Role of PVME on the ionic conductivity and morphology of a TPU based electrolyte

M. Digar, Ten-Chin Wen*

Department of Chemical Engineering, National Cheng Kung University, Tainan 701, Taiwan, ROC

Abstract

Ionic conductivity and morphology of a two-component hybrid polymer electrolyte comprising a polymer blend, $LiClO_4$ and propylene carbonate (PC) have been studied. The hybrid polymer electrolyte has been made by mixing $LiClO_4$ in required proportions with a blend of thermoplastic polyurethane (TPU) and polyvinylmethylether (PVME) and then adding PC to it. TPU used in this study was a segmented urethane having a 1:1 mixture of polypropylene glycol (PPG) and polytetramethylene glycol (PTMG) as the soft segment and $4,4'$-diphenyl methane diisocyanate (MDI) extended with ethylene diamine (EDA) as the hard segment. The morphology and ionic conductivity of these hybrid polymer electrolytes were studied by using differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR) and AC impedance measurements. Electrochemical stability of the electrolyte was studied by cyclic voltammetry (CV). Blending with 20-wt% PVME leads to: (i) ~100% increase in absorption of PC compared to pure TPU; and (ii) increase in dissolution of $LiClO_4$ up to ~2.0 mmol/g of the blend which was otherwise only 0.4 mmol/g in pure TPU. Room temperature ionic conductivity of the polymer electrolyte containing 1.5 mmol of $LiClO_4$ per gram of the blend and 40% PC is 10^{-4} S/cm. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Quite a large number of studies have been carried out on solid state batteries utilizing hybrid films composed of polymer, salt and plasticizer as gelled polymer electrolytes (GPEs) [1–7]. These electrolytes are not true polymer electrolytes, as ionic transport resembles that of a liquid system and the polymer serves primarily as a support for the conductive matrix. The plasticizer used for this purpose is generally an aprotic solvent such as ethylene carbonate (EC) or propylene carbonate (PC) [3,8–10] or low molecular weight polymer such as polyethylene glycol (PEG) or polyethylene glycol dimethyl ether (PEGDME) [7,11,12]. The required characteristics of a GPE are: (a) high ionic conductivity ($>10^{-3}$ S/cm); (b) good mechanical strength; (c) good chemical and electrochemical stability; (d) good thermal stability (up to ~90°C); and (e) compatibility with other cell components. The role of the plasticizer in the GPE is to solvate the ions more easily and hence to increase the ionic conductivity of the plasticized electrolytes. But these systems have got some disadvantages too. The major ones

are the poor mechanical properties due to high degree of plasticization, solvent volatility and the reactivity of the plasticizer (if sufficiently polar) with lithium electrode.

Linear segmented polyurethane has emerged as one of the important class of polymers for use as matrix material in polymer electrolytes [13–20]. These segmented polyurethanes have got a two-phase morphology, where interconnected or isolated hard segment domains are distributed in the soft segment matrix. The primary driving force for the phase separation or domain formation is the strong intermolecular interaction of the urethane units, which are capable of forming interurethane hydrogen bonds. In our previous work [20], we reported the efficacy of a thermoplastic polyurethane (TPU) as a solid polymer electrolyte made from a 1:1 mixture of polypropylene glycol (PPG) and polytetramethylene glycol (PTMG) as the soft segment and $4,4'$-diphenyl methane diisocyanate (MDI) extended with ethylene diamine (EDA) as the hard segment. This system shows a conductivity of $\sim 10^{-6}$ S/cm at 85°C when doped with 0.35 mmol/g of $LiClO_4$. The mechanical properties of this polymer electrolyte system were very good, owing to the presence of hard segment domains which are in the glassy state and act as a reinforcing filler to the soft segment matrix.

But one problem associated with this TPU electrolyte

* Corresponding author. Tel.: +886-6-2757575, ext. 62656; fax: +886-6-2344496.

E-mail address: tcwen@mail.ncku.edu.tw (T.-C. Wen).

Table 1
List of reagents and chemicals

Designation	Chemical identification	Source
MDI	4,4′-diphenylmethane diisocyanate	DuPont Company. Inc.
PPG 2000	Polypropylene glycol ($M_w = 2000$)	DuPont Company, Inc.
PTMG 2000	Polytetramethylene glycol ($M_w = 2000$)	DuPont Company, Inc.
EDA	Ethylene diamine	Aldrich Chemical Company, Inc.
DMF	Dimethylformamide	Mallinckredt Baker Inc.
MeOH	Methyl alcohol	Mallinckredt Baker Inc.
LiClO$_4$	Lithium perchlorate	Aldrich Chemical Company, Inc.
PVME	Polyvinylmethylether	Aldrich Chemical Company, Inc.
PC	Propylene carbonate	Aldrich Chemical Company, Inc.

system is that it cannot solvate LiClO$_4$ more than 0.4 mmol/g nor can it absorb PC more than 20%. As it cannot solvate more LiClO$_4$, the number of charge carriers in the electrolyte system is less. Moreover, the inability to absorb higher amount of PC cannot increase the solvating power of the plasticized TPU substantially. In order to overcome this problem, we blended another polymer, namely polyvinylmethylether (PVME) with the TPU. Differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR) and ionic conductivity of the blend system were studied by doping with different concentrations of LiClO$_4$ and adding different amounts of PC as plasticizer. Such two-component systems have been reported earlier by many researchers [21–24], where one phase contains polymer/s that can absorb the plasticizer and the other component contains polymer/s that enhance the mechanical properties of the blend. In our blend system, TPU component imparts good mechanical properties whereas the PVME component

absorbs more of the plasticizer and solvates the Li$^+$ ions. The idea of selecting PVME as the second component comes from its molecular structure containing pendent ether groups, which may also coordinate with the Li$^+$ ions and hence may increase the ability of the blend to dissolve more Li salts. In fact, from our study it has been found that a 4:1 blend of TPU and PVME can dissolve LiClO$_4 > 1.5$ mmol/g and can absorb >40% PC with very little deterioration of the mechanical properties of the blend. Room temperature conductivity of the blend doped with 1.5 mmol/g LiClO$_4$ and containing 40% PC is of the order of 10^{-4} S/cm.

