymer electrolyte films. The semicircle fitting was accomplished to obtain R_b value. The R_b of the polymer electrolyte is calculated from the interception of high–frequency depressed semicircle with low–frequency spike.

Figure 5 depicts the logarithm of ionic conductivity with respect to PC mass fraction. As can be seen, the ionic conductivity increases with PC mass loadings, up to 10 wt% of PC. The optimum ionic conductivity of 5.10×10^{-7} Scm^{-1} is achieved with this mass fraction of PC. Plasticizing effect is the main attributor for this phenomenon. This effect would weaken the dipole–dipole interactions in the polymer chains and reduce the solvation of Li cations (Li$^+$) by polymer matrix. Hence, it promotes the ionic decoupling and enhances the dynamic free volume of the polymer system and thereby increases the ionic conductivity. It suggests that the plasticizer is not only weakening the polymer–polymer chain interactions, but also decreasing the dipole–ion interactions in the dopant salt. For the dipole–dipole interactions within the polymer chains, the hydrogen atom from the methyl group of PC may interact with the chloride anions in the polymer backbone. On the contrary, it proposes that the hydrogen from the methyl group of PC would weaken the O–Li bond of the Li$_2$B$_4$O$_7$. As a result, it promotes the dissociation of lithium cations from the bonding and hence favors the ionic transportation within the polymer matrix, improving the ionic conductivity.

In addition, the plasticizing effect lowers the T_g. Thus, it softens the polymer backbone and increases the segmental mobility when an electric field is applied onto the polymer electrolytes. Consequently, it disrupts the crystalline phase of polymer side chains and produces voids, which enables the easy flow of ions through polymer membrane when the

electric field is applied. The ionic conductivity is eventually enhanced with these higher amorphous and more flexible polymer chains. The increase in ionic conductivity is also owing to the high dielectric constant of PC. High dielectric constant could allow the greater dissolution of $Li_2B_4O_7$ and offers a result in increasing the number of charge carriers, promoting the ionic hopping mechanism. The ionic conductivity is reduced to 4.20×10^{-8} Scm^{-1} with increasing the PC mass loadings further. This is suggestive of the decrease in effective number of charge carriers for ionic transportation as a result of the domain of short–range ion–plasticizer interactions within the polymer matrix (Stephan et al., 2002). Hence, the ionic conductivity is lower than of other plasticized–polymer electrolytes because of the reduced amount of lithium cations.
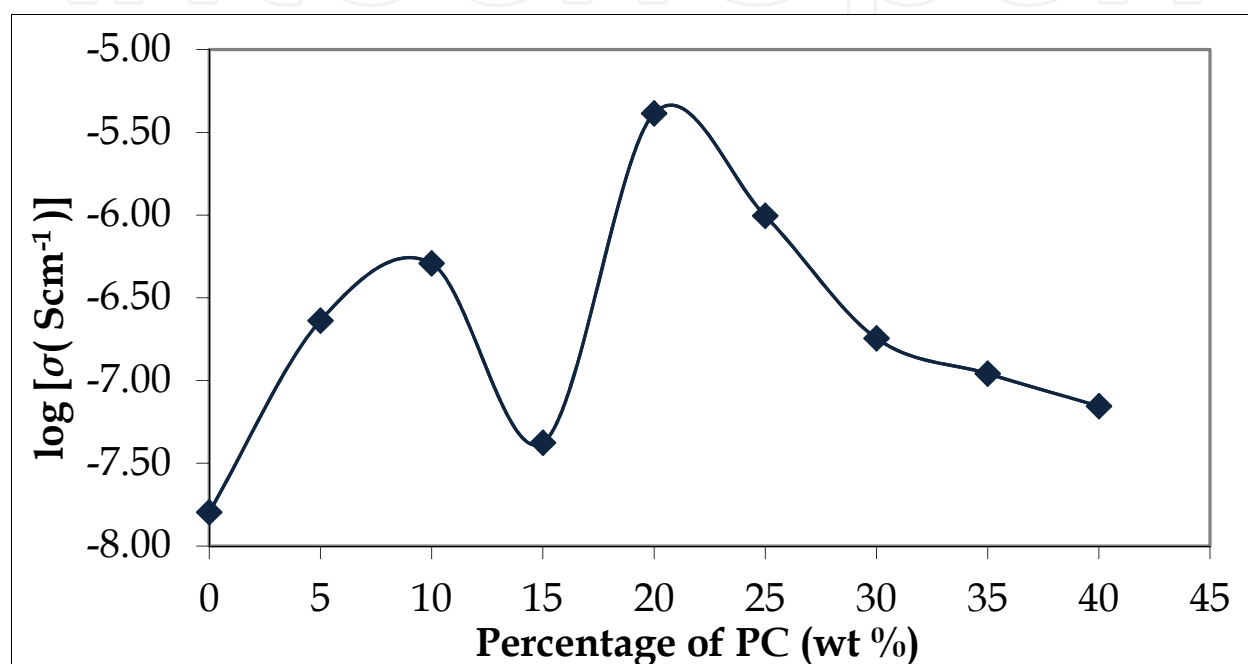
Fig. 5. The variation of logarithm of ionic conductivity of plasticized–based polymer electrolytes as a function of weight percentage of PC at ambient temperature.

