

Morphology and Ionic Conductivity of Thermoplastic Polyurethane Electrolytes

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ABSTRACT: Thermoplastic polyurethane (TPU) with a mixture of soft segments [poly(ethylene glycol) (PEG) and poly(tetramethylene glycol) (PTMG)], denoted TPU-M, was prepared as an ion-conducting polymer electrolyte. TPUs with PEG and PTMG as soft segments were also synthesized individually as polymer electrolytes. The changes in the morphology and ion conductivity of the phase-segregated TPU-based polymer electrolytes as a function of the lithium perchlorate concentration were determined with differential scanning calorimetry, Fourier transform infrared spectroscopy, alternating-current impedance, and linear sweep voltammetry measurements. Both solid and gelatinous polymer electrolytes were characterized in this study. The effect of temperature on conductivity was studied. The conductivity

changes revealed the combined influence of PTMG and PEG units in TPU-M. The swelling characteristics in a liquid electrolyte and the dimensional stability were evaluated for the three TPUs. Because of its dimensional stability and ionic conductivity, the TPU system containing both PEG and PTMG as soft segments was found to be more suitable for electrolyte applications. A room-temperature conductivity of approximately 1×10^{-4} was found for TPU-M containing 50 wt % liquid electrolyte. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1154–1167, 2004

Key words: polyurethanes; polymer electrolyte; ionic conductivity

INTRODUCTION

Because of the increased usage of portable electronics, the need for secondary batteries has increased in definite proportions. Accordingly, the market for secondary lithium batteries has been steadily growing at a higher rate since the emergence of commercial lithium-ion batteries around 1992. These batteries are expected to occupy a dominant position with respect to alkaline batteries, NiCd, and NiMH batteries by the end of this century.

Most of the current research is related to lithium-ion batteries and has been very much focused on the use of polymer electrolytes.^{1–10} A distinguishing feature of polymer electrolytes is that the ion motion takes place without long-range displacement of the solvent. Ion transport in polymer electrolytes is a complex process involving ion motion, the local motion of polymer segments, and interpolymer and intrapolymer transitions between ion-coordinating sites.¹¹

Polymer electrolytes can be classified into two types: solid polymer electrolytes (SPEs) and gelati-

nous polymer electrolytes (GPEs). Since the discovery of ionic conductivity in a poly(ethylene oxide)/alkali-metal-ion complex in 1975,¹² the research and development of SPEs has been quite active and focused particularly toward the improvement of the ionic conductivity. Ever since Armand et al.¹³ proposed the application of SPEs to lithium batteries, this area has been studied. SPEs have been developed for a variety of uses, and much work has been done to understand the movement of ions through the polymer host.^{14,15}

GPEs are polymers swollen by salt solutions. They can also be considered liquid electrolytes entrapped in a polymer matrix. Some gel electrolytes containing lithium salt have been found to possess ionic conductivity, electrochemical stability, and mechanical properties suitable for battery electrolytes.^{16,17} Optimized gel electrolytes are expected to have transport properties comparable to those of their liquid counterparts, but they can also be processed into films. Although gel electrolytes are somewhat less convenient than SPEs in film preparation, their conductivity outperforms the solid type by several orders of magnitude at ambient temperature. Therefore, gel electrolytes provide an attractive alternative for new generations of batteries. In both SPEs and GPEs, the conductivity, strength, and stability are the most important factors for use in lithium batteries.

Earlier investigations into the structural properties and conduction behavior of these electrolyte systems

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have indicated that ionic conduction occurs in the amorphous phase of the materials. Therefore, it depends on the macromolecular chain dynamics (increasing flexibility and free-volume density imply increasing conductivity) and the degree of ionic aggregation. Fast ionic transport in polyether-based electrolytes is associated with the presence of a flexible, amorphous phase characterized by a low glass-transition temperature (T_g).¹⁴ Unfortunately, the mechanical strength and stability of amorphous polyether matrices are known to be poor, and polymer electrolytes often creep under the pressures applied in electrochemical devices. Therefore, several studies have been made on obtaining amorphous and mechanically stable polyether hosts as matrices for polymeric electrolytes.¹⁸ This has led to the use of polymer blends or composites as polymer electrolytes containing more than one polymer or a mixture of one polymer and some finely dispersed inorganic or organic fillers¹⁹ and polymer networks prepared by either chemical or physical crosslinking processes. Recently, thermoplastic polyurethanes (TPUs) doped with various alkali metal salts have also been studied as matrices for polymer electrolytes.^{20–23}

In our previous study,²⁴ TPUs doped with lithium perchlorate (LiClO_4) were used as electrolytes in which poly(ethylene glycol) (PEG) and poly(tetramethylene glycol) (PTMG) were used as soft segments with methylene bis(*p*-cyclohexyl isocyanate) (H_{12}MDI) as the hard segment. The synthesized PEG-based GPE showed high conductivity but poor mechanical properties. It may be possible to increase the mechanical strength through the simultaneous introduction of PTMG and PEG units so that the electrolyte can have sufficiently high conductivity and better mechanical strength for practical use.

Results from our earlier study²⁴ using the H_{12}MDI /PEG/PTMG system revealed that the electrolyte was good enough to be used as an SPE. However, the mechanical strength was not sufficient enough for it to be used as a GPE. In this study, we wanted to enhance the mechanical properties of the TPU system by replacing H_{12}MDI with methylene bis(*p*-phenyl isocyanate) (MDI). The presence of more rigid aromatic rings (MDI) was expected to provide better mechanical strength to the TPU system than the less rigid alicyclic rings in H_{12}MDI .

Also, we anticipated structural influences of the TPU prepared with a mixture of PTMG and PEG as soft segments on the morphology and ionic conductivity. To this end, we synthesized TPU-M with MDI as a hard segment and with a mixture of PEG and PTMG as soft segments. To elucidate the relationships between the structures and properties of the TPU, we performed studies with added LiClO_4 and also in the presence of a plasticizer (LP-30) consisting of 1M LiPF_6 in a 1:1 (w/w) mixture of ethylene carbonate (EC) and

propylene carbonate. To bring out the individual influences of the PEG and PTMG soft segments on the thermal properties and conductivity of TPU-M, we independently synthesized TPUs with PEG and PTMG as soft segments and studied them under conditions similar to those of TPU-M. The interaction between the Li^+ ions and groups (hard and soft) of these TPUs were investigated with differential scanning calorimetry (DSC) and Fourier transform infrared (FTIR) measurements. The differences in the interactions between the soft and hard segments of these TPUs with Li^+ ions in SPEs and GPEs are expected to influence the ionic conductivity.

The ionic conductivity of these three TPUs was determined by alternating-current (AC) impedance measurements and was correlated with FTIR and DSC results. The electrochemical stability of a suitable electrolyte system (TPU-M) was tested by linear sweep voltammetry to explore the possibility of using the electrolyte in lithium batteries.

EXPERIMENTAL

Synthesis of the TPUs

The TPUs were synthesized in a batch reactor consisting of a 2000-mL, four-necked, round-bottom flask with an anchor stirrer, a nitrogen inlet and outlet, and a thermocouple connected to the temperature controller. The polyols, PEG-2000 [weight-average molecular weight (M_w) = 2000 g mol^{-1}] and PTMG-2000 (M_w = 2000 g mol^{-1}), and the chain extender, 1,4-BD (M_w = 90 g mol^{-1}), were kept in a vacuum oven at 80°C for 1 day to remove moisture from the chemicals. The polyols (0.05 mol) and 0.20 mol of the chain extender were put in the reactor first and mixed well at 50°C . After 30 min, the temperature was increased to 85°C , and two drops of the catalyst, dibutyltin dilaurate, were added to the reactor. Then, 0.25 mol (5:1 NCO/OH) of the hard segment, MDI, was added stepwise to the reaction mixture. Dimethylformamide (DMF) was used to control the viscosity of the TPUs during the polymerization. To monitor the molecular weights of the TPUs, during the synthesis, small amounts of the TPUs were taken out intermittently for gel permeation chromatography (GPC) analysis. In this way, all of the TPUs were controlled to an M_w value of approximately 200,000 and a polydispersity index [PDI; weight-average molecular weight/number-average molecular weight (M_w/M_n)] of 1.5–2.0 through the addition of MDI. At the end, a few drops of methyl alcohol were added to terminate the reaction.