2. Experimental

2.1. Reagents and chemicals

The chemicals and reagents used in this study are given in Table 1. PPG and PTMG (both having molecular weight 2000) were dehydrated under reduced pressure at 80°C for 24 h before use. LiClO$_4$ was dehydrated at 120°C under reduced pressure for 72 h. PVME was obtained as a 50% solution in water. It was purified through three cycles of dissolution in cold water and separation by warming. It was then dried under vacuum at 60°C for 72 h. All other reagents and solvents were used without further purification.

2.2. Synthesis of TPU

The TPU was synthesized by a two-step addition process, where the prepolymer was made in the first step by reaction of excess of MDI with the polyols and then extending the chain length by reaction of the prepolymer with the chain extender in the second step. The prepolymer was made by allowing the mixture of MDI and polyols to react at 85°C for 6 h with stirring under a constant dry nitrogen blanket. After the prepolymer formation was over, it was dissolved in
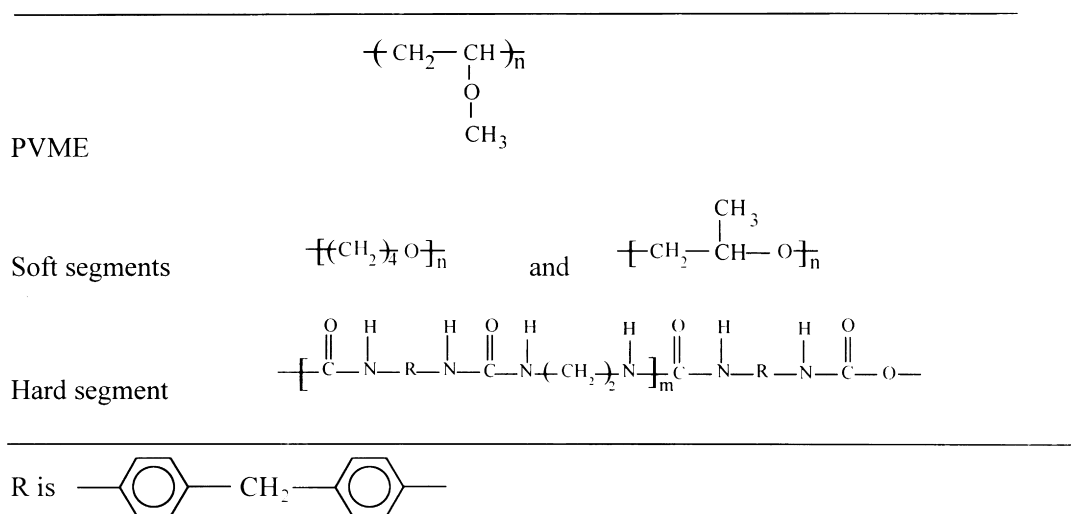
Scheme 1.

DMF and the temperature of the mass was reduced to $-5°C$. Then a 3-wt% solution of EDA in DMF was slowly added to the prepolymer solution at $-5°C$ with constant stirring. After the addition of EDA solution was over, the temperature of the mass was increased to $85°C$ and the reaction was allowed to continue for 1 h at this temperature. The concentration of the polymer at this stage was ~20%. The polymer solution was cooled to room temperature and precipitated into excess methanol. It was reprecipitated twice from DMF into excess methanol, washed several times with methanol and dried in vacuum at $100°C$ for 72 h.

2.3. Molecular weight

The structure of PVME and TPU soft and hard segments are summarized in Scheme 1. The molar ratio of MDI, PPG, PTMG and EDA was maintained at 6:1:1:4. The molecular weight and the molecular weight distribution of the TPU were measured using a Shimadzu Gel Permeation Chromatograph connected to a Shimadzu HPLC pump and an RI detector. A 1 wt% solution of the TPU in DMF was injected into the GPC column (Jordi Gel DVB mixed bed) at a flow rate of 2 ml/min. The system was calibrated with 10 polystyrene standards. The TPU has a number average molecular weight of ~75 000 and a polydispersity of 1.91.

2.4. Sample preparation

Blends of TPU and PVME were made by mixing 10-wt% solutions of TPU and PVME in DMF under stirring with the help of a magnetic stirrer. Films for DSC and AC impedance measurements were made on glass substrates by casting from a 10-wt% solution of the blends in DMF. Doping was done by solution blending, where the required amount of 10-wt% solution of $LiClO_4$ in DMF was mixed with the blend solutions by stirring for 12 h with the help of magnetic stirrer. Drying of the doped as well as the undoped films was done at $100°C$ under vacuum for 72 h. For FTIR analysis, films were cast on KBr pellets from a 5-wt% solution in DMF and dried at $120°C$ under vacuum for 72 h. The samples were then shifted to a glove box where they were transferred into airtight containers to avoid absorption of moisture. The containers were opened only at the time of measurement of FTIR spectra.

2.5. Swelling measurement

Swelling study of the TPU and the blend films were carried out inside a glove box (Vacuum Atmosphere Company, USA) by dipping a preweighed film (~500 mg) in ~20 ml PC. The films were kept immersed for various periods of time after which the films were withdrawn, the surface PC was removed by soaking with a filter paper and then reweighed. Percent swelling (S_w) is expressed as

$$S_w = 100(W - W_0)/W_0$$

where W_0 is the initial weight of the film and W is the weight after swelling.

2.6. DSC measurement

DSC measurements were carried out using a DSC 2010 Differential Scanning Calorimeter (TA Instruments, USA) over a temperature range of -120 to $150°C$ at a scan rate $10°C/min$. All the thermograms were base line corrected and calibrated using Indium metal. The experimental specimens (6–8 mg) were cut from cast films dried at $100°C$ under vacuum for 72 h. Glass transition temperatures were reported for the midpoint of the transition process, and the melting temperatures were the peak temperatures. All the samples were annealed at $150°C$ for 2 min, cooled to $-120°C$ using liquid nitrogen and then scanned for measurement of T_g and T_m.

2.7. FTIR measurement

FTIR spectra were measured at ambient temperature using a Nicolet 550 equipment with a wave number resolution of $4 cm^{-1}$. 128 scans were signal averaged to increase the s/n ratio. The –NH stretching region was deconvoluted using a commercial software (Grams 386 Software from Galactic Industries Corporation). The maximum error associated with the deconvolution study is expected to be ^ 10%.

