

Morphology and Conductivity Changes in a Thermoplastic Polyurethane-Based Copolymer Consisting of Different Soft Segments

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ABSTRACT: Three different segmented thermoplastic polyurethanes (TPUs) were synthesized with 4,4'-methylenebis(phenyl isocyanate) as a hard segment and poly(ethylene glycol) (PEG) or poly(propylene glycol) (PPG) or an equal mixture of PEG and PPG with molecular 2000 as soft segments. The soft-segment component of TPU was changed to monitor modifications in chemical and physical properties among the three TPUs. Differential scanning calorimetry (DSC) and thermogravimetric analysis were used to monitor changes in thermal characteristics. Fourier transform infrared spectroscopy (FTIR) was employed to predict the interaction between the lithium cation and the hard or soft segment in the presence of added LiClO_4 . The deconvolution results of spectral bands associated with the N—H groups of these TPUs were used to obtain such information. Impedance spectroscopy was used to inspect the changes in the bulk conductivity of these TPUs caused by alteration of the soft-segment component. The conductivity changes were explained through combined DSC and FTIR results. The electrochemical stability of the TPU systems was studied by linear sweep voltammetry. The results showed that the copolymer system had better thermal and electrochemical stability than the other systems. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1462–1473, 2001

Key words: thermoplastic polyurethane; copolymer; ionic conductivity; morphology; thermogravimetric analysis (TGA); FTIR; electrochemical stability

INTRODUCTION

A large number of experimental investigations have been conducted on the properties of polyether–alkali metal salt complexes after the important work by Wright¹ and Armand.² For polymer electrolytes, in the presence of added alkali metal salts, the formation of transient crosslinks

between ether oxygens in the host polymer and alkali metal cations have been reported. Most researchers have concentrated on the design of novel polymer materials that possess high ionic conductivity, mechanical strength, and thermal stability for technological applications.^{3–5} Although the main interest has been to enhance ionic conductivity, morphological studies have also been carried out for a few of the solid polymer electrolytes (SPEs). Generally, a polymer electrolyte is required to exhibit elastomeric properties in addition to high ionic conductivity. To provide suitable ambient-temperature conductivity, the temperature of application should be above its glass-transition temperature (T_g).

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The interest in the use of thermoplastic polyurethanes (TPUs) as matrices for polymer electrolytes is related to the possibility of increasing the mechanical strength of linear polyethers. TPUs are composed of a polyether or polyester soft segment and a diisocyanate-based hard segment that can be characterized by a two-phase morphology.⁶ The phase separation caused by the immiscibility of the hard and soft phases leads to the formation of a hard-segment domain, a soft-segment matrix, and an ill-defined interphase. The hard-segment domains act as physical crosslinks and filler particles to the soft-segment matrix and, hence, are responsible for the good mechanical properties of these polymers. The soft-segment domain dissolves most of the ions and, thus, contributes to the conductivity of this complex. Measurements on systems with various soft-segment contents have shown that conductivity occurs through soft-segment domains.⁷ The domain formation is derived from the strong intermolecular hydrogen bonding between the hard-hard (H-H) segments of urethane or urea linkages and the hard-soft (H-S) segments of urethane or urea and ether.⁸⁻¹¹

IR spectroscopy has been extensively used to study the hydrogen bonding in TPUs and has been demonstrated as a powerful tool for identifying the characteristics of hydrogen bonding.⁹⁻²³ Hydrogen bonding is characterized by a frequency shift to values lower than those corresponding to the free groups (i.e., with no hydrogen bonding). The extent of the frequency shift is normally used to estimate the hydrogen-bonding strength. Particularly, for polyether-based TPUs, the fraction of hydrogen-bonded carbonyls is a measure of the H-H segment hydrogen bond (NH· · O=C bond), and this can be taken as a measure of the degree of phase separation. On the other hand, the fraction of the hydrogen-bonded ether oxygens (NH· · O bond) represents the degree of phase mixing between hard and soft segments. Recently, several studies have attempted to elucidate the relationships between the structure and properties within TPUs with Fourier transform infrared (FTIR) spectroscopy¹²⁻²³ and differential scanning calorimetry (DSC).²³⁻²⁶ Seki and Sato²⁷ and McLennaghan and colleagues^{28,29} proved that the doping of lithium salt to TPUs results in an increase in the soft-segment T_g and a loss of the higher temperature endothermic transitions. More recently, results from our laboratory³⁰ showed that the addition of LiClO₄ increases the overall bulk conductivity of a phase-segregated