In this study, three different TPUs were prepared with PEG, PEG and PTMG, or PTMG as soft segments. These TPUs are designated TPU-A, TPU-M, and TPU-B, respectively.

TABLE I
Compositions and GPC Results of the TPUs

Code	Composition	Molar ratio	M_w (g/mol)	M_n (g/mol)	M_w/M_n (PDI)
A	PEG + 1,4-BD + MDI	1:4:5	1.95×10^5	1.26×10^5	1.55
M	PEG/PTMG + 1,4-BD + MDI	1:1:8:10	1.90×10^5	1.11×10^5	1.71
B	PTMG + 1,4-BD + MDI	1:4:5	1.93×10^5	1.17×10^5	1.65

Molecular weight distribution

The M_w and M_n values of the synthesized polymers were measured with a Shimadzu GPC instrument fitted with a Shimadzu HPLC pump and a differential refractometer. The polymers, taken out from the reactor, were diluted with DMF and then injected into the GPC column (Jordi DVB gel mixed-bed column 10 mm in the inside diameter and 250 mm long) at a flow rate of 2.0 mL/min. The compositions and GPC results of the TPUs are shown in Table I.

Preparation of the electrolytes

The prepared TPUs (TPU-A, TPU-M, and TPU-B) were diluted with DMF to obtain 10 wt % solutions and were mixed with 10 wt % solutions of $\text{LiClO}_4/\text{DMF}$ in different proportions to contain 0.5, 1.0, or 1.5 mmol of LiClO_4/g TPU. Films were cast onto glass petri dishes, DMF was evaporated slowly *in vacuo*, and the films were dried at approximately 50°C *in vacuo* for 72 h. The SPEs prepared from TPU-A were denoted A1, A2 and A3; these contained 0.5, 1.0, and 1.5 mmol of LiClO_4/g TPU, respectively. Similarly, M1–M3 and B1–B3 were derived from TPU-M and TPU-B, respectively.

However, the GPEs were prepared via the dipping of dry polymer films into a commercial liquid electrolyte (LP-30, E. Merck, Germany), which was 1M LiPF_6 in 1:1 (w/w) EC and dimethyl carbonate. Swelling was continued until the swollen percentage reached the required value. The percentage of swelling (S_w) can be expressed as follows:

$$S_w = (w - w_0)/w_0 \times 100 \quad (1)$$

where w is the weight of the swollen film and w_0 is the original weight of the dry film.

GPEs were named by the addition of the number equivalent to S_w beside the corresponding TPUs.

Thermal analysis

The thermal analysis of the TPUs and SPEs was performed with a DuPont TA DSC 2010 differential scanning calorimeter at a heating rate of 10°C/min from –100 to 100°C. Before the DSC analysis, the samples were dried *in vacuo* for several days. About 3 mg of

each sample was placed in an aluminum capsule for DSC analysis. T_g 's were reported as the midpoint of the thermal transition. All thermograms were baseline-corrected and calibrated against indium metal.

Infrared analysis

FTIR was used to investigate the functional groups present in TPUs. The FTIR samples were prepared by the dripping of a dilute polymer solution in DMF onto KBr pellets. The samples were placed in a vacuum oven at 120°C for at least 72 h for the removal of the residual solvent and moisture. The infrared spectra were recorded with an average of 64 scans at a wavenumber resolution of 2 cm^{-1} with a Nicolet 550.

Conductivity measurements

The conductivity of the SPEs and GPEs was measured by AC impedance analysis with electrochemical cells consisting of electrolyte films sandwiched between two blocks of stainless steel sealed with an o-ring in a jacketed glass tube within which heating/cooling water was circulated through the outer jacket. The temperature of the cell was controlled with a water thermostat (D8&G, Haake) and calibrated with a Pt resistance thermometer. All the processes of cell assembly were performed inside a glove box filled with pure argon. The impedance analysis was performed with an Autolab PGSTAT 30 (Eco Chemie B.V., The Netherlands) with the help of frequency response analysis software in the frequency range of 1 kHz to 1 Hz under an oscillation potential of 200 mV for the SPEs. For the GPEs, the experiments were performed at an oscillation potential of 10 mV from 100 kHz to 1 kHz.

Linear sweep voltammetry

Linear sweep voltammetry of the three electrode laminated cells was performed with Autolab PGSTAT 30 equipment (Eco Chemie B.V.) with the help of general-purpose electrochemical system software with a sweep rate of 1 mV/s in the potential range of 2–8 V after equilibration at 2 V for 10 min. The laminated cells were assembled inside the glove box, in which stainless steel was used as a working electrode and

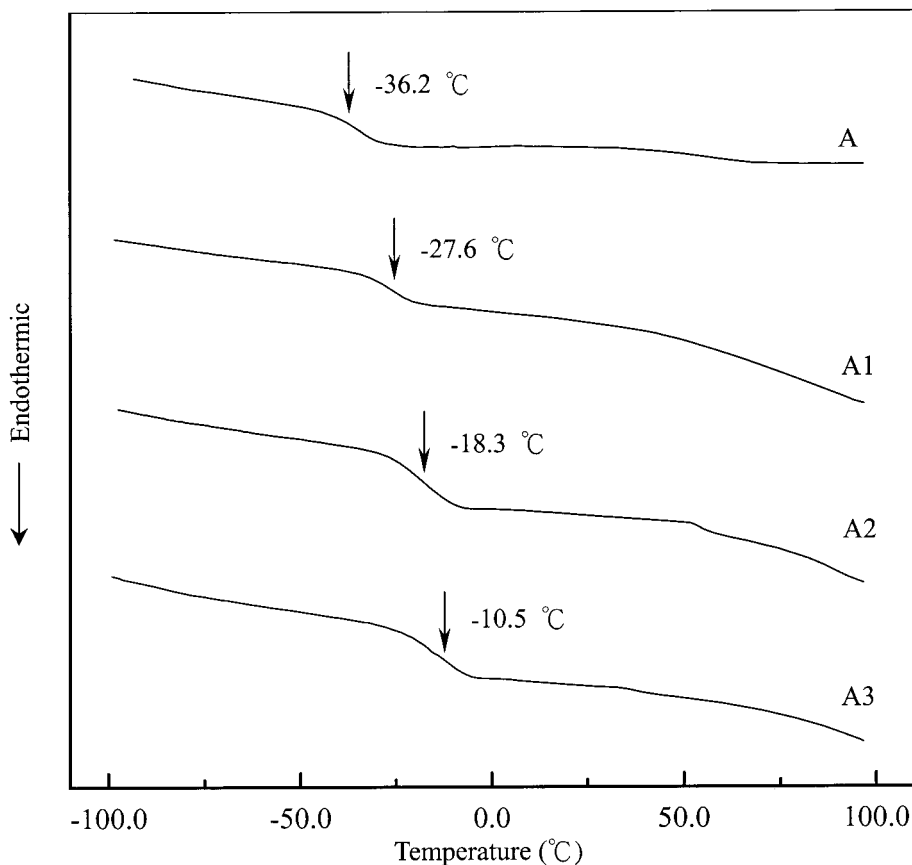


Figure 1 DSC thermograms of TPU-A with different concentrations of LiClO_4 .

lithium metal was used as counter and reference electrodes.