2.8. AC impedance measurement

Impedance measurements of the solid polymer electrolytes were performed using thin films made by casting from solution and subsequent drying. Film thickness was maintained in the range of $150–200\mu$ and the area of contact was $0.785 cm^2$. The GPEs were prepared from the solid polymer electrolytes by dripping required amount of PC on the doped films and by allowing it to stand up to 2 h for complete absorption of PC. Samples were sandwiched between two stainless steel electrodes and fixed in an airtight double wall glass cell, through the outer jacket of which thermostated water was circulated for measurements at different temperatures. Gelled electrolyte preparation and cell assembly were carried out in dry argon atmosphere inside a glove box (Vacuum Atmosphere Company, USA). Ionic conductivity of the samples was measured using an Autolab PGSTAT 30 equipment (Eco Chemie B.V., Netherlands) with the help of a frequency response analysis system software under an oscillation potential of 20 mV.

2.9. Cyclic voltammetry (CV)

Three electrode laminated cells were assembled inside the glove box for the cyclic voltammetric experiments. Stainless steel (SS) was used as the working electrode and lithium metal was used as the counter as well as the reference electrode. Cyclic voltammetric measurements were
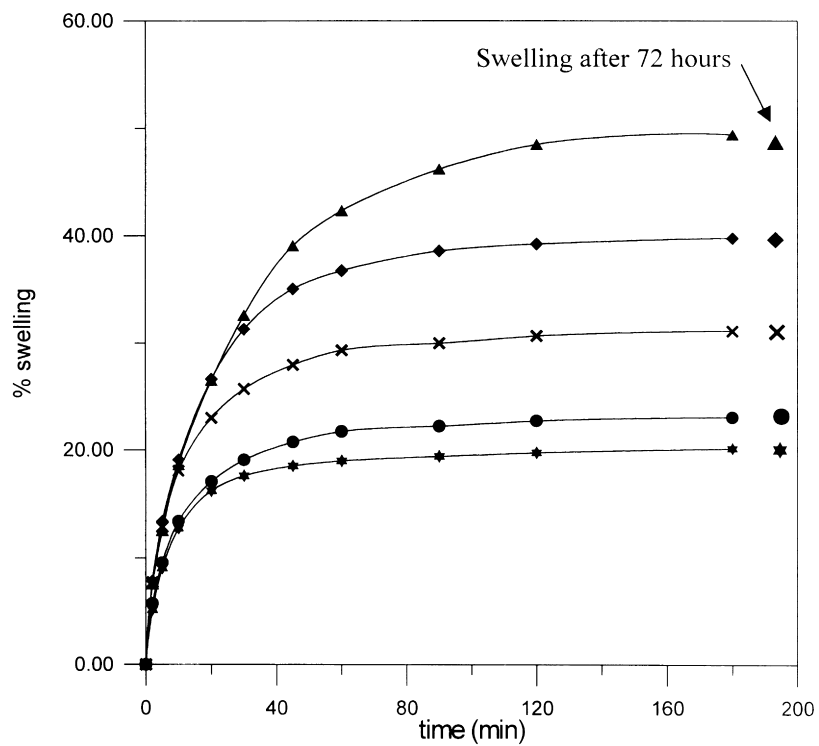
Fig. 1. Swelling study of TPU and its blends with PVME in PC: ★ = TPU; ✕ = 5% PVME; ✕ = 10% PVME; ∇ = 20% PVME; ○ = 30% PVME.
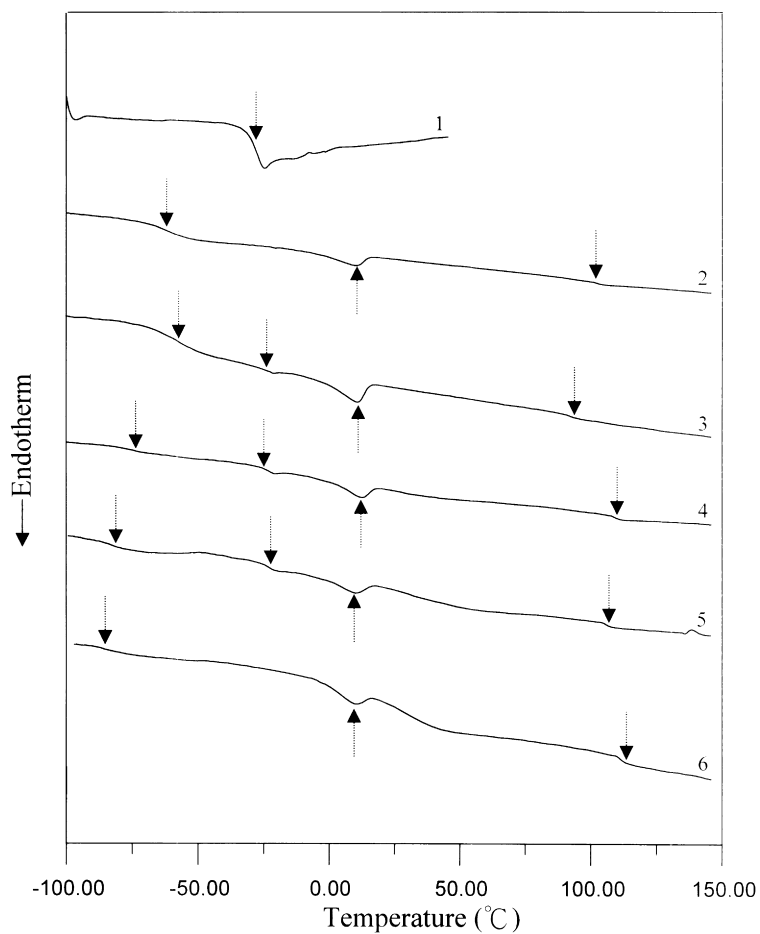

Fig. 2. DSC thermograms of: (1) PVME; (2) pure TPU; (3) sample B1; (4) sample B2; (5) sample B3; and (6) sample B4.