water-borne polyurethane (WPU) composed of soft segments of poly(propylene glycol) (PPG) and hard segments of isophorone diisocyanate and ethylenediamine. Significant changes in the FTIR spectrum of the WPU were observed when the critical salt concentration was above 1.0 mmol/g WPU, suggesting changes in the interaction between the lithium cation and the segments of TPU. Thus, the characteristics of the phase-segregated morphology of the WPU was altered as a result of the interaction of lithium cations within the polar hard domains and by the changes in phase intermixing caused by the coupling of the hard and soft phases. Significant effects of ions on phase-separated morphology have also been observed on polyurethane-based ionomers.⁷

Few parameters, such as the kind of raw materials, the soft-segment molecular weight, and the hard-segment concentration,^{28-29,31} could affect the elastomeric properties of TPU. Furtado et al.³² investigated the morphology and ionic conductivity of electrolytes prepared from poly(tetramethylene glycol-co-ethylene glycol) copolymer reinforced by condensation with hexamethyldiisocyanate. They focused on the effects of added LiClO₄ concentration on the structure and bulk impedance of linear polyurethane. A change in the soft segments of TPU will enable us to understand more about the interaction of lithium cations with the soft and hard segments of TPU.

In this study, three TPUs were synthesized by the incorporation of PPG, poly(ethylene glycol) PEG, and a 1:1 mixture PEG and PPG as soft segments and used as SPEs. FTIR spectroscopy, thermogravimetric analysis (TGA), DSC, and electrochemical impedance measurements were used to monitor the changes in hydrogen-bonding characteristics, thermal transition, and conductivity in the process of establishment of the role of the soft segments. The effects of added LiClO₄ on the previous characteristics were also investigated. The three TPUs were gelled with a plasticizer [propylene carbonate (PC)], and the effect on conductivity was also studied.

EXPERIMENTAL

Synthesis of TPU

The raw materials employed in this study are listed in Table I. PPG (PPG-2000) and PEG (PEG-2000) were dried and degassed in a vacuum oven under 85°C for 1 day. All other chemicals were

Table I Raw Materials for the Synthesis of the TPU Series

Designation	Chemical Identification	Supplier
PEG	Poly(ethylene glycol), $M_w = 2000$	Showa Chemical, Inc.
PPG	Poly(propylene glycol), $M_w = 2000$	Showa Chemical, Inc.
MDI	4,4'-methylenebis(phenyl isocyanate)	Aldrich Chemical, Inc.
DMF	Dimethylformamide	Tedia Company, Inc.
1,4BD	1,4-Butanediol	Aldrich Chemical, Inc.
MeOH	Methyl alcohol	Tedia Company, Inc.
DBTDL	Di- <i>n</i> -butyltin (IV) dilaurate	Wako Chemical Co.

used without any further treatment. The TPU prepolymer was synthesized by a one-step addition reaction in a 2-L four-necked round-bottomed flask complexed with an anchor-propeller stirrer, a nitrogen inlet and outlet, and a thermocouple connected to the temperature controller.

PPG (200 g, 0.20 mole), PEG (200 g, 0.20 mole), or the mixture of PEG and PPG in a 1:1 ratio (PPG 100 g, 0.10 mole/PEG 100 g, 0.10 mole) and the chain extender, 1,4-butanediol (7.2 g, 0.80 mole) were simultaneously added to the reactor under a nitrogen gas atmosphere to make the prepolymer of TPU. The temperature was kept at 50°C initially. After the proper mixing (at 150 rpm), two drops of dibutyltin dilaurate were added into the batch to catalyze the reaction, and 4,4'-methylenebis(phenyl isocyanate) (250 g, 1.01 mole) was then added stepwise into the reactor to keep the ratio of isocyanate (NCO)/polyol at 5. The temperature of the reactor was increased to 85°C. After 6 h of reaction at this temperature, *N,N'*-dimethylformamide (DMF) was added to control the viscosity of TPUs during preparation. After 30 min of reaction, few drops of methyl alcohol were added to terminate the reaction. A small amount of polymer solution was diluted with DMF and then injected into a gel permeation chromatograph to determine the molecular weight and distribution. All of the TPUs were controlled to have a weight-average molecular weight (M_w) of about 200,000 and a Poly Dispersity Index (PDI) [M_w /number-average molecular