Upon addition of 20 wt% of PC, the ionic conductivity is rising up further to the maximum level of 4.12×10^{-6} Scm^{-1} at room temperature. Again, the contribution from plasticizer is the main attributor for this enhancement of ionic conductivity. The incorporation of plasticizer increases the ionic conductivity through two ways. High plasticizer concentration would open up the narrow rivulets of plasticizer–rich region and lead to greater ionic migration. Moreover, it provides a large free volume of a relatively superior conducting region by reducing the crystalline degree of the polymer electrolytes (Rhoo et al., 1997; Stephan et al., 2000b). General expression of ionic conductivity of a homogenous polymer electrolyte is illustrated as below:

$$\sigma(T) = \sum_i n_i q_i \mu_i$$

where n_i is the number of charge carriers type of i, q_i is the charge of ions type of type of i, and μ_i is the mobility of ions type of i. Based on the equation above, the quantity and mobility of charge carriers are the main factors that could affect the ionic conductivity of

polymer electrolytes as the charge of the mobile charge carriers are negligible. Therefore, it can be concluded that the mobility and concentration of mobile charge carriers have been optimized in SPC5 as it achieves the highest ionic conductivity compared to other polymer complexes. However, the ionic conductivity is drastically declined with increasing the PC concentration further. It is ascribed to the restricted ionic and segmental mobility of mobile charge carrier in a rigid polymer matrix (Cha et al., 2004).

5.2 Temperature dependence-ionic conductivity studies

The temperature dependence study of ionic conductivity is further investigated in order to understand the mechanism of ionic conduction in this plasticized–polymer electrolyte. SPC5 is chosen as it achieves the highest ionic conductivity. Figure 6 illustrates the logarithm of ionic conductivity against reciprocal absolute temperature of SPC5, from ambient temperature to 373 K. As expected, the ionic conductivity increases with temperature. Polymer expansion effect plays an important role in this phenomenon. The polymer matrix expands with temperature, which in turn to the formation of local empty spaces and voids for the segmental migration. Therefore, it facilitates the migration of ions and diminishes the ion clouds effect between the electrodes and electrolyte interface (Ramesh et al., 2010). The enhancement of charge carriers and segmental motions could assist the ionic transportation and compensate for the retarding effect of the ion cloud virtually, inducing to higher ionic conductivity.

A linear relationship is perceived in the figure with regression value of 0.99. Therefore, it can be concluded that SPC5 follows Arrhenius rules as its regression value is close to unity. In this thermally activated principle, the conductivity is expressed as below:

$$\sigma = A\, exp\left(\frac{-E_a}{kT}\right)$$

where A is the pre–exponential factor which is proportional to the amount of charge carriers, E_a is the activation energy, k is Boltzmann constant and T is the absolute temperature. The Arrhenius relationship indicates the presence of the hopping mechanism. This theory states the ion jumps from its normal position on the lattice to an adjacent equivalent but empty site. As the temperature increases, the vibrational modes of polymer segments are also increased. Thus, it weakens the interaction between the polar group of the polymer backbone and Li^+, and promotes the decoupling process of charge carriers from the segmental motion of polymer matrix, leading to formation of vacant sites in the polymer chain. Hence, the neighboring ions from adjacent sites tend to occupy these vacant sites and coordinate with the polymer chain again. Eventually, the ionic hopping mechanism is generated. In this study, it implies that the methyl group from PC and the C–H group from PVC could weaken O–Li coordinative bond of $Li_2B_4O_7$ through the hydrogen bonding. As a result, it initiates the decoupling of Li^+ from the bond and therefore generates the ionic hopping process. In order to probe the ion dynamic of polymer electrolytes further, activation energy (E_a) is determined by fitting it in Arrhenius equation as shown above. E_a is defined as the energy required to overcome the reorganization and reformation of the polymer chain with Li^+. Based on the calculation, the E_a of SPC5 is 0.08eV. This activation energy is considered low. Therefore, it can be concluded that Li^+ would break and re–bind the coordination bond easily with lower energy barrier.
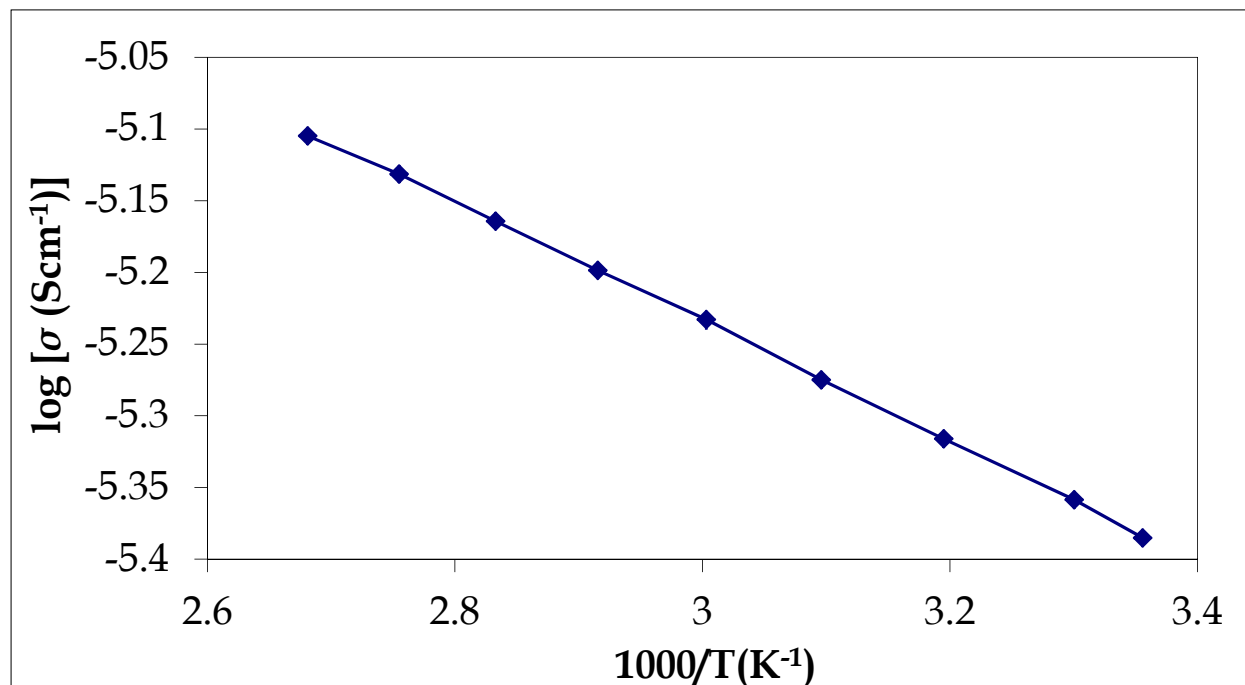
Fig. 6. Arrhenius plot of SPC5 in the temperature range of 298–373 K.