Table 2
Thermal transition temperatures of PVME, TPU and the blend systems

Sample[a]	Salt concentration (mmol/g)	T_g (SS) (°C)	T_g (PVME) (°C)	T_m (SS) (°C)	T_g (HS) (°C)
PVME	0.0	–	−27.95	–	–
TPU	0.0	−64.53	–	10.32	102.25
B1	0.0	−57.57	−21.82	10.80	92.13
B2	0.5	−73.86	−22.97	12.76	108.92
B3	1.0	−82.66	−23.18	9.93	105.78
B4	1.5	−86.30	–	9.54	110.96

[a] Samples B1–B4 are the 4:1 blends of TPU and PVME containing 0.0, 0.5, 1.0 and 1.5 mmol of LiClO$_4$ per gram of the blends, respectively; SS = soft segment, HS = hard segment.

carried out using Autolab PGSTAT 30 potentiostat/galvanostat equipment (Eco Chemie B.V., Netherlands).

3. Results and discussion

3.1. Swelling study

In order to find out the effect of PVME on the absorption of PC by the blends of TPU and PVME, we made six blends having 5, 10, 20, 30, 40 and 50-wt% PVME. Swelling behavior of the first four blends was studied in PC at ambient temperature. The other two blends containing 40 and 50% PVME were not tried, as the mechanical properties of the blends were not suitable for use as polymer electrolyte. The swelling behavior of the above-mentioned four blends was shown in Fig. 1 along with that of pure TPU. It is evident from the figure that all the four blends are sufficiently stable in PC even after 72 h. All the films show no decrease in weight even after 72 h immersion in PC except the blend containing 30% PVME, where slight decrease in percent swelling was observed after 72 h. The blend containing 5% PVME does not show any appreciable increase in absorption of PC. It can absorb only 23% PC, which is close to the value for pure TPU ($\sim$20%). With an increase in the amount of PVME in the blend from 5 to 30%, percent swelling is increased from 23% to above 50%. The blend containing 10% PVME absorbs only 31% PC, still in the lower level for use as a gelled electrolyte. For the 20% PVME containing blend, swelling percent (40%) is double that for the pure TPU. The swelling percent can be increased even beyond 50% (for the blend containing 30% PVME), but the mechanical property of the 50% swelled film is slightly inferior for use as a polymer electrolyte. In our present study, we, therefore, use a blend of TPU with 20-wt% of PVME, which shows about 100% more swelling in PC.

3.2. DSC study

The thermal behaviors of TPU, PVME and the blend of TPU and PVME are shown in Fig. 2 along with three other curves for the three doped blend samples containing 0.5, 1.0 and 1.5 mmol of LiClO$_4$ per gram of the blends. The T_g and the T_m data for the above samples are presented in Table 2. Two glass transition temperatures and one melting temperature characterize the thermal behavior of the TPU. The T_g in the region of −60°C or less is associated with the transition of the soft segment from the glassy state to the rubbery state, whereas that in the region of 90–110°C is associated with the short range ordering of the hard segment domains. The melting temperature in the region of 10–20°C is associated with the melting of the crystalline soft segment arising from PTMG 2000. The DSC curve of PVME shows its glass transition in the region of −30°C. All the four blends presented in Fig. 2 containing either or no LiClO$_4$ show all the transitions of the TPU and PVME with shifting to higher or lower temperature regions. As is evident from the figure, the blend containing no LiClO$_4$ shows two low temperature transitions at slightly higher temperatures than the corresponding transitions of the soft segment and PVME. The high temperature transition associated with the hard segment was found to decrease to the lower temperature region. In pure TPU the transition was found at $\sim$102°C whereas in the blend it arises at $\sim$92°C. This behavior may be due to the mixing of soft and hard segments induced by the presence of PVME. Having ether oxygens, PVME may also have some van der Waals type interaction with the urethane –NH groups, and hence there may be slight increase in the T_g of PVME also.

Curves 4, 5 and 6 of Fig. 2 show the thermal behavior of the blend system doped with 0.5, 1.0 and 1.5 mmol of LiClO$_4$ per gram of the blend, respectively. An examination of the curves shows that the soft segment T_g is decreased with increase in salt concentration. This is in contrast to our earlier observation [20] of the pure TPU system where T_g of the soft segment was increased with increase in salt concentration. In our present study, PVME in the doped blends was found to have higher T_g than the original one. This may be due to the coordination of Li$^+$ ions to the ether oxygens of PVME. The decrease and increase of T_g of the soft and the hard segments, respectively, may be due to the higher degree of phase separation in the presence of PVME and LiClO$_4$. However, the reason behind this is not very much clear. As PVME has a better solvating power for the Li$^+$ ions (as is evident from the dissolution of higher amount of LiClO$_4$ in the blends compared to the TPU alone), Li$^+$ ions
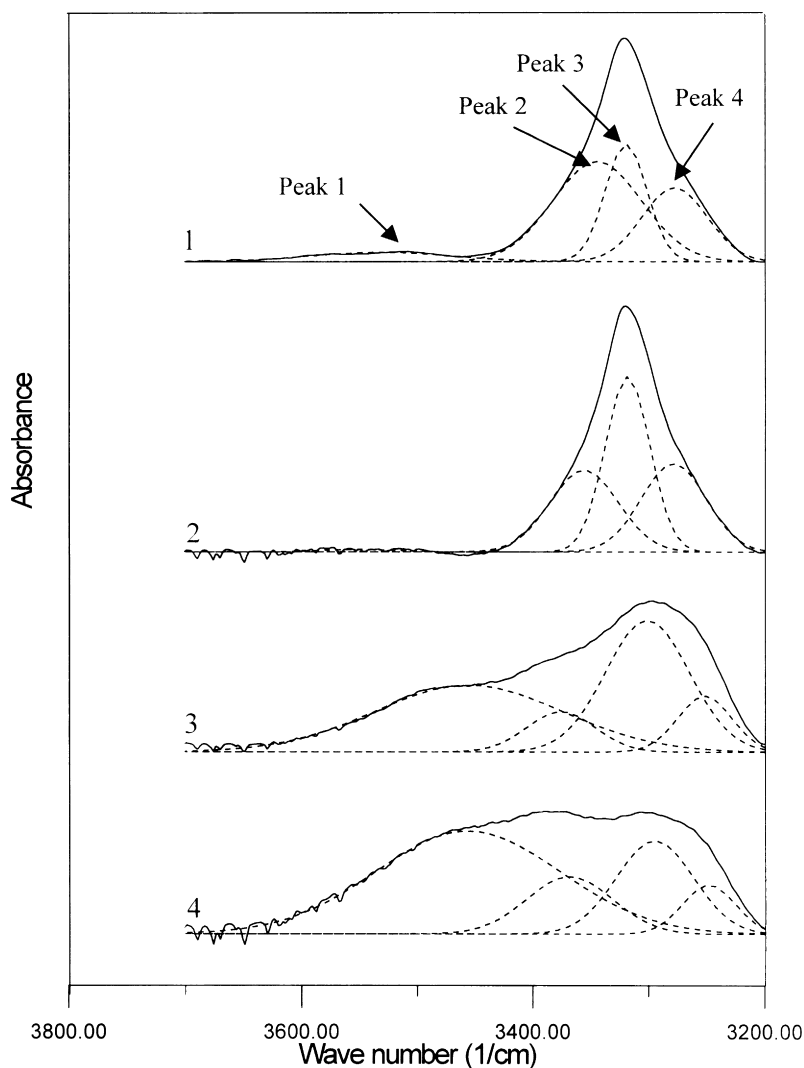
Fig. 3. Deconvolution on the FTIR spectra in the −NH stretching region: (1) pure TPU; (2) sample B1; (3) sample B2; and (4) sample B4.