weight (M_n)] between 1.80 and 2.20. In this study, three kinds of TPU system were prepared with PEG, a copolymer (PEG-PPG), and PPG as soft segments; these were named TPU-E, TPU-C, and TPU-P, respectively.

Molecular Weight

M_n and M_w were determined with a Shimadzu (Kyoto, Japan) gel permeation chromatograph fitted with a Shimadzu HPLC (High Performance Liquid Chromatograph) pump and a differential refractometer. A Jordi (USA) gel divinylbenzene mixed-bed 250 × 10-mm column was employed for the analysis. DMF was used as the continuous phase and was pumped through the column at a flow rate of 2.0 mL/min. This system was calibrated against 10 polystyrene standards. The molecular weight distribution of the synthesized TPU systems is given in Table II.

Preparation of the Polymer Film

Lithium perchlorate (LiClO_4) was dissolved in DMF to make a 10 wt % LiClO_4 /DMF solution. TPU solutions (~ 10 wt %) were blended with different amounts of 10% LiClO_4 solution to incorporate different concentrations of LiClO_4 in the TPU systems. The blended solutions were poured into glass dishes to make the desired lithium-salt-doped polymer films. The solution was dried in a vacuum oven for 2 days at 80°C. Two

Table II Molecular Weights and the Distributions of the Synthesized TPU Series

Molecular Weight	TPU-E × 10 ⁵	TPU-P × 10 ⁵	TPU-C × 10 ⁵
M_n	0.98	1.24	1.22
M_w	1.99	2.29	2.69
PDI (M_w/M_n)	2.03	1.85	2.20

different concentrations of LiClO_4 were chosen for each type of TPU, 0.20, and 0.70 mmol LiClO_4/g TPU. For comparison with doped TPUs, TPU films were also made without LiClO_4 addition. In this study, the TPU-P polymer electrolytes, with the addition of electrolyte concentrations of 0.00, 0.20, and 0.70 mmol LiClO_4/g TPU, were designated as samples P0, P1, and P2, respectively. TPU-C systems were denoted as C0, C1, and C2, for 0.00, 0.20, and 0.70 mmol LiClO_4/g TPU concentrations, respectively, and TPU-E systems were denoted as E0, E1, and E2, for 0.00, 0.20, and 0.70 mmol LiClO_4/g TPU concentrations, respectively.

After drying, the films were transferred into a glove box filled with dry argon. The water and oxygen content in the glove box were kept below 1 and 5 ppm, respectively. Before all tests, the water content of these films was maintained below 10 ppm ($< 9.8 \times 10^{-6}$ water/g of TPU) by a Karl Fisher moisture titrator (model 275KF, Denver Instruments, Norfolk, UK).

FTIR

FTIR analyses were made by the casting of film from a 2% polymer solution onto a potassium bromide window at room temperature. After evaporation of the solvent, the films were placed in a vacuum oven at about 80°C for over 24 h to remove residual solvent and moisture.

FTIR spectra were collected with a Nicolet 550 (Madison, WI, USA) system at a resolution of 2 cm^{-1} , and a minimum of 64 scans were signal-averaged at room temperature. Band deconvolution of the resulting spectra was obtained by analysis with Grams 386 software (Galactic Industries Corporation). The maximum error associated in the deconvolution of the IR spectral bands was expected to be $\pm 5\%$ with respect to peak area. In most cases, the deconvolution was executed by the fitting of the spectra to different functions to assure the accuracy of the deconvolution results.

TGA

TGA was performed with a PerkinElmer TGA-7 (USA) instrument with a scan rate of 20°C/min up to 600°C under a N_2 atmosphere.