5.3 Fourier Transform Infrared (FTIR) studies

The FTIR spectra and description of vibration modes of pure PVC, pure $Li_2B_4O_7$, SPC1, PC and SPC5 are shown in Figures 7(a)–(e) and Table 2, respectively. Comparing SPC1 with pure PVC, there are 10 new peaks have been formed. All of these new peaks are the characteristic bonds of $Li_2B_4O_7$. Five new peaks have been detected in the wavenumber range of 1200 cm^{-1}–700 cm^{-1}. These peaks are assigned as B–O(B) stretching mode of BO_4 tetrahedral shape of $Li_2B_4O_7$ at 710 cm^{-1}, 815 cm^{-1}, 905 cm^{-1}, 1034 cm^{-1} and 1120 cm^{-1}. In contrast, for B–O(B) stretching mode of BO_3 triangle shape, $Li_2B_4O_7$ portrays two characteristic peaks at 1246 cm^{-1} and 1376 cm^{-1}. However, only one peak is observed at 1253 cm^{-1} for SPC1. This indicates the interaction between PVC and $Li_2B_4O_7$ and further reveals the decoupling of Li^+ from the B–O(B) coordinative bonds. Four new peaks at 451 cm^{-1}, 504 cm^{-1}, 565 cm^{-1} and 670 cm^{-1} are designated as O–B–O deformation mode of BO_4 tetrahedral in $Li_2B_4O_7$. All the vibration modes exhibit peak shifting, except the weak peak at 1331 cm^{-1} which is denoted as CH_2 deformation of PVC.

As shown in Figure 7(a), the transmittance peaks at 616 cm^{-1} and 969 cm^{-1} are corresponding to cis and trans C–H wagging modes, respectively. Upon addition of $Li_2B_4O_7$, these peaks are shifted towards higher wavenumber to 637 cm^{-1} and 973 cm^{-1}, respectively. Apart from that, they exhibit changes in shape. For cis wagging mode, it has been changed from weak peak to shoulder peak, whereas a medium peak has been changed to a broad band for trans wagging mode. A sharp peak is observed at 1067 cm^{-1} in Figure 7(a), which designated as C–H rocking mode of PVC. However, it turns to a broad band with inclusion of $Li_2B_4O_7$ and manifests a downward shift to 1062 cm^{-1}. The peak at 833 which corresponds to C–Cl

stretching mode of PVC also shifted to 825 cm^{-1} upon impregnation of lithium salt. Similarly, C–H stretching mode of CH$_2$ group which is located at 1434 cm^{-1} for pure PVC spectrum also exhibits downward shift to 1420 cm^{-1}. This discloses the interactions between C–H, C–Cl and Li$^+$. It suggests that the Li$^+$ would be dissociated from O–Li interactive bond by forming hydrogen bonds to hydrogen atom from C–H group in PVC. Hence, these mobile Li$^+$ would re–interact with chloride anions in PVC as chloride anions have three electron lone pairs. The ionic hopping mechanism is eventually generated. The vibrational modes of characteristic peaks not only undergo the changes in shift and shape, but they also demonstrate the change in intensity. An apparent proof has been observed in the wavenumber region of 3000 cm^{-1}–2800 cm^{-1}. Two sharp peaks are located at 2867 cm^{-1} and 2979 cm^{-1}, and are denoted as CH$_3$ asymmetric stretching mode of PVC. The first transmittance peak is found to be shifted to higher wavenumber of 2910 cm^{-1}, meanwhile it has been moved to 2971 cm^{-1}, for latter peak. Upon the addition of Li$_2$B$_4$O$_7$, the intensity of both peaks is greatly reduced by comparing Figure 7(a) with 7(c). Regarding to the changes in peak intensity, changes in shape, changes in shift, formation of new peaks and disappearance of the peak, it reflects the establishment of polymer–salt complex.