RESULTS AND DISCUSSION

Thermal analysis

Because of the presence of a two-phase microstructure, the thermal behavior of TPUs is very complex. Apart from T_g of the soft segment, the hard segment shows three different endothermic transitions at 70–100, 120–170, and above 200°C.²⁶ These three transitions are associated with short-range ordering of the hard-segment domains, long-range ordering, and microcrystallinity in the hard domain, respectively. In this article, we report the effects of added LiClO_4 on the thermal behavior of the soft segment of a TPU system (TPU-M) consisting of a mixture of PTMG and PEG as soft segments. The thermal transitions of the parent TPUs (TPU-A and TPU-B), arising from the interactions of Li^+ ions with groups in the TPUs, have also been followed to identify the influence of the presence of the mixture of soft segments in TPU-M on T_g . The presence of a mixture of PTMG and PEG in TPU-M showed significant effects on the thermal transitions, ionic conductivity, and swelling characteristics

in the presence of a plasticizer, LP-30. These effects are elaborated in the forthcoming discussion.

Figures 1–3 show DSC thermograms of the three TPUs containing various concentrations of LiClO_4 . The soft-segment T_g of TPU-M was found to be between those of TPU-A and TPU-B. T_g of the TPU-A soft segment was higher than that of TPU-B. This could be attributed to the structures of these two polyols.

When TPU-M was doped with various concentrations of LiClO_4 , a different trend for the changes of T_g with the lithium salt concentration was observed in comparison with TPU-A and TPU-B. These changes were attributed to the variations in the number of oxygens coordinated to Li^+ ions and the polarity of the soft segments.

When these TPUs were doped with various concentrations of LiClO_4 , the lithium salt complexes showed increases in the soft-segment T_g in all three cases (Table II). Such an increase in the soft-segment T_g has already been reported by many researchers^{20–27} and attributed to the formation of transient crosslinks between the Li^+ ion and the ether oxygen of the soft segments. The interaction of the Li^+ ion restricts the segmental motion of the polymer chains, leading to an

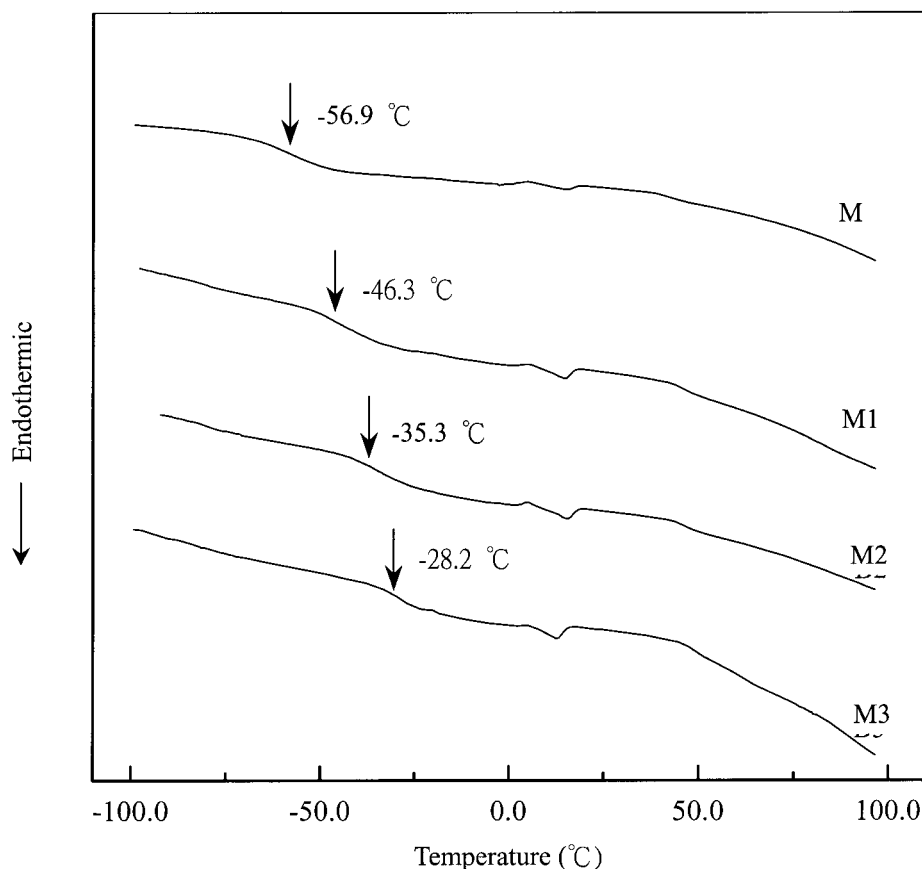


Figure 2 DSC thermograms of TPU-M with different concentrations of LiClO_4 .

increase in T_g . Although T_g increased with the addition of LiClO_4 in all three TPUs, the three TPUs had different increases in T_g (Table II). This became clear after an analysis of the normalized T_g data with respect to the LiClO_4 concentration ($\Delta T_g/\Delta C$; Table II). For the TPU-A system, the increase in T_g of the soft segment was almost linear with the salt concentration. However, for TPU-B, the $\Delta T_g/\Delta C$ values gradually decreased with increasing salt concentration. This indicated that at higher salt concentrations, most of the salt remained as either ion pairs or aggregates and hence did not interact with the ether groups of PTMG. The lower polarity of PTMG, compared with that of PEG, may be the reason for the lower solvating power for LiClO_4 . Additionally, in PTMG, the number of ether oxygens, which can be coordinated by Li^+ ions, was lower (27/mol) than in PEG (45/mol). In fact, a portion of added LiClO_4 was found to salt out (seen as a white powder on the surface) from the TPU-B surface when it was doped with 1.0 or 1.5 mmol of LiClO_4/g of TPU-B (samples B2 and B3).

TPU-M showed an intermediate behavior between TPU-A and TPU-B. The $\Delta T_g/\Delta C$ values indicated an almost linear relationship with the salt concentration up to approximately 1.0 mmol/g, but beyond that, there was a decreasing trend in $\Delta T_g/\Delta C$, which may

have been due to the plasticizing effect of ion pairs and aggregates. Like TPU-B, some of the added LiClO_4 separated out from the surface of the M3 film upon drying. The separation of the salt from the M3 film was found to be much less than that in the B films.

The changes in the T_g 's of the three TPUs were expected from the interactions of Li^+ ions with hard-segment and soft-segment groups ($-\text{C}=\text{O}$, $-\text{NH}$, and $-\text{O}-$) of the TPUs, which disturbed the hydrogen-bonding interactions. Otherwise, the competitive interaction of Li^+ ions against hydrogen bonding could cause morphological changes, and these aspects were analyzed through FTIR spectroscopy.

Infrared spectroscopy

N—H stretching region

Many researchers^{28–36} have reported the presence of strong hydrogen-bonding interactions in poly(ether urethane)s that lead to changes in the two-phase microstructure of TPUs. The presence of such hydrogen-bonding interactions is evident from the shifting of the N—H stretching frequency in the FTIR spectra. It has been reported³⁴ that the frequency shift for the formation of a hydrogen bond with a urethane $\text{C}=\text{O}$ is