DSC Thermograms

Thermal analysis of TPU was carried out with a differential scanning calorimeter (TA DSC 2010,

New Castle, DE, USA). The temperature was equilibrated first to -100°C and then scanned from -100 to 100°C at a heating rate of $10^\circ\text{C}/\text{min}$. A sample was taken from the TPU film and sealed in aluminum capsules and transferred out of a dry box to perform the thermal analysis.

Impedance Spectroscopy

Impedance measurements were performed for the cast films of about 150–200 μm in thickness and 0.785 cm^2 in area. The ionic conductivity of the TPU films sandwiched between two stainless steel (SS) electrodes was measured with an Autolab PGSTAT 30 (Eco Chemie B.V., Utrecht, The Netherlands) with the help of Frequency Response Analysis system software (Autolab, The Netherlands) under an oscillation potential of 10 mV from 100 kHz to 1 Hz. The conductivity was calculated with the relation

$$\sigma = \frac{1}{R_b} \times \frac{\ell}{A},$$

where R_b is the bulk resistance from alternating current impedance, ℓ is the film thickness, and A is the surface area of electrode.

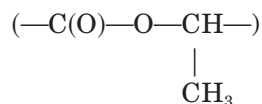
Linear Sweep Voltammetry (LSV)

The three laminated electrode cells were assembled inside the glove box for LSV experiments. Lithium metal was used as a counter and a reference electrode, and SS was used as a working electrode. LSV measurement was carried out with an Autolab PGSTAT 30 potentiostat/galvanostat (Eco Chemie B.V.).

RESULTS AND DISCUSSION

DSC

DSC was used to examine the morphology-based thermal transitions associated with polyether soft segments of the three TPU systems. Table III gives the T_g 's of the soft segments of P0, E0, and C0, which contained the same proportion of hard segment (NCO/polyol = 5). E0 had a higher T_g than P0. This may be due to the lesser extent of hydrogen bonding between ether groups of the soft segment of P0



with the hard-segment (N—H) group. The presence of a pendant group (—CH₃) in P0 may have provided steric hindrance and caused a decrease in intermolecular hydrogen bonding. The reduced hydrogen bonding may have lowered the T_g for P0 as observed here. With the copolymer that consisted of PEG and PPG units in a 1:1 ratio, DSC thermograms showed a single T_g , which was found to be even lower than that for P0. This demonstrated that there could be variations in the H—H and H—S hydrogen bonding as well as order—disorder proportions in hydrogen bonding. As a result of this, different extents of phase intermixing between hard and soft groups (PEG and PPG) could be present, which made the T_g become lower than even that of E0 and P0.

DSC thermograms were recorded for the three TPUs with the addition of lithium salt in various concentrations (Table III and Fig. 1). It was evident from the results that T_g of the soft segment increased with salt concentration in all the three TPU systems but to different extents. This is in line with earlier observations of LiClO₄-doped TPU-containing poly(ethylene oxide) or poly(propylene oxide)^{25,29,33–34} as soft segments and also with an increase in T_g with salt concentration for the polyether—LiCF₃SO₄ complex system.³⁵ In this study also, the increase in T_g could arise from the arresting of the local motion of the polymer through transient crosslink formation between electron-rich parts (oxygen atoms) of soft segments and Li⁺ ions. However, an interesting point comes out on normalizing the T_g data with respect to LiClO₄ concentrations. The addition of