In order to investigate the complexation between PC and polymer matrix, SPC5 is further examined as it achieves the maximum ionic conductivity. Comparing SPC1 with SPC5, seven new peaks have been formed. These peaks are denoted as ring deformation of PC, ring stretching and breathing modes of PC, C–O stretching mode of PC, B–O(B) stretching mode of BO$_3$ triangle shape of Li$_2$B$_4$O$_7$, C–H symmetric deformation mode of PC and C=O symmetric stretching mode of PC at 795 cm^{-1}, 959 cm^{-1}, 1054 cm^{-1} and 1187 cm^{-1}, 1351 cm^{-1}, 1388 cm^{-1} and 1794 cm^{-1}, respectively. Upon PC loadings, some of the characteristic peaks are disappeared. These peaks are the weak peaks in PC at 950 cm^{-1} and 910 cm^{-1}, and the shoulder peak of SPC1 at 1035 cm^{-1}. The characteristic peaks at 446 cm^{-1}, 503 cm^{-1}, 566 cm^{-1} and 668 cm^{-1} are designated as O–B–O deformation mode of BO$_4$ tetrahedral in Li$_2$B$_4$O$_7$. The weak peak at 446 cm^{-1} is originated from the medium sharp peak at 451 cm^{-1} in SPC1 spectrum. In term of intensity, this characteristic peak is reduced around 18%, from 23% to 5%, in transmittance mode. For the weak peaks at 503 cm^{-1} and 566 cm^{-1}, they show signs of changes in shape. It has been changed to broad band and slightly shifted from 504 cm^{-1} for the first peak. On the other hand, the latter peak displays a somewhat upward shift from 565 cm^{-1} and changed to shoulder peak. An oppose result is obtained for the peak at 702 cm^{-1}, which assigned as B–O(B) stretching mode of BO$_4$ tetrahedral in Li$_2$B$_4$O$_7$. This peak illustrates downward shift from 710 cm^{-1} to 702 cm^{-1} and the change in shape, from shoulder peak to weak peak.

Noticeable change in shape is observed in the wavenumber range of 700 cm^{-1}–600 cm^{-1}. A weak peak at 668 cm^{-1} with a shoulder peak at 637 cm^{-1} has been changed to two weak peaks at 670 cm^{-1} and 636 cm^{-1}, respectively, by doping PC into the polymer complex. As aforementioned, the peak at 670 cm^{-1} is the characteristic peak of O–B–O deformation mode of BO$_4$ tetrahedral, whereas cis C–H wagging mode in PVC is the assignment for the latter peak. Therefore, it implies the interaction between PVC, Li$_2$B$_4$O$_7$ and PC. There is another evidence to prove the complexation between PVC, Li$_2$B$_4$O$_7$ and PC at 830 cm^{-1}. Two shoulder peaks have been changed to a broad band. This arises from the combination of B–O(B) stretching mode of BO$_4$ tetrahedral shape of Li$_2$B$_4$O$_7$ at 815 cm^{-1}, C–Cl stretching

mode of PVC at 825 cm^{-1} , and ring stretching and breathing modes of PC at 850 cm^{-1}. As explained in section 5.1, we propose that the hydrogen atom from methyl group in PC would break the O–Li coordination bond through hydrogen bonding. Thus, the dissociated Li$^+$ would interact with the chloride anion of the C–Cl interactive bond in PVC and ultimately form CH–Cl–Li linkage. A broad band is observed at 1062 cm^{-1} in SPC1 spectrum. However, this C–H rocking mode of PVC has been changed to weak shoulder peak at 1074 cm^{-1} with adulteration of PC. The effect of PC is also observed for the shoulder peak at 1120 cm^{-1}. As tabulated in Table 2, this peak is assigned as B–O(B) stretching mode of BO$_4$ tetrahedral of Li$_2$B$_4$O$_7$. Nevertheless, a medium sharp peak is attained at 1117 cm^{-1}. The change in shape is due to the merging of this stretching mode with C–O stretching mode of PC as a medium sharp peak is obtained at 1118 cm^{-1}, as shown in Figure 7(d). This interaction further proves the mechanism of complexation that we proposed as above.