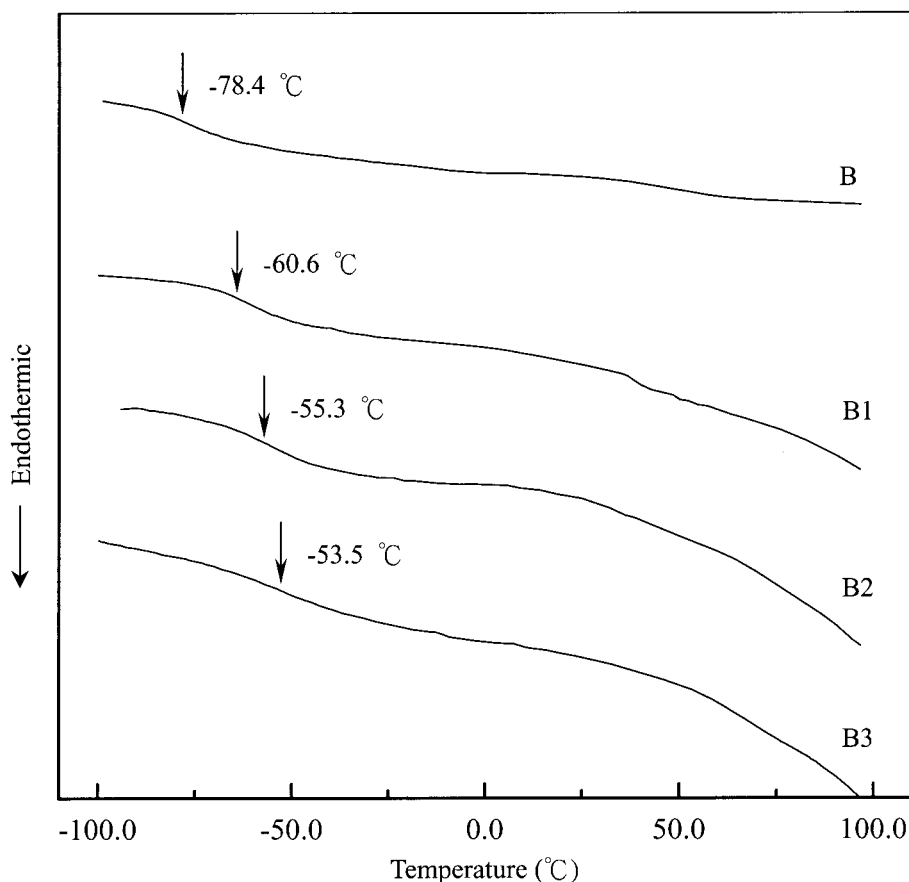


Figure 3 DSC thermograms of TPU-B with different concentrations of LiClO_4 .

$90\text{--}110\text{ cm}^{-1}$, whereas for bonding with the ether oxygen, it is approximately 150 cm^{-1} . The groups responsible for hydrogen bonding depend on the composition of the TPU. At high urethane concentrations, the main group responsible for hydrogen bonding is the urethane $\text{C}=\text{O}$, whereas the ether group becomes the predominant acceptor when the urethane concen-

tration is low. In a system containing appreciable concentrations of hard and soft segments, —NH groups have been found to interact with both $>\text{C}=\text{O}$ and —O— groups.

For the purpose of investigating the effects of LiClO_4 on the phase behavior of TPU, the —NH stretching regions of the spectra ($3250\text{--}3550\text{ cm}^{-1}$) for TPU-A and TPU-M have been deconvoluted by the Gaussian fitting method. TPU-B has not been investigated because it shows the separation of LiClO_4 beyond the concentration of 0.5 mmol/g of TPU-B. As reported by others,²⁷ the deconvolution of the —NH stretching region results in three distinct peaks at $3450\text{--}3550$, $3320\text{--}3450$, and $3260\text{--}3325\text{ cm}^{-1}$. The first peak is assigned to the free —NH stretching vibration. Both the second and third peaks are also assigned to the —NH stretching vibration, in which the —NH groups are hydrogen-bonded to the carbonyl and ether oxygens, respectively. One typical FTIR spectrum of the TPUs is presented in Figure 4 along with the deconvoluted spectra of undoped and doped samples in the inset. The deconvoluted spectra of the other samples are not shown. The deconvolution results of all the samples are presented in Table III. It is evident from Figure 4 and Table III that the extent of free —NH groups is

TABLE II
DSC Data for TPUs with Different Concentrations of LiClO_4

Code	LiClO_4 (mmol/g of TPU)	T_g ($^\circ\text{C}$)	$\Delta T_g / \Delta C$ ($^\circ\text{C}/\text{mmol/g}$ of TPU)
A	0	-36.2	—
A1	0.5	-27.6	17.2
A2	1.0	-18.3	18.5
A3	1.5	-10.5	15.6
M	0	-56.9	—
M1	0.5	-46.3	21.1
M2	1.0	-35.3	22.1
M3	1.5	-28.2	14.1
B	0	-78.4	—
B1	0.5	-60.6	35.5
B2	1.0	-55.3	10.6
B3	1.5	-53.5	3.6

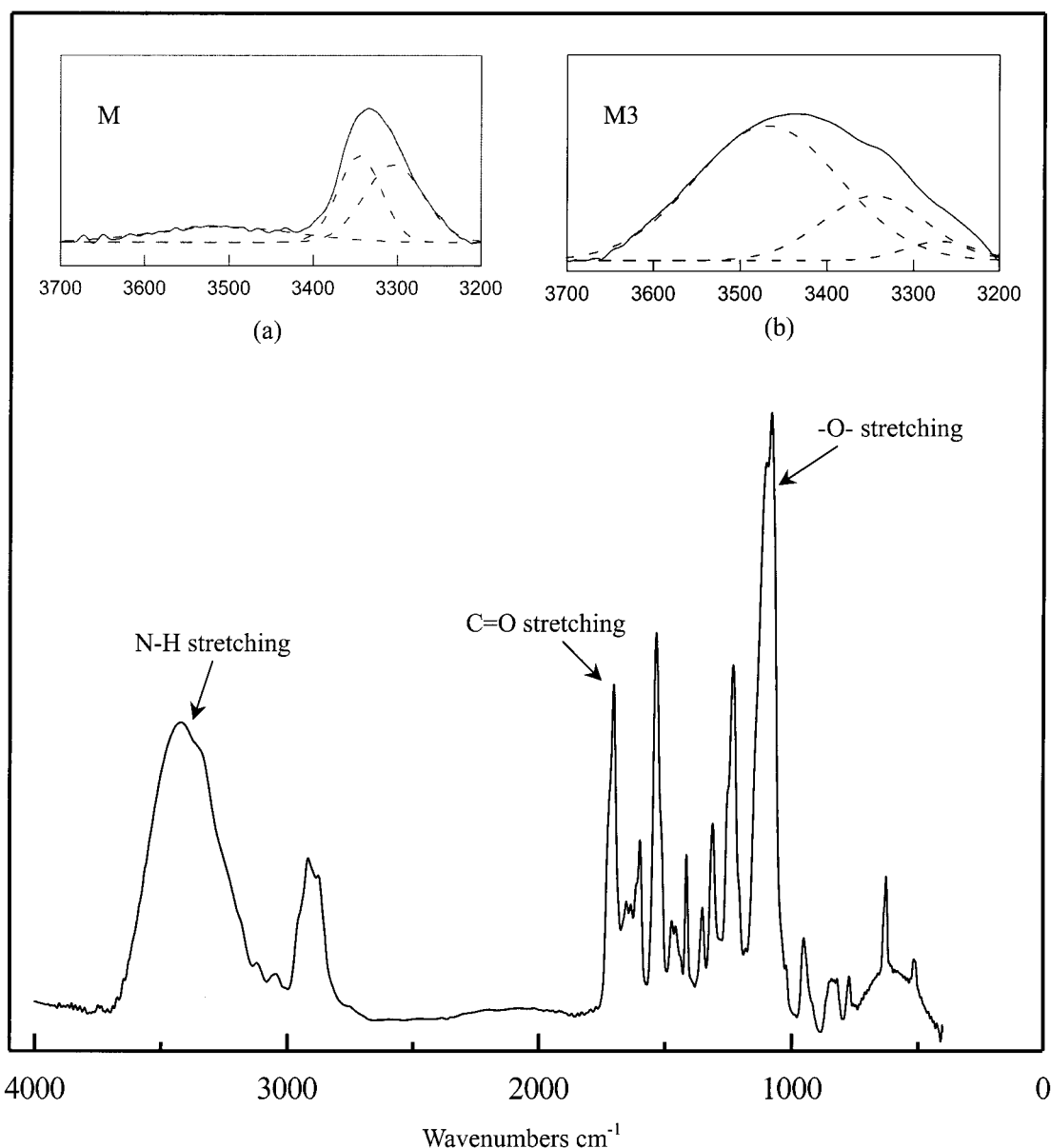
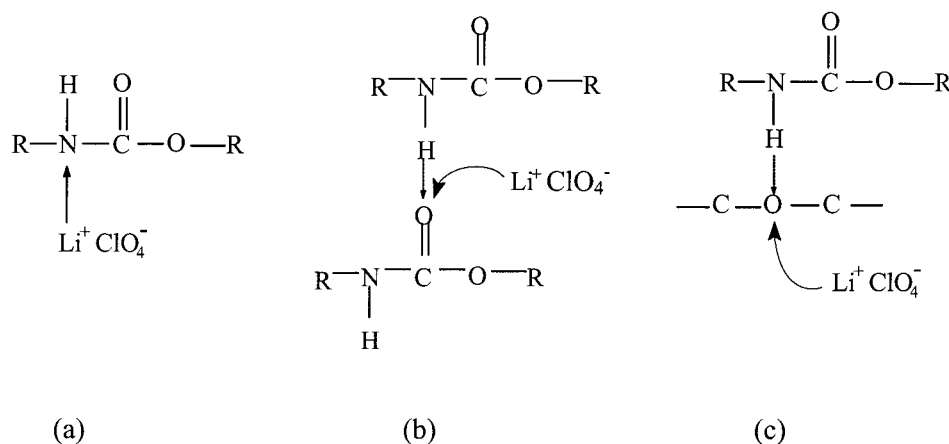