may get coordinated preferentially with the PVME ether groups. This may lead to an increase in Tg of PVME.

3.3. FTIR study

FTIR was employed to investigate the effect of PVME on the phase behavior of TPU in presence of LiClO$_4$. The −NH stretching region (3700–3200 cm^{-1}) of the spectrum has been deconvoluted to respective peaks for this purpose. The deconvoluted spectra of the −NH stretching region for the samples TPU, B1, B2 and B4 are shown in Fig. 3 and the corresponding peak positions and percent areas are given in Table 3. As is evident from Fig. 3 and Table 3, all the four samples show four characteristics peaks after deconvolution. As reported by others [25–29], peak 1 can be assigned to the free −NH stretching vibration. Peak 3 is

Table 3
Deconvolution results of the FTIR spectra in the −NH stretching region

Sample	Salt concentration (mmol/g)	Peak positions (cm^{-1})				Percent area			
		Peak 1	Peak 2	Peak 3	Peak 4	Peak 1	Peak 2	Peak 3	Peak 4
TPU	0.00	3530.0	3343.4	3318.8	3277.2	6.67	45.12	24.04	24.17
B1	0.00	3546.8	3357.6	3317.7	3276.6	0.97	26.90	44.10	28.03
B2	0.50	3454.8	3375.4	3300.3	3251.2	42.84	9.24	38.12	9.81
B4	1.50	3452.4	3372.5	3294.4	3248.8	56.38	14.61	21.33	7.68
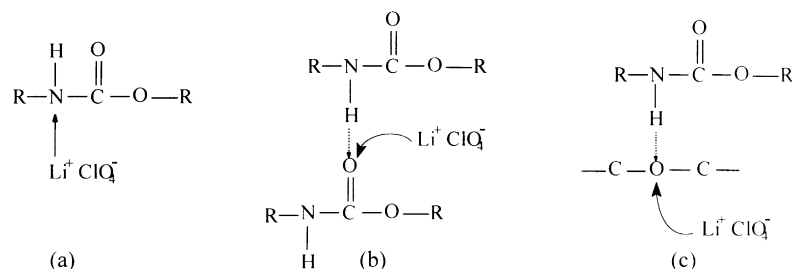
Scheme 2.

assigned to the –NH stretching vibration where the –NH groups are H-bonded to the carbonyl oxygens of the hard segment. Peak 4 is also assigned to the –NH stretching vibration but this time the –NH groups are H-bonded to the ether oxygens of the soft segment. The other peak (peak 2) can be assigned as the overtone to the fundamental in carbonyl region [25]. For polyether urethanes the fraction of H-bonded carbonyl oxygens (peak 3) is usually employed to evaluate the extent of phase separation between the hard and soft segments. On the other hand, the fraction of the H-bonded ether oxygens (peak 4) represents the extent of phase mixing.

An examination of the band position of peak 1 for pure TPU and the blends show that there is little shift in the band position when TPU is blended with PVME, but there is considerable ($\sim$80 cm^{-1}) shifting of the band position when the blends were doped with LiClO$_4$. This shifting of the free –NH band position to lower frequency in the presence of LiClO$_4$ may be attributed to the coordination of Li$^+$ ions to the nitrogen atoms of the free –NH groups (Scheme 2a). Owing to this ionic coordination of Li$^+$ ions to the nitrogen atoms of free –NH groups, the N–H bond becomes weaker and hence the band position is shifted to lower frequency. The two H-bonded peaks of TPU (peaks 3 and 4) show no change in band position when blended with PVME. With addition of salt, both the band positions were shifted to lower frequency. Shifting of the H-bonded –NH band positions to lower frequency can be explained with the help of Scheme 2b and c. As peaks 3 and 4 correspond to the –NH stretching vibrations shown in Scheme 2b and c,
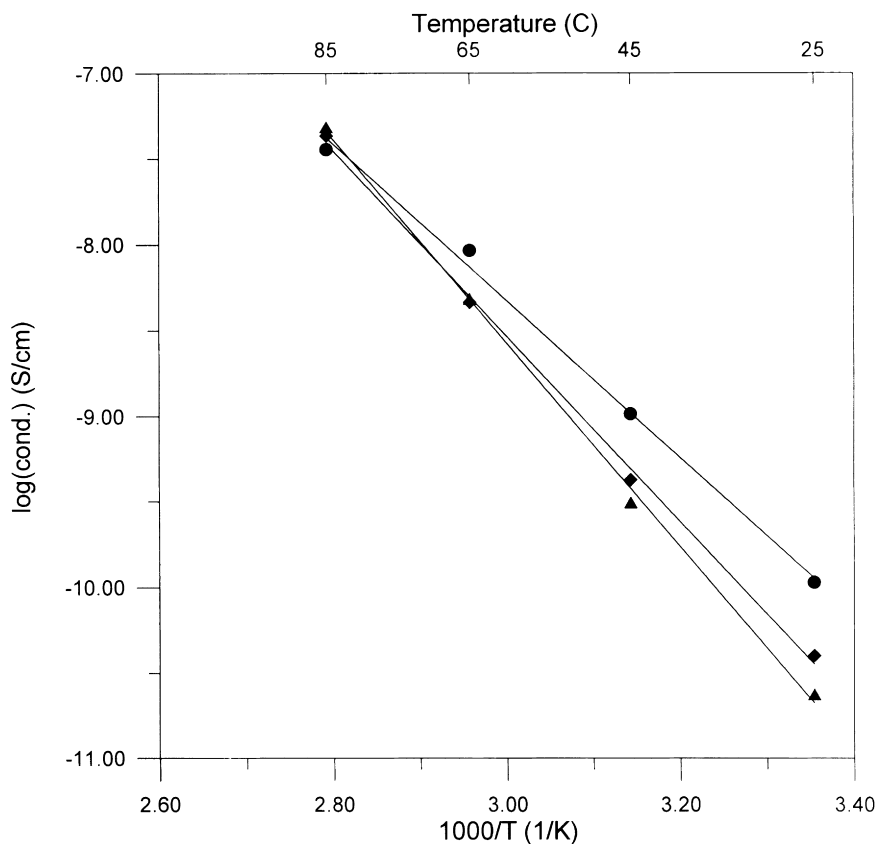