SPC1 exemplifies two weak peaks at 1331 cm^{-1} and 1426 cm^{-1}. The first peak is designated as CH$_2$ deformation of PVC, whereas the C–H stretching mode of CH$_2$ group of PVC is for latter peak. Upon inclusion of PC, these two peaks are still appearing in the spectrum. The first peak is shifted upward to 1332 cm^{-1}, whereas the latter peak remains unchanged. Two more new weak peaks have been discovered in this band. These peaks are the B–O(B) stretching mode of BO$_3$ triangle of Li$_2$B$_4$O$_7$ and C–H symmetric deformation mode of PC at 1351 cm^{-1} and 1388 cm^{-1}, respectively. Moreover, the change in intensity is one of the aspects to determine the complexation of this plasticized–polymer electrolyte. The peak shifting of B–O(B) stretching mode of BO$_3$ triangle shape in Li$_2$B$_4$O$_7$ at 1253 cm^{-1} still remain the same. However, its peak intensity is slightly declined, from 28% to 21%, in transmittance mode, as illustrated in Figure 8. In contrast, the increase in peak intensity is obtained at high wavenumber range of 3000 cm^{-1}–2900 cm^{-1}. Only two peaks are observed in this range. Both of these peaks are denoted as CH$_3$ asymmetric stretching mode of PVC and shifted to 2912 cm^{-1} (from 2910 cm^{-1}) and 2975 cm^{-1} (from 2971 cm^{-1}). In term of intensity, the peaks are gradually increased. For the first peak, it rises up around 7%, from 5% to 12%, in transmittance mode. The peak intensity of latter peak enhances around 10%, from 7% to 17%, in transmittance mode. This reveals the interaction between PVC and PC and further verifies the establishment of polymer complex.

Some of the characteristic peaks of PC are not be found in the SPC5 spectrum compared to PC spectrum. These peaks include CH$_2$ bending deformational mode of CH$_3$ group of PC, in plane CH$_2$ scissoring mode of PC and the combinations of CH$_2$ rocking and ring breathing mode of PC at 1460 cm^{-1}, 1482 cm^{-1} and 1555 cm^{-1}, respectively. In PC spectrum, an intrinsic vibrational band of the C=O symmetric stretching mode is located at ~1800 cm^{-1}. This strong and broad band splits into two components (at 1787 cm^{-1} and 1900 cm^{-1}). The overtone is produced at 1900 cm^{-1} as a consequence of Fermi resonance of the C=O stretching mode with the ring breathing mode that lies at ~950 cm^{-1}. However, this overtone of PC is not being observed in SPC5 spectrum. This disappearance of characteristic divulges the interaction between PC and polymer system. The changes in position, changes in shape, changes in intensity, formation of new peaks and disappearance of peak infers the interaction between PVC, Li$_2$B$_4$O$_7$ and PC. Therefore, it can be concluded that PC is associated in the polymer matrix.
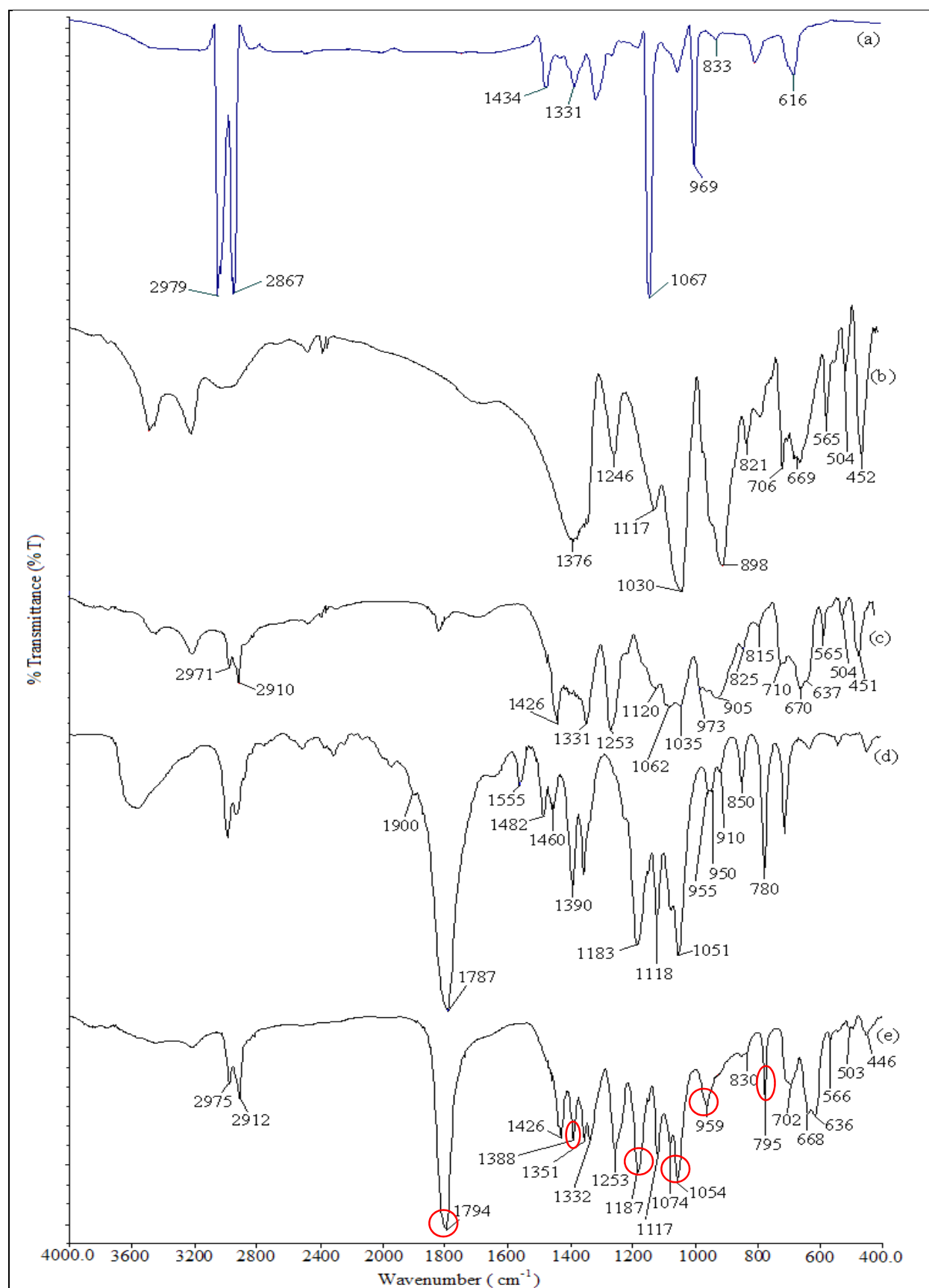
Fig. 7. The FTIR spectra of (a) pure PVC, (b) pure $Li_2B_4O_7$, (c) SPC1, (d) PC and (e) SPC5.