Figure 4 FTIR spectrum of the TPUs. The inset shows the deconvolution of the —NH stretching region for (a) sample M and (b) sample M3.

greater in doped TPUs than in undoped TPUs. In the absence of LiClO_4 , most of the —NH groups remain hydrogen-bonded to either carbonyl or ether oxygen atoms. Hence, the free —NH stretching absorption was observed as a shoulder to the main peak. With the addition of LiClO_4 , the extent of hydrogen-bonded —NH absorption, with respect to free —NH absorption, is reduced. The decrease in hydrogen-bonded —NH absorption, and the increase in free —NH absorption, may be due to the competition of Li^+ -ion coordination with hydrogen bonding. Such a competition of Li^+ -ion coordination with hydrogen bonding was reported earlier by Ferry et al.³⁷ Our results for the area percentage (Table III) indicate the presence of

TABLE III
Deconvolution Results of the FTIR Spectra
in the N—H Stretching Region

Code	Peak position			Area (%)		
	1	2	3	1	2	3
A	3536	3438	3325	47.9	10.2	41.8
A1	3498	3383	3321	50.4	21.8	20.3
A2	3484	3363	3302	62.6	24.4	12.9
A3	3468	3350	3309	69.9	21.1	8.9
M	3505	3330	3297	39.0	26.3	34.6
M1	3485	3328	3274	51.8	16.2	12.5
M2	3473	3322	3261	62.4	14.0	6.9
M3	3464	3327	3255	73.4	14.5	4.7



Scheme 1 Representation of the coordination of Li⁺ ions to different positions: (a) the nitrogen atoms of free N—H groups, (b) the hydrogen-bonded carbonyl oxygens, and (c) the hydrogen-bonded ether oxygens.

such competition, which results in more free —NH groups from the hydrogen-bonded ones with an increase in the salt concentration. However, a quantitative estimation of free and hydrogen-bonded —NH groups from band areas may lead to erroneous results, as the absorptivity coefficient for the hydrogen-bonded —NH bands is a function of the strength of the hydrogen bond and the band frequency.^{38,39}

It is evident from Table III that the band position of —NH groups of TPU-M and TPU-A shifts to a lower frequency with increasing salt concentration. The variation of the N—H bond strength as a result of a change in the extent of hydrogen bonding due to complexation with Li⁺ ions is responsible for such shifting of the peak positions. The coordination of Li⁺ ions to different positions of the TPUs is shown in Scheme 1. Scheme 1(a) indicates the interaction of Li⁺ ions with N atoms of free —NH groups. Because of this ionic coordination to N atoms, the N—H bond becomes weaker, and so the band position is shifted to a lower frequency. The shifting of peaks 2 and 3 can be explained with the help of Scheme 1(b,c), respectively. The shifting of the band position to a lower frequency indicates that the N—H bond of the hydrogen-bonded —NH groups to either carbonyl or ether oxygens is weakened by the inductive effect of the coordination of the Li⁺ ions with the electron-rich oxygen atoms. The change in the band position of peak 3, which is due to the coordination of Li⁺ ions to the ether oxygen of the soft segment, is also evident from the DSC measurements and the increase in T_g of the soft segment with the salt concentration.

C=O stretching region

To investigate further the hydrogen-bonding interaction of —NH groups with the carbonyl oxygens, we deconvoluted the carbonyl stretching region into three

different peaks. The results of the deconvolutions are presented in Table IV. As reported by others,²³ the three peaks are due to free or non-hydrogen-bonded C=O (1727–1730 cm⁻¹), disordered hydrogen-bonded C=O (1718–1721 cm⁻¹), and ordered hydrogen-bonded C=O (1703–1704 cm⁻¹) vibrations, respectively. The disordered hydrogen-bonded C=O corresponds to the hydrogen-bonding interactions with —NH groups in both amorphous and crystalline regions, whereas the ordered hydrogen-bonded C=O occurs within the crystalline hard domain.^{38,39} The positions of all three absorptions remain unaffected by doping (Table IV). However, the area percentage for peaks 1 and 3 shows definite variations with an increase in the salt concentration. This indicates that the C=O region is indeed affected by the introduction of salt, possibly because of the coordination of Li⁺ ions with carbonyl oxygen atoms.

There were striking variations in the effect of temperature on the conductivity between TPU-M and TPU-A. The presence of PTMG units in TPU-M provides different polarities to ionize the Li salt in comparison with TPU-A. We monitored these aspects by

TABLE IV
Deconvolution Results of the FTIR Spectra in the C=O Stretching Region

Code	Peak position			Area (%)		
	1	2	3	1	2	3
A	1726	1718	1704	35.8	10.7	53.4
A1	1727	1719	1703	29.9	9.5	60.4
A2	1728	1721	1703	21.2	17.5	61.2
A3	1727	1718	1703	24.8	6.7	68.4
M	1729	1719	1703	27.9	7.0	65.0
M1	1728	1719	1703	24.8	4.2	70.9
M2	1729	1719	1703	23.0	3.7	73.2
M3	1727	1718	1703	24.5	7.0	68.4