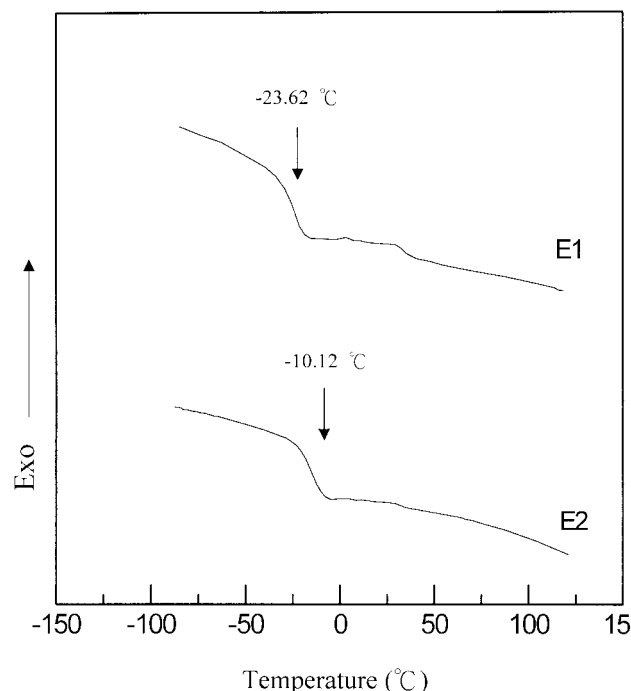


Figure 1 DSC thermograms for TPU-E doped with various LiClO₄ concentrations: (E1) 0.20 and (E2) 0.70 mmol/g TPU.

the same concentration of Li⁺ ion (0.20 mmol/g) to the three TPUs resulted different $\Delta T_g/\Delta C$ s. Table III shows that $\Delta T_g/\Delta C$ followed the order C1 > E1 > P1. A similar trend with $\Delta T_g/\Delta C$ was also noticed for the three TPU systems (E2, P2, and C2) with the addition of 0.70 mmol/g of LiClO₄. However, when lithium salt addition was increased from 0.20 to 0.70 mmol/g, $\Delta T_g/\Delta C$ decreased. The increase in lithium salt concentration at this stage produced a plasticizing effect by the production of undissociated lithium salt or charge-neutral contact ion pairs.^{30,36} The lower ability of these contact ion pairs to make ion crosslinks caused a decrease in $\Delta T_g/\Delta C$.

Hence, the copolymer possessed the beneficial characteristics of a polymer electrolyte with a lower T_g and a higher tendency to interact with added lithium ions. The $\Delta T_g/\Delta C$ value for the TPU-E was found to be higher than that of TPU-P (Table III). Based on this, we envisaged that the added lithium salt had more of a tendency to interact with PEG soft segments in the copolymer. Hence, the observed variations in T_g among E0, P0, and C0 could be viewed as caused by the possible differences in molecular interactions between the hard and soft segments of the TPU to alter the hydrogen-bonding characteristics. Also,

Table III Thermal Properties of the TPU-E, TPU-P, and TPU-C Systems

Polymer	T_g (°C)	$\Delta T_g/\Delta C$
E0	-35.1	
E1	-23.6	57.6
E2	-10.1	27.0
P0	-44.1	
P1	-34.3	49.1
P2	-22.3	24.0
C0	-49.3	
C1	-37.2	60.3
C2	-22.4	29.6

for the doped TPU systems with LiClO_4 salt, changes in interactions between the groups in TPU and Li^+ ions were expected, and this aspect is the subject of further discussion in the later part of the article.

TGA

The thermal stability test will be useful for the employment of electrolytes in the applications related to technological device. Figure 2 represents the thermogram of the three polymers E0, P0, and C0. C0 had a higher initial thermal decomposition temperature (372°C) in comparison with E0 (365°C) and P0 (351°C). This demonstrates that the copolymer possessed better thermal stability than E0 and P0. The first decomposition temperature was lowered on addition of LiClO_4 salt and generated a second stage of decomposition, which resulted from the ionic crosslink formation between Li^+ ion and soft-segment units.³¹ The result was the weakening of the $\text{C}=\text{O}$ bond by the decrease in the electron density on oxygen. On the addition of 1.20 mmol/g of LiClO_4 (Fig. 3), a striking decrease in the first and second decomposition temperatures was noticed. This might be