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Description of vibration modes	Wavenumber (cm^{-1})			References
	PVC/ Li$_2$B$_4$O$_7$/PC	SPC1	SPC5	
O–B–O deformation mode of BO$_4$ tetrahedral of Li$_2$B$_4$O$_7$	452, 504, 565 and 669	451, 504, 565 and 670	446, 503, 566 and 668	Ge et al., 2007
Cis C–H wagging mode in PVC	616	637	636	Rajendran et al., 2008a
B–O(B) stretching mode of BO$_4$ tetrahedral shape of Li$_2$B$_4$O$_7$	706, 821, 898, 1030 and 1117	710, 815, 905, 1035 and 1120	702 and 1117	Ge et al., 2007
Ring deformation of PC	780	–	795	Deepa et al., 2004
C–Cl stretching mode of PVC	833	825	830	Li et al., 2006a
Ring stretching and breathing modes of PC	850, 910, 950 and 955	–	959	Deepa et al., 2004
Trans C–H wagging mode of PVC	969	973	Disappear	Achari et al., 2007
C–O stretching mode of PC	1051, 1118 and 1183		1054, 1117 and 1187	Deepa et al., 2004
C–H rocking mode of PVC	1067	1062	1074	Achari et al., 2007
B–O(B) stretching mode of BO$_3$ triangle shape of Li$_2$B$_4$O$_7$	1246 and 1376	1253	1253 and 1351	Ge et al., 2007
CH$_2$ deformation of PVC	1331	1331	1332	Rajendran et al., 2000b
C–H symmetric deformation mode of PC	1390	–	1388	Sharma and Sekhon, 2007
C–H stretching mode of CH$_2$ group of PVC	1434	1426	1426	Rajendran et al., 2008a
CH$_2$ bending deformation mode of CH$_3$ group of PC	1460	–	Not appear	Deepa et al., 2004
In plane CH$_2$ scissoring mode of PC	1482	–	Not appear	Deepa et al., 2004
Combinations of CH$_2$ rocking and ring breathing mode of PC	1555	–	Not appear	Deepa et al., 2004
C=O symmetric stretching mode of PC	1787	–	1794	Sharma and Sekhon, 2007
Overtone of PC (2×ring breathing mode of PC at 950 cm^{-1})	1900	–	Not appear	Sharma and Sekhon, 2007
CH$_3$ asymmetric stretching mode of PVC	2867 and 2979	2910 and 2971	2912 and 2975	Rajendran et al., 2000b