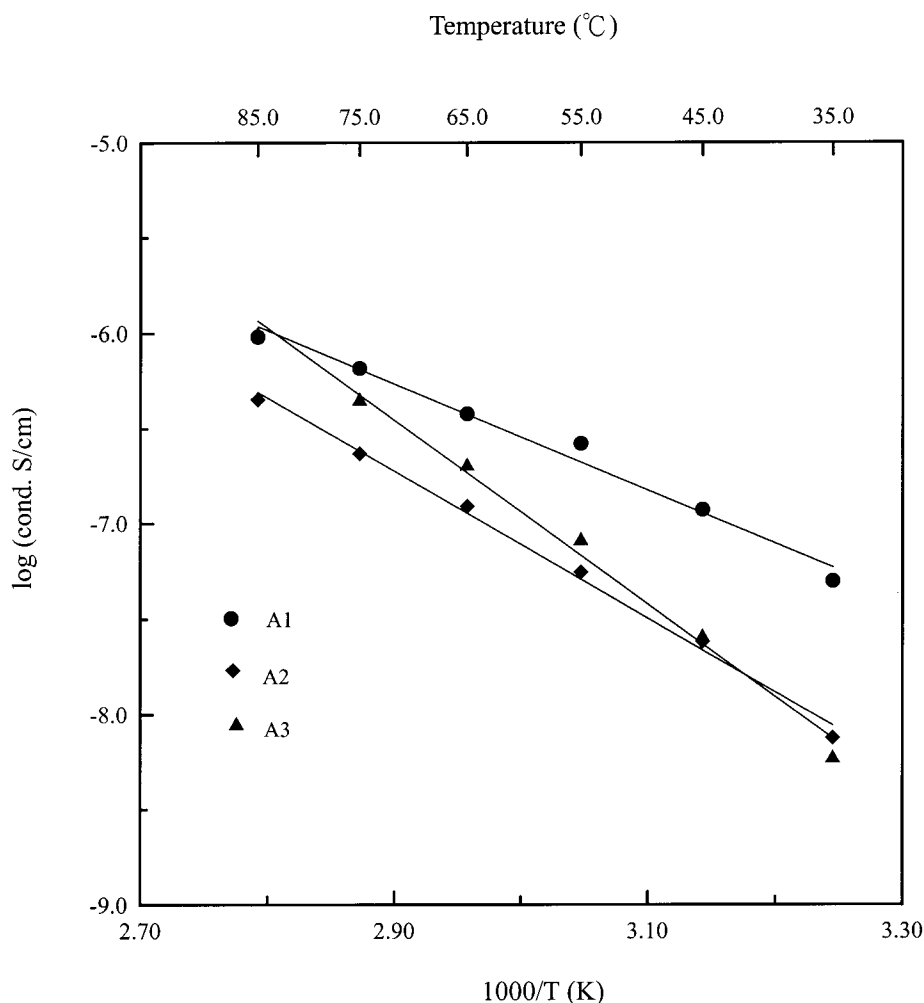


Figure 5 Temperature dependence of the conductivity of TPU-A as an SPE with different concentrations of LiClO_4 .

following the conductivity of TPU-M and TPU-A samples with various concentrations of LiClO_4 .

Conductivity measurements

SPEs

The conductivity of poly(ether urethane)-based polymer electrolytes has been reported by many researchers.^{20–27,37} The variation of conductivity with temperature is represented by the Vogel–Tammann–Fulcher (VTF) [eq. (2)] or Arrhenius [eq. (3)] relationship, depending on whether the ion mobility is coupled with the segmental motion of the polymer or not:

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

$$\sigma(T) = A \exp[-E/k_B T] \quad (3)$$

where A is a constant, E is the activation energy, B is the pseudoactivation energy related to polymer segmental motion, k_B is the Boltzmann constant, and T_0 is

a reference temperature usually associated with the ideal T_g at which free volume disappears or the temperature at which the configurational entropy becomes zero. In either case, T_0 usually lies 35–50 K below T_g .

The application of the VTF relationship to ion transport requires the coupling of the charge carriers with the segmental motion of the polymer chains. However, the Arrhenius relationship is applicable when the charge carriers are decoupled from the polymer host. In Figures 5 and 6, the ionic conductivity data for TPU-A and TPU-M with various concentrations of LiClO_4 are presented against the reciprocal of the temperature. TPU-B, unable to dissolve a sufficient amount of LiClO_4 , was not tested. According to Figures 5 and 6, both systems follow an Arrhenius relationship for ion transport; that is, ion movement occurs by an activated hopping mechanism. The ionic conductivity of TPU-A was found to be always approximately one order of magnitude higher than that of the corresponding TPU-M samples with equivalent

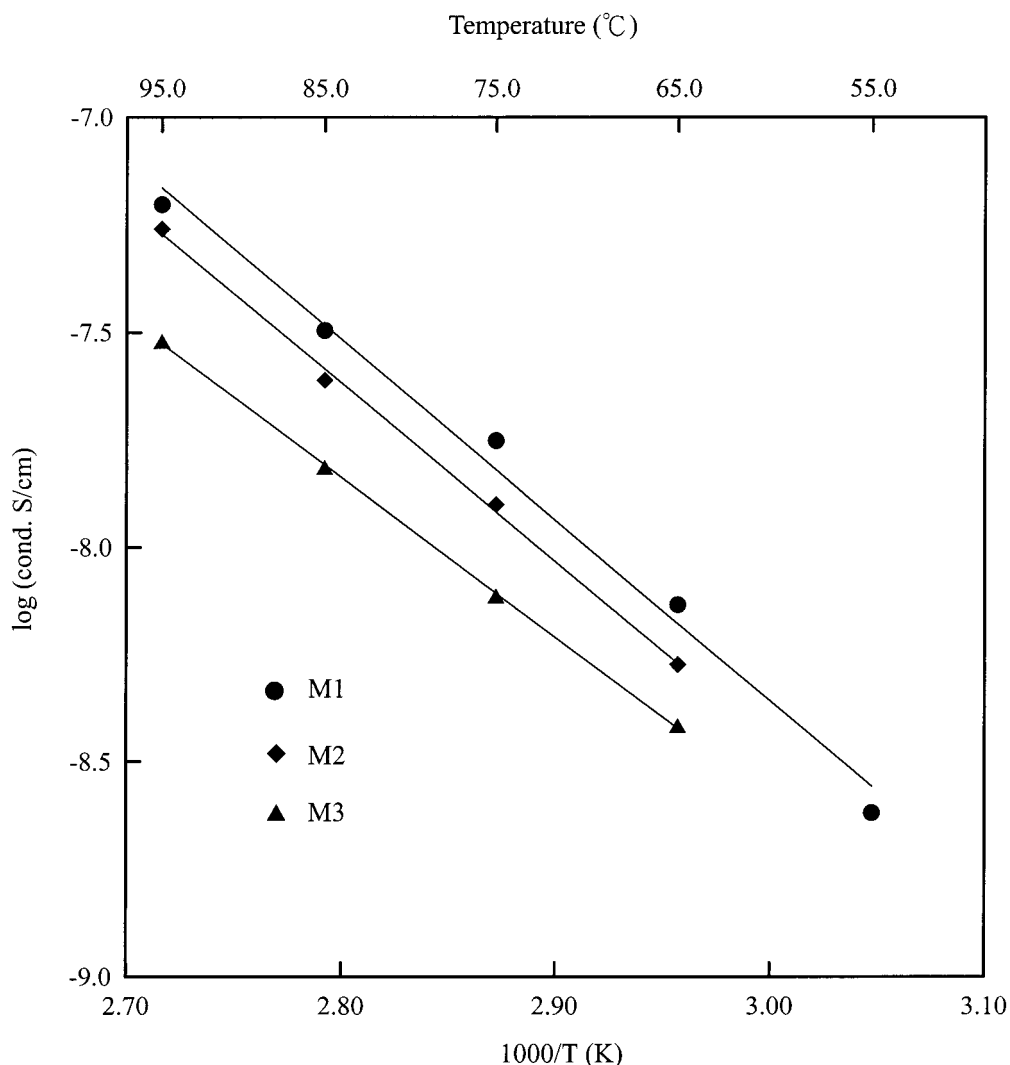


Figure 6 Temperature dependence of the conductivity of TPU-M as an SPE with different concentrations of LiClO_4 .

concentrations of LiClO_4 . This may be attributed to the higher polarity of PEG (in comparison with PTMG), which facilitates easier dissociation of LiClO_4 and, therefore, leads to an increased number of charge carriers.