Fig. 4. Temperature dependence of ionic conductivity of the 4:1 blend of TPU and PVME having different concentration of LiClO$_4$, x = 0.5 mmol/g; ∇ = 1.0 mmol/g; ○ = 1.5 mmol/g.
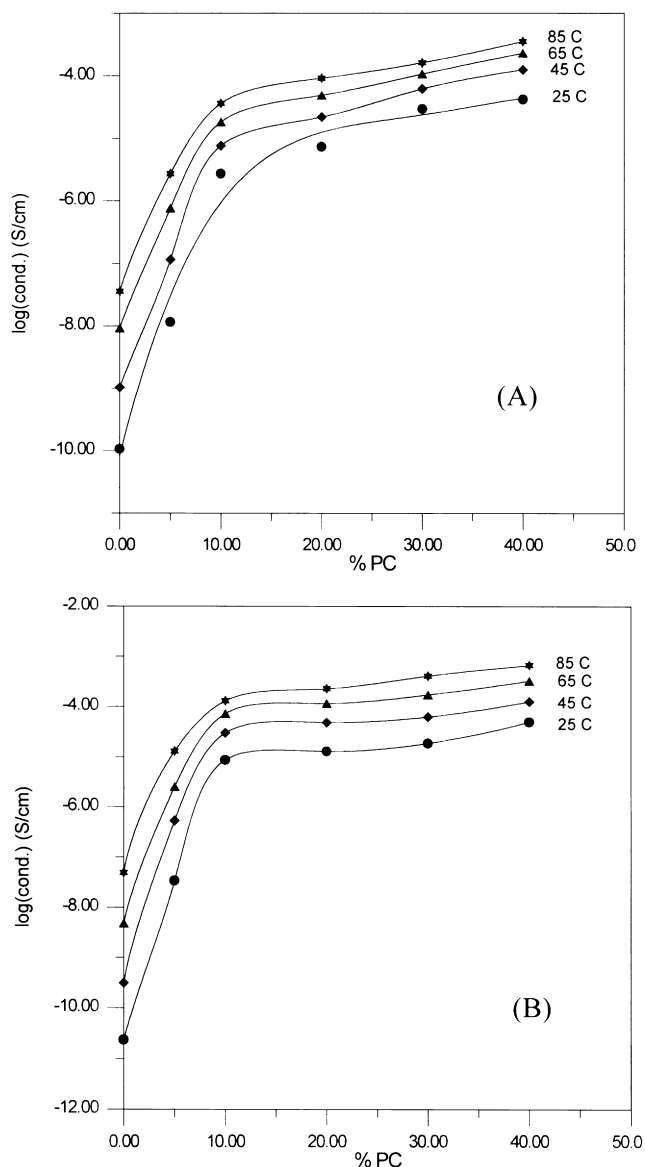
Fig. 5. Effect of PC on the ionic conductivity of the blends: (A) sample B2; and (B) sample B4.

respectively, any interaction of the carbonyl or ether oxygens (with which –NH groups are H-bonded) with Li^+ ions will weaken the N–H bond due to the inductive effect of coordination of Li^+ ions with the electron rich oxygen atoms (the schematic representation of coordination of Li^+ ions to different positions: (a) to the nitrogen atoms of free –NH groups; (b) to the hydrogen bonded ether oxygens; and (c) to the hydrogen bonded carbonyl oxygens is shown in Scheme 2).

Table 3 also shows the respective peak areas for all the –NH bands. All the peak areas were normalized on the basis of total –NH stretching band area. It is evident from the data of pure TPU and the undoped blend (sample B1) that the percent area for peak 1 was decreased when the TPU was blended with PVME with a simultaneous increase in percent area for both peak 3 and peak 4. This may be attributed to

the fact that PVME offers more favorable environment for interaction of the soft and hard segments of TPU. Hence more of the free –NH groups of TPU will be H-bonded to either carbonyl or ether oxygens leading to a consequent increase in the area of peaks 3 and 4, respectively. Such an enhanced interaction of soft and hard segments in the presence of PVME is also evident from our DSC results. Sample B1 was found to show a bit higher phase mixing compared to pure TPU, which is evident from the smaller T_g difference of hard and soft segments in sample B1.

It is also evident from Table 3 that with the addition of salt, the peak area for free –NH band (peak 1) was increased with a simultaneous decrease in the area of H-bonded peaks (peaks 3 and 4). The data reveal that some of the –NH groups which were H-bonded to either carbonyl or ether oxygens, become free when Li salt was added. This may be due to interaction of Li^+ ions with the lone pair of electrons of N atoms leading to decrease in the electron density on N atoms. This in turn may decrease the ability of the –NH groups to form a H-bond with either the carbonyl or the ether groups. In our DSC experiment also it has been noticed that the interaction of hard and soft segments was decreased with salt concentration. This is evident from the increase in T_g difference of hard and soft segments of doped blends with increase in salt concentration.