Table 2. Assignments of vibrational modes of pure PVC, pure Li$_2$B$_4$O$_7$, PC, SPC1 and SPC5.
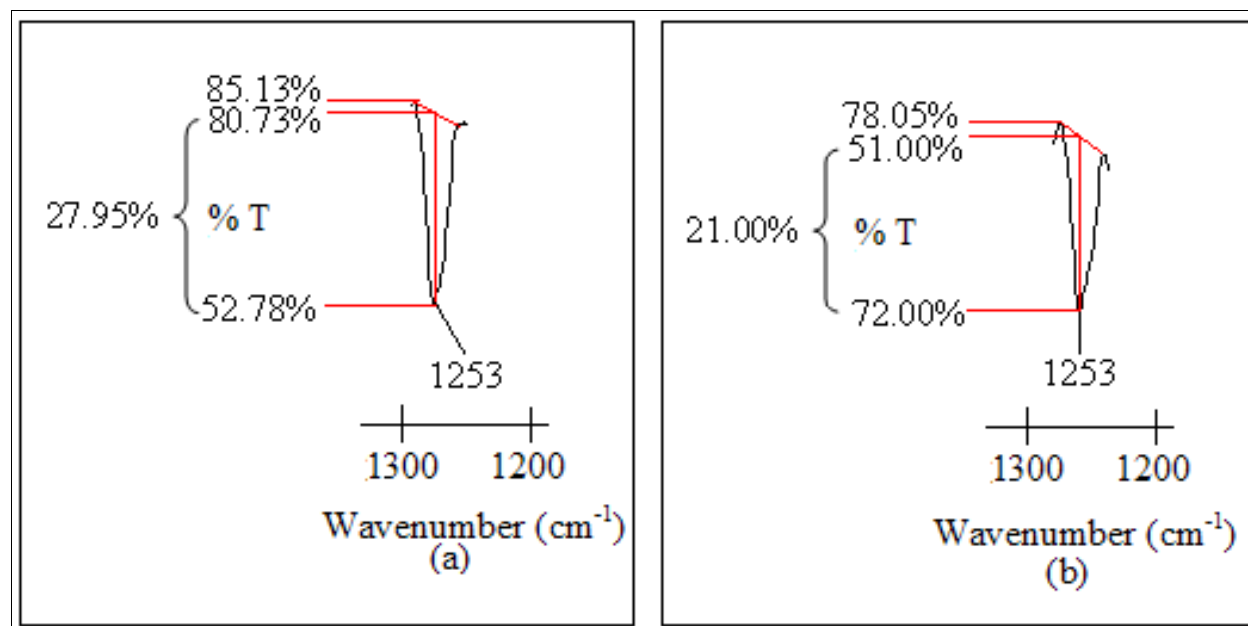
Fig. 8. The change in intensity of B–O(B) stretching mode of BO_3 triangle shape of $Li_2B_4O_7$ at 1253 cm^{-1} for (a) SPC1 and (b) SPC5.

5.4 Thermogravimetric analysis (TGA)

Figure 9 describes the thermogravimetric curves of SPC1, SPC5, SPC7 and SPC9. Two distinct stages have been observed in the temperature regime. The first weight loss is credited to the evaporation of residual THF solvent and dehydration of entrapped moisture (Ramesh et al., 2010). A moderate mass loss is initially observed. Pure PVC and SPC1 elucidate around 6% and 1% of mass losses at 159 °C and 150 °C, respectively. Even though the adulteration of PC increases the weight loss, but it also boosts up the decomposition temperature. As observed, the drop in weight is further increased with increasing the PC concentration. Around 11%, 31% and 32% of weight losses are attained for SPC5, SPC7 and SPC9 at 160 °C, 169 °C and 180 °C, respectively. After complete the dehydration, a stable weight is followed up in the thermal range.

Beyond this stable range, the weight of polymer complexes is drastically reduced in this stage. Dehydrochlorination process is the main contributor for this weight loss. At high temperature, the degrading products such as Cl free radicals are produced initially upon combustion. For further propagation, these free radicals would react with the methyl group of PC and hence break up the interactive bond, leading to the dehydrochlorination mechanism. The HCl cleavage would produce allyl chloride. Then, this allyl chloride favors the unzipping process and results in polyene linkage. This unzipping reaction induces many degradation reactions such as random chain scission reaction, depolymerization, inter–molecular transfer reaction and intra-molecular transfer reaction whereby dimers, trimers and oligomers are produced as well as polymer fragments. As a result, the monomer and oligomers which chemi–adsorbed onto the polymer matrix is volatilized in this region (Ramesh et al, 2011a). Pure PVC has mass loss of 63%, starting from 250 °C to 389 °C, with a residual mass of 31%. As can been seen, the weight losses have been improved by doping of $Li_2B_4O_7$ and PC. SPC1 delineates the mass loss of 46%, from 230 °C to 390 °C, with residual mass of around 51 %. The effect of PC onto the weight loss is further observed. SPC5 has lost