Another important feature of Figures 5 and 6 is the variation of the ionic conductivity with the salt concentration. Figure 5 reveals that the relationship between the conductivity and salt concentration for TPU-A is a complex one. At a lower temperature region, electrolytes containing more salt have lower conductivity, whereas at a higher temperature region, the opposite relationship can be observed. Although sample A2 showed lower conductivity than A1 throughout the temperature range studied, the slopes of the two curves indicate that they may intersect each other at a higher temperature. Samples containing larger amounts of salts improved in their conductivity because of an increasing number of charge carriers, but the T_g of the soft segment was also simultaneously

increased, and this reduced the mobility. Hence, at a lower temperature region, the samples containing higher amounts of salts, though containing an increased number of charge carriers, showed lower conductivity because the mobility was restricted on account of the higher T_g value of the soft segment. Moreover, ion-pair/aggregate formation is not ruled out at higher salt concentrations.⁴⁰ According to the FTIR results, some of the Li^+ ions may be coordinated to the hard-segment urethane groups and so will not contribute conductivity unless the temperature becomes close to the hard-segment T_g . This might be another reason for the low conductivity of TPU-A with a larger amount of salt.

The conductivity-temperature relation (Fig. 6) for TPU-M was found to be anomalous. In Figure 6, the three curves representing different LiClO_4 concentrations are almost parallel to one another and unlike those of TPU-A. The conductivity was found to show a decreasing trend with an increase in the salt concen-

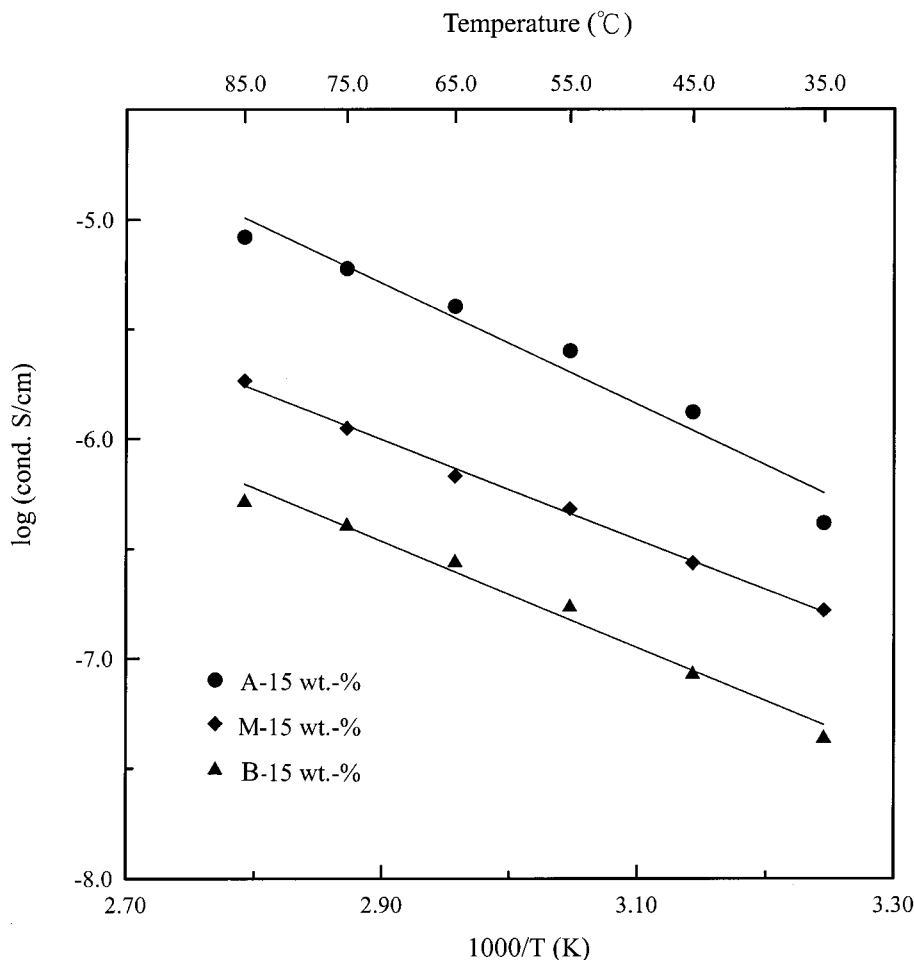


Figure 7 Temperature dependence of the conductivity of TPUs as a GPE containing 15 wt % LP-30.

tration. The reason behind the lower conductivity of TPU-M containing a larger amount of salt may be associated with the inability of TPU-M to dissolve a larger amount of salt. As mentioned earlier, M3 showed the separation of LiClO_4 while a cast film was dried from a mixture of TPU-M and LiClO_4 in DMF. M2 apparently did not show such separation of LiClO_4 . As the polarity of the PTMG-containing soft segment of TPU-M was low, an increase in salt just increased the number of undissociated salt or ion pairs and not the charge carriers. Hence, the conductivity of the TPU-M samples was found to decrease with an increase in the salt concentration.

GPEs

As the conductivity of the dry films was very low even at 85°C ($\sim 10^{-7}$ to 10^{-6} S/cm), we attempted to verify the utility of these samples as GPEs. In view of the practical applications of these systems, one commercial liquid electrolyte, LP-30, was used for making gelatinous electrolytes. The temperature dependence of the ionic conductivity of the three TPU films

swelled with 15 wt % LP-30 is shown in Figure 7. TPU-B absorbed a maximum of 15 wt % of the liquid electrolyte. Hence, the liquid electrolyte content of the other two polymers (TPU-A and TPU-M) was also maintained at 15 wt %. It is evident from Figure 7 that the conductivity behavior can be well described by an Arrhenius equation and that the trend is TPU-A > TPU-M > TPU-B. Although the role of the matrix polymer is secondary (most of the ions are being solvated and transported by the plasticizer) for a gelatinous electrolyte, at a lower concentration of the plasticizer, the matrix polymer plays a significant role in solvating and transporting the charge carriers. However, the improvement of the conductivity by the matrix polymer domains will be very low in comparison with that improved by the plasticizer-rich domains. A slight enhancement of the number of charge carriers is expected because of the solvation of some of the Li^+ ions by the matrix polymer. As TPU-A contains more polar PEG units as soft segments and the soft-segment polarity was in the order TPU-A > TPU-M > TPU-B, the order of conductivity, TPU-A > TPU-M > TPU-B, observed in Figure 7 is justified. Otherwise, the con-