3.4. AC conductivity

Fig. 4 shows the temperature dependence of ionic conductivity of the blend doped with different concentrations of $LiClO_4$. All the three samples show the Arrhenius type temperature dependence of ionic conductivity in the studied temperature range of 25–85°C. In the lower temperature region, ionic conductivity of the three samples increases with decrease in salt concentration, whereas at higher temperatures the reverse phenomenon was observed. Conductivity of the samples was increased with increase in salt concentration. These results may be explained by considering two factors. Firstly, ion pair or aggregate formation increases with alkali-metal salt concentration [30]. Samples containing higher concentration of salt might have more aggregates (free ion concentration is low) at lower temperature and hence conductivity of higher salt containing samples may be lower than those containing lower amount of salt. At higher temperatures, some of the aggregates may dissociate leading to increased number of free ions, and hence conductivity becomes higher than samples containing lower amount of salt. Secondly, a considerable amount of salt is interacting or coordinating with the hard domain as has been observed by FTIR (Scheme 2a and b) and DSC experiments. The salt coordinated to the hard segment is unable to participate in the conductive process until the temperature region of the hard segment T_g (~100°C) is reached [17]. It is evident from Fig. 4 that the conductivity of these dry samples is very low ($<10^{-7}$ S/cm) even at 85°C. We, therefore,
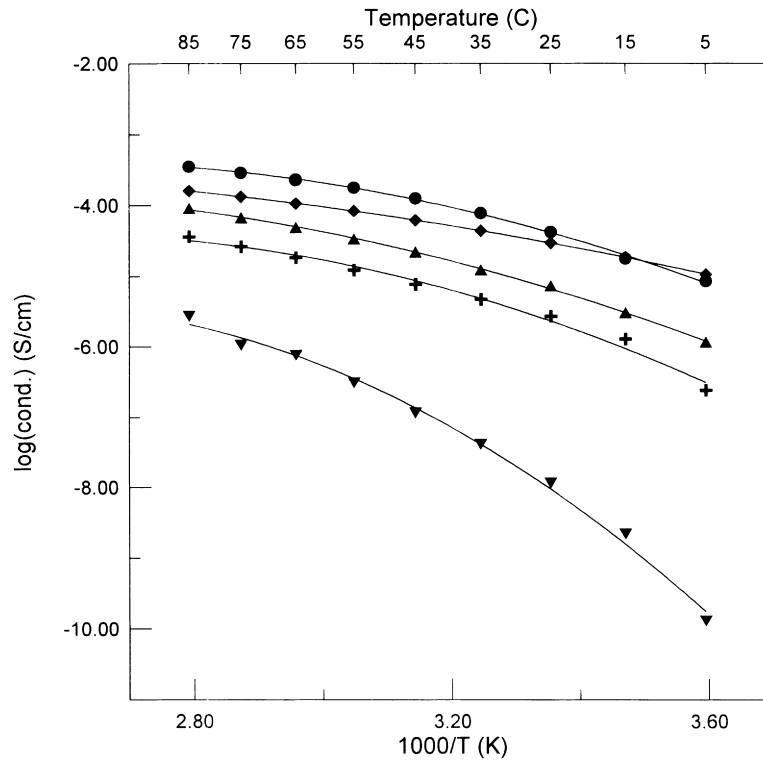
Fig. 6. Temperature dependence of ionic conductivity of sample B2 with different concentration of PC, P = 5.23%; + = 10.68% PC; O = 20.00% PC; V = 33.63% PC; X = 40.30% PC.
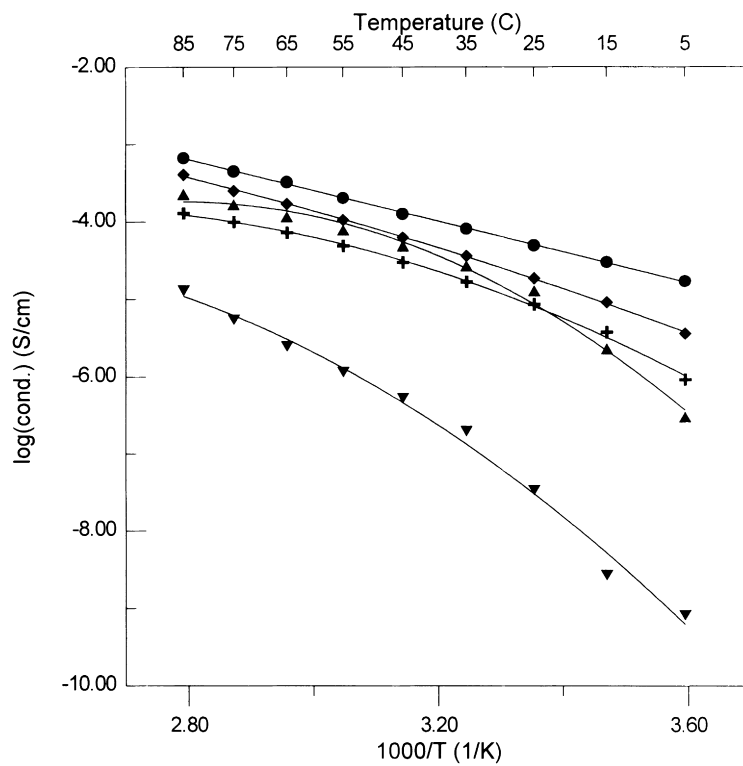

Fig. 7. Temperature dependence of ionic conductivity of sample B4 with different concentration of PC, P = 5.38%; + = 10.78% PC; O 19.84% PC; V = 31.11% PC; X = 40.77% PC.
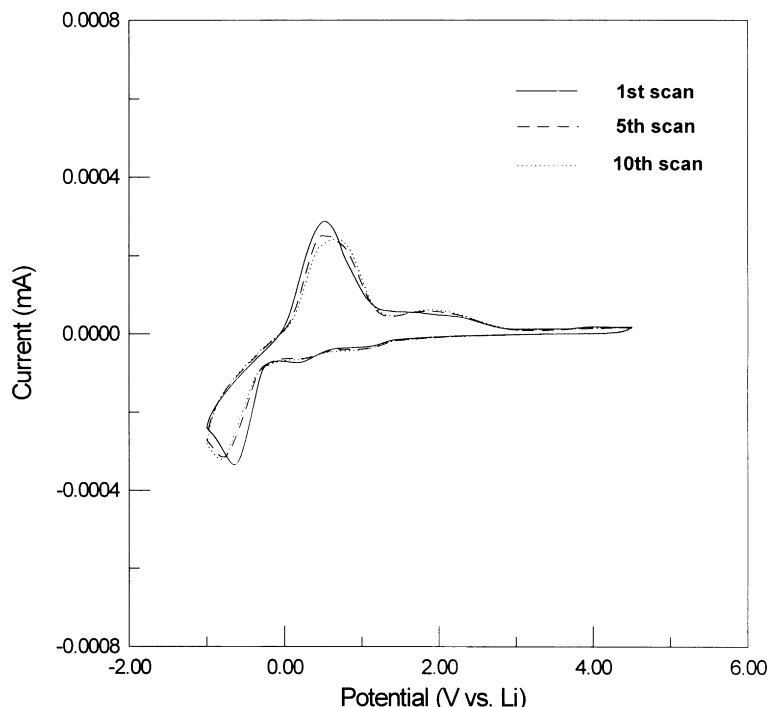
Fig. 8. Cyclic voltammogram for the laminated Li/GPE/SS cell.