around 45 % of its weight with around 43% residual mass, from 230 °C to 390 °C. In contrast, for SPC7, it is around 29% with 37% residual mass, starting from 238 °C to 388 °C. SPC9 starts to decompose at 239 °C and exemplifies a modest weight loss of 37% at 389 °C, with residual weight of 28%. Among the plasticized–polymer electrolytes, SPC5 portrays the lowest total weight loss of 57%. SPC5 is still a promising candidate as polymer electrolyte although its total weight loss is higher than SPC1. SPC5 exhibits excellent thermal stability as its stability is up to 230 °C, whereby the normal working range is 40–70 °C.
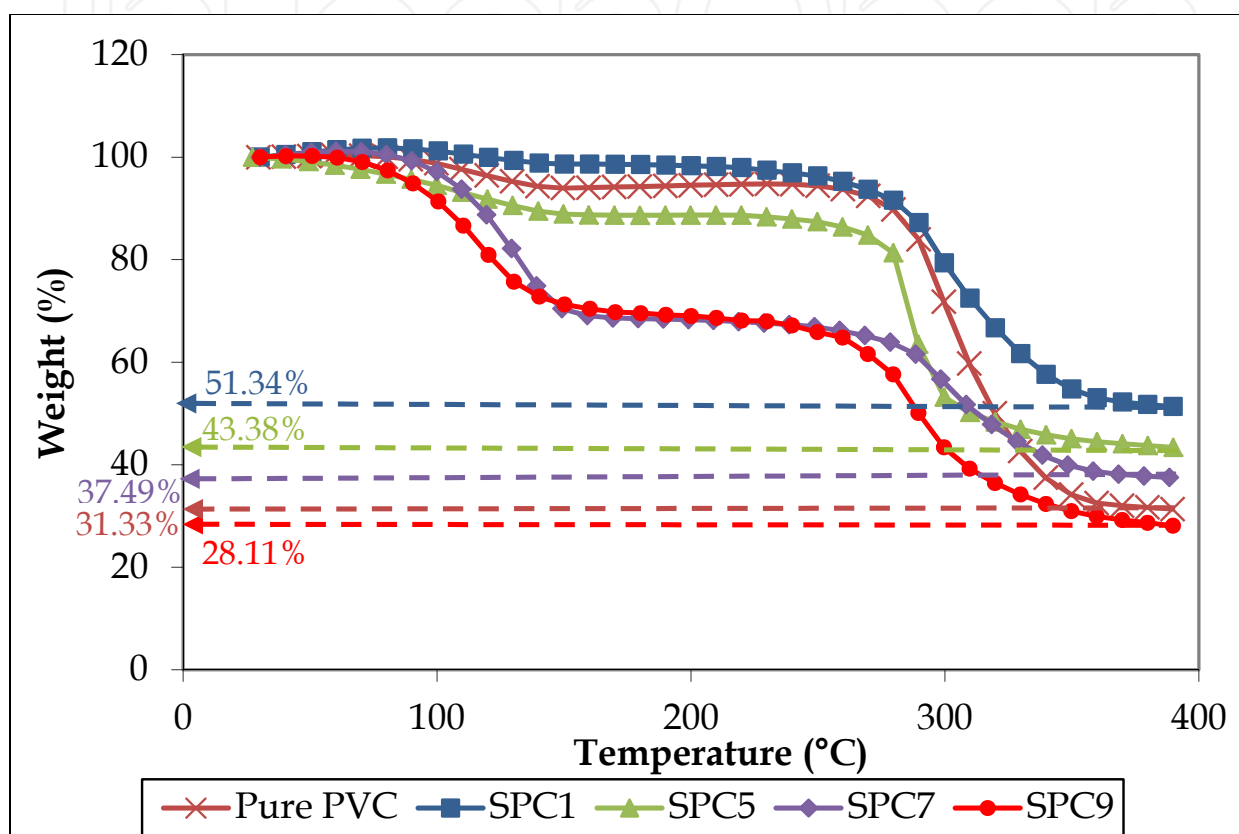
Fig. 9. Thermogravimetric analysis of pure PVC, SPC1, SPC5, SPC7 and SPC9.

6. Conclusion

The PVC–Li$_2$B$_4$O$_7$–PC plasticized–polymer system has been prepared and investigated in this project. Upon addition of 20wt% of PC (or designated as SPC5), the highest conductivity of 4.12×10^{-6} Scm^{-1} is achieved at ambient temperature. Plasticizer plays a fundamental role to weaken the interaction within the polymer matrix and hence increases the ionic conductivity with a flexible polymer backbone. The polymer electrolytes obey the Arrhenius behavior and indicate the ionic hopping mechanism, as proven in temperature dependence–ionic conductivity studies. In addition, FTIR studies help us to confirm the complexation of PVC–Li$_2$B$_4$O$_7$–PC system by determining the, changes in intensity, changes in shape and changes in shift, appearance and disappearance the peaks. Moreover, the thermal stability of the polymer films is contradictory to the PC mass loadings. By analyzing the TGA thermograms, it divulges that SPC5 exhibits good thermal stability in comparison with SPC7 and SPC9.

7. Further research

Upon addition of plasticizer, some limitations are obtained such as low flash point, slow evaporation, decreases in thermal, electrical and electrochemical stabilities. Low performances, for instance, small working voltage range, narrow electrochemical window, high vapor pressure and poor interfacial stability with lithium electrodes are the disadvantages of plasticized–gel polymer electrolytes (Pandey and Hashmi, 2009). Therefore, ionic liquid will be incorporated into the plasticizer in our further study. Room temperature ionic liquid (RTIL) possesses many attractive properties, such as wider electrochemical potential window (up to 6V), wider decomposition temperature range, non–toxicity and non–volatility as well as non–flammability with low melting point. Other features are better safety performance, relatively high ionic conductivity due to high ion content, and excellent thermal, chemical and electrochemical stabilities (Jiang et al., 2006; Cheng et al., 2007).

8. Acknowledgement

9. References

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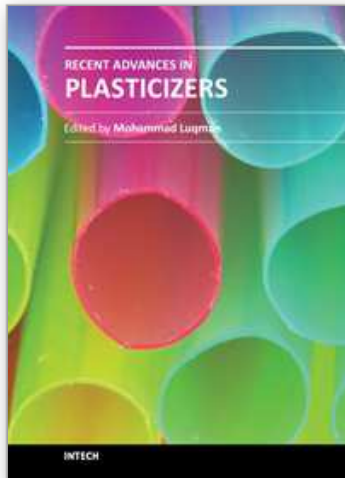
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