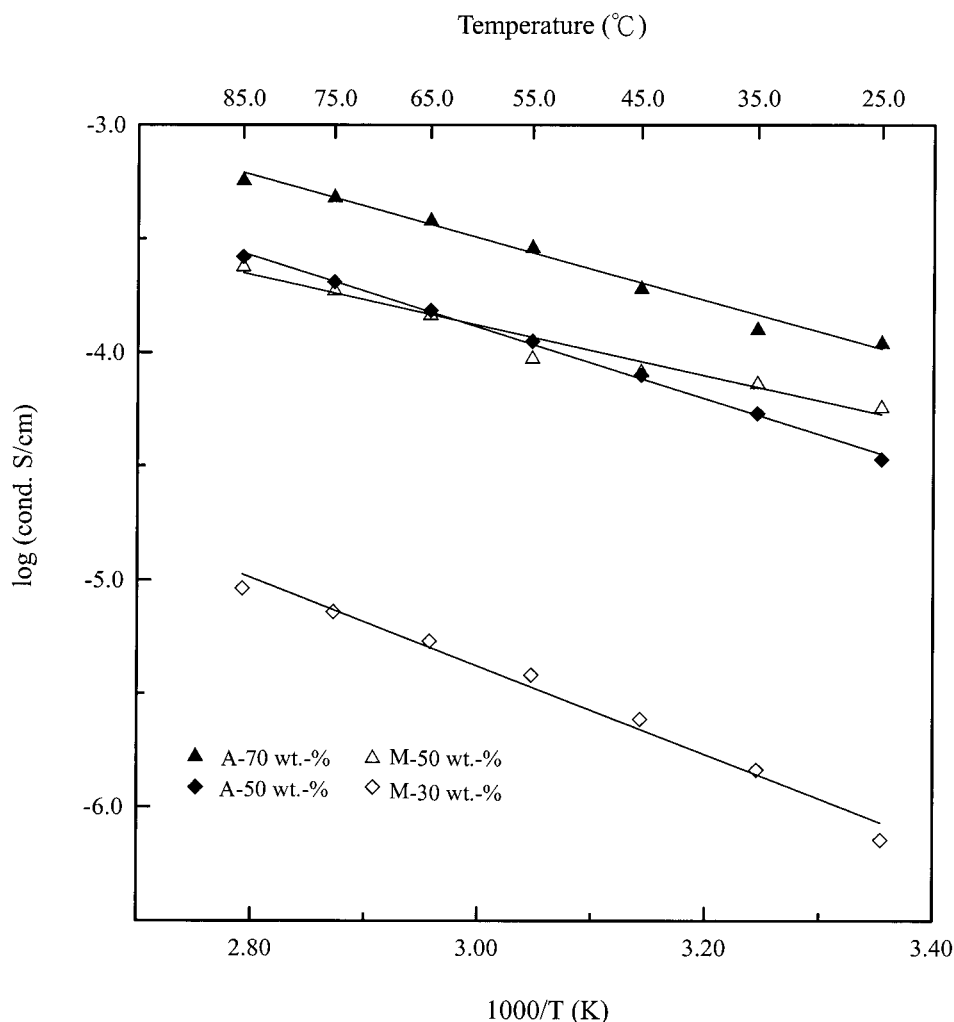


Figure 8 Temperature dependence of the conductivity of TPU-A and TPU-M as GPEs with different concentrations of LP-30.

ductivity of TPU-M is influenced by the matrix structure because it contains a mixture of PEG and PTMG.

Dimensional stability

It was possible to take up the liquid electrolyte (LP-30) by TPU-M, TPU-A, and TPU-B to different extents. The dimensional stability of the aforementioned gelatinous electrolytes was found to be very good for practical use. As the conductivity of these electrolytes was still in the lower side, we tried to increase the conductivity by increasing the liquid electrolyte content. As TPU-B could not absorb more than 15 wt % of the liquid electrolyte, we increased the swelling percentages of TPU-A and TPU-B up to the saturation level. TPU-A could absorb a maximum of 70 wt %, whereas TPU-M could absorb only 50 wt %. The temperature dependence of the conductivity data for the gelatinous electrolytes of TPU-A and TPU-M with different concentrations of the liquid electrolyte is presented in Figure 8. All the gelatinous electrolytes were found to follow the Arrhenius relation-

ship, and the conductivity increased with the increase in the liquid electrolyte concentration for both TPUs. A comparison of the conductivities of TPU-A and TPU-M with equivalent concentrations of the liquid electrolyte revealed that the difference in conductivity was approximately 1 decade when the liquid electrolyte concentration was low, whereas at higher concentrations, the TPUs had almost the same conductivity. As mentioned earlier, at lower electrolyte concentrations, the matrix polymer also significantly contributed toward the conductivity. Hence, TPU-A, having PEG as the soft segment, showed somewhat increased conductivity over TPU-M. At higher concentrations of the liquid electrolyte, the effect of the matrix polymer became negligible, and so the difference in the conductivities of TPU-A and TPU-M was reduced.

The mechanical strength of the TPU-M gelatinous systems containing equivalent amounts of the liquid electrolyte was better than that of TPU-A. In fact, the TPU-A gelatinous system containing a liquid electrolyte concentration greater than 50 wt % was very

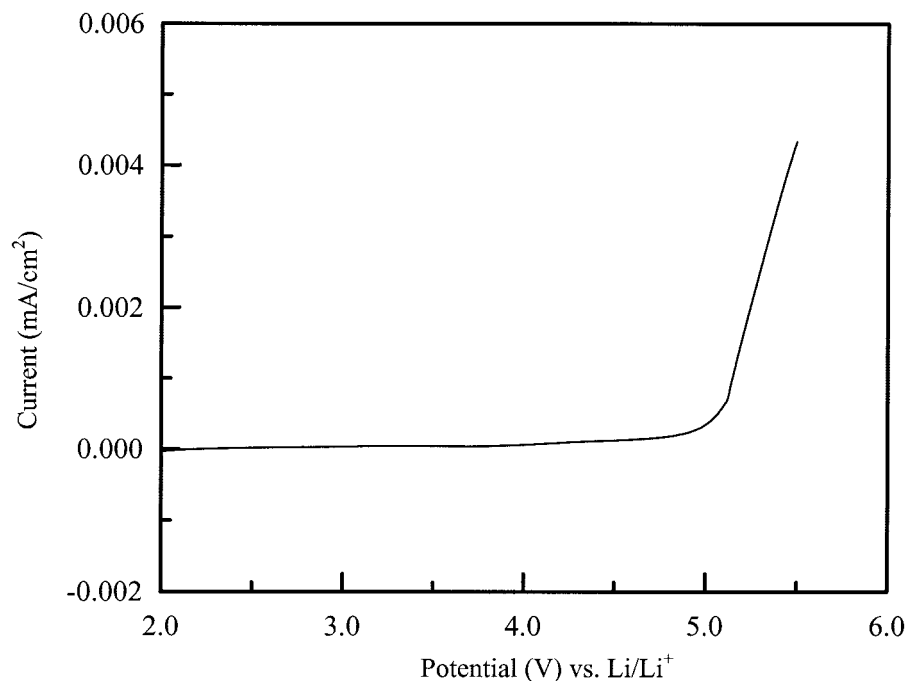


Figure 9 Linear sweep voltammetric behavior of TPU-M as a GPE.

difficult to use for practical purposes. In light of the better ionic conductivity and mechanical properties, the TPU-M gelatinous system containing 50 wt % liquid electrolyte was the best choice of the three TPUs for use as a polymer electrolyte in lithium batteries.

Stability of the GPEs

For appropriate operation temperatures and voltages, polymer electrolytes must have good thermal and electrochemical stability. During the conductivity measurements, the TPU-M electrolyte did not show any short circuits throughout the entire temperature range studied (5–85°C). This revealed that the electrolyte was thermally stable.

To ascertain the electrochemical stability of the gelatinous electrolytes, we performed linear sweep voltammetry for TPU-M containing 50 wt % liquid electrolyte. Figure 9 shows the linear sweep voltammetric behavior of TPU-M as a GPE. It is evident from Figure 9 that for TPU-M, the current onset occurred beyond 5.0 V, and this suggested that the electrochemical stability of the GPE was as high as 5.0 V versus Li/Li⁺. Such stability would be suitable for the practical use of GPEs in lithium-ion batteries.

CONCLUSIONS

Changes in the morphology and ionic conductivity were evident between the TPU-LiClO₄ complexes based on PEG, PTMG, and mixtures of PEG and PTMG as soft segments. The DSC results clearly

showed different trends in the changes of T_g with the LiClO₄ concentration for the TPU with a mixture of PTMG and PEG as soft segments and the parent TPUs. The lower polarity of PTMG in comparison with that of PEG altered the extent of dissociation of LiClO₄ and influenced the ionic conductivity. FTIR and conductivity results provide evidence for the involvement of combined interactions of both PEG and PTMG soft segments with lithium ions for TPU-M. A gel-type electrolyte with dimensional stability could be made with TPU-M with various weight percentages of LP-30. With respect to conductivity and mechanical strength, the TPU system containing equimolar portions of PEG and PTMG as soft segments was superior to the parent systems. A room-temperature conductivity of approximately 1×10^{-4} was obtained for the gel electrolyte containing 50 wt % of the liquid electrolyte (LP-30) and having good dimensional stability. TPU-M was shown to possess good electrochemical stability in a wider potential window (2.0–5.0 V), and its suitability for use as a GPE in lithium batteries was justified.

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