attempted to see the efficacy of these samples as GPEs by adding PC to the doped samples. Ionic conductivity of the GPEs containing 0.5 and 1.5 mmol of $LiClO_4$ per gram of the blend has been studied in the temperature range of 5–85°C.

The data on the effect of PC on the ionic conductivity of both the aforementioned samples has been presented in Fig. 5 for four different temperatures. An examination of Fig. 5 shows that the conductivity of the gelled electrolytes increases with increase in the amount of PC in the temperature range of 25–85°C. The role of PC is to act as a plasticizer to the polymer electrolyte which incorporates structural features to the electrolyte that increase the mobility and the concentration of the ionic charge carriers. PC has a high dielectric constant (64.4), which leads to a significant gain in the ionic charge carriers along with an increase in ionic mobility. Many researchers [31,32] have reported such an increase in conductivity by the addition of plasticizer where the polymers are insoluble in the plasticizing solvents. From our study it is to be noted that for all four temperatures, conductivity is increased rapidly up to the addition of 10% PC. With PC beyond 10%, the rate of increase in conductivity is very slow. The nonlinear dependence of conductivity with amount of PC does not appear to be unreasonable because with higher amount of PC, the system may not have sufficient aggregates or contact ion pairs to be dissociated to free ions due to the presence of more amount of PC. Almost all the ion pairs might have been dissociated to free ions with 10% PC. The slight increase in conductivity beyond 10% addition of PC may be due to the increased mobility of the free ions in a more

favorable environment. As a result of the addition of PC, room temperature conductivity of our blend system containing 1.5 mmol of $LiClO_4$ per gram of the blend and 40% PC approaches to $\sim 10^{-4}$ S/cm. One more order increase in conductivity was observed at 85°C. As far as the dimensional stability of the GPE film is concerned, it has very good mechanical properties. In our swelling study (Fig. 1), dipping the films even up to 72 h does not lead to any deterioration of the mechanical properties of the films.

The temperature dependence of ionic conductivity of our blend polymer electrolytes has been presented in Figs. 6 and 7. The ionic conductivity data of these samples were analyzed using the Arrhenius relationship and the Vogel–Tamman–Fulcher (VTF) relationship

$$\sigma(T) = A \exp[-E/k_B T] \tag{1}$$

$$\sigma(T) = AT^{-1/2} \exp[-B/k_B(T - T_0)] \tag{2}$$

where $\sigma(T)$ is the conductivity at temperature T, A a constant proportional to the number of charge carriers, E the activation energy, k_B the Boltzmann constant, B the pseudo activation energy related to polymer segmental motion and T_0 the temperature at which the configurational entropy of the polymer becomes zero and is close to the glass transition temperature.

The VTF relationship is applicable for the transport of ionic species in polymer electrolytes when the transport of the charge carriers is coupled with the segmental motion of the polymer matrix. On the other hand, the Arrhenius relationship is applicable when the motion of the charged species is decoupled from the segmental motion of the polymer

matrix. The results presented in Figs. 6 and 7 show that the temperature dependence of conductivity is best described by the VTF equation when the amount of added PC is low. When the plasticizer concentration is low, the ions are residing in a polymer rich phase where the movement of the ions is associated with the segmental motion of the polymer chains. With a higher amount of PC, the curves become linear or close to linearity, which is best described by the Arrhenius equation. With the increase in PC, the mobility of the charge carriers is increased as they are in the plasticizer rich phase and the system becomes more liquid-like. With a higher concentration of PC, the mobility/transport of the charge carriers become less coupled with the segmental motion of the polymer matrix and hence the temperature dependence of ionic conductivity follows the Arrhenius equation.

3.5. Cyclic voltammetry study

In order to ascertain the electrochemical stability of the hybrid polymer electrolyte, CV of the laminated three electrode cells were performed at ambient temperature. Three representative cyclic voltammograms of sample B4 were presented in Fig. 8. The cells were cycled from -1.0 to $+4.5$ V (vs. Li) at a sweep rate of 5 mV/s. The cyclic voltammograms are typical of a liquid or gel polymer electrolyte. It is evident from Fig. 8 that there is no electrochemical reaction in the potential range 1.0–4.5 V. The onset of deposition of Li was found at ~ 0.3 V and stripping of lithium occurred at ~ 0.5 V. The Li plating–stripping process is reversible and there are no other oxidation peaks up to 4.5 V. This indicates that the blend (TPU/PVME) does not have any effect on the electrochemical stability of the electrolyte. This can be safely used as a hybrid polymer electrolyte in rechargeable lithium batteries.

4. Conclusion

A new two-component hybrid polymer electrolyte has been prepared by blending a polyether urethane with PVME. The blend system containing 20-wt% PVME shows ionic conductivity of the order of 10^{-4} S/cm at ambient temperature when doped with 1.5 mmol of $LiClO_4$ per gram of the blend and plasticized with 40% PC. Blending with PVME leads to a higher degree of solvation of $LiClO_4$ (~ 2.0 mmol/g) compared to only 0.4 mmol/g in the case of pure TPU. The blend polymer can absorb $\sim 100\%$ more PC compared to the pure TPU. It shows no deterioration with respect to the mechanical properties even after 72 h immersion in PC. The CV study of the laminated cell using this hybrid system as the GPE shows no electrochemical reaction in the potential range 1.0–4.5 V vs. lithium. Hence it

can be concluded that this new hybrid polymer system is suitable for use as a GPE in rechargeable lithium batteries.

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