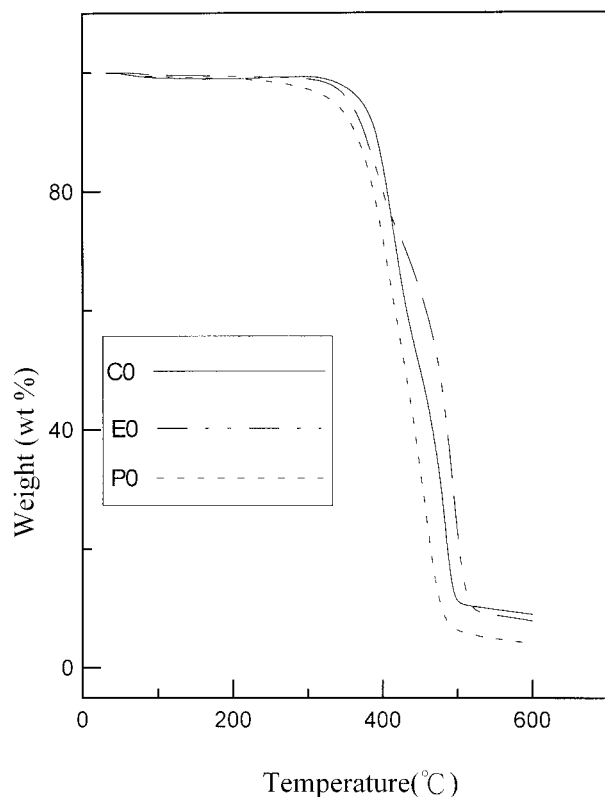


Figure 2 TGA of E0, P0, and C0.

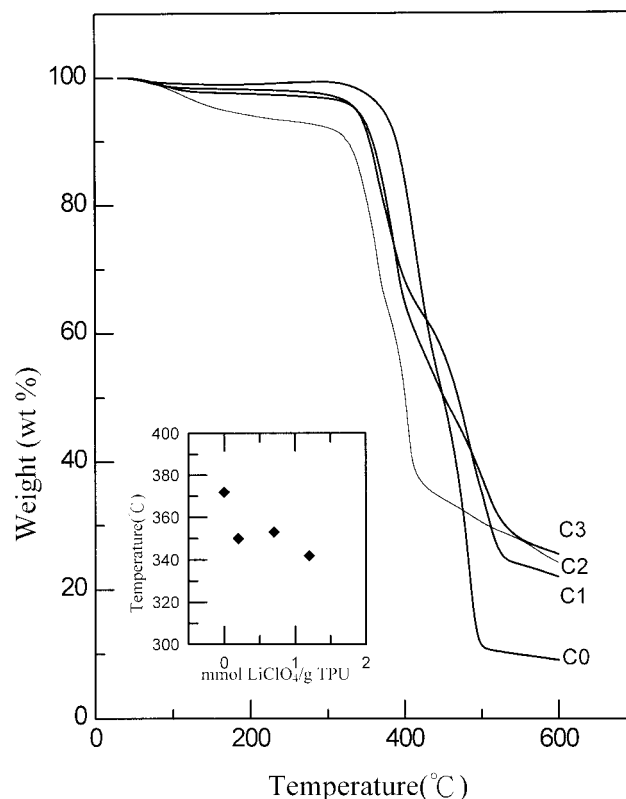


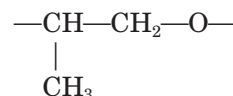
Figure 3 Effect of added salt (LiClO_4) concentration on the initial decomposition temperature of TPU-C.

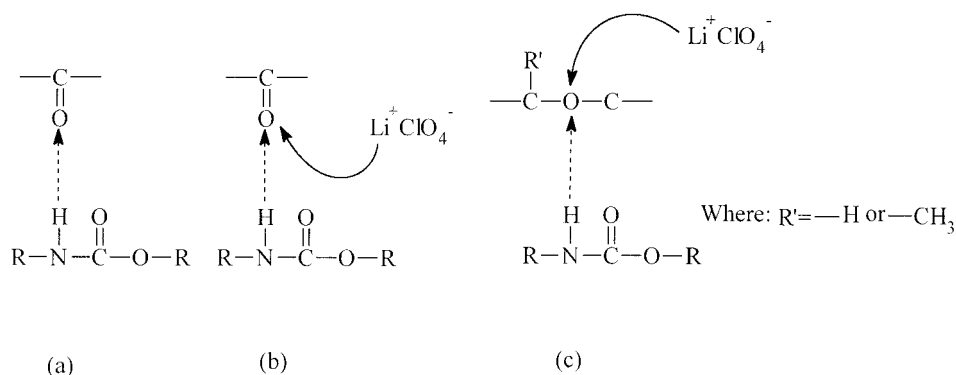
due to the additional influence of excess LiClO_4 not involved in crosslinking with the segments of TPU.

The analysis of FTIR spectroscopic band positions of the $\text{N}-\text{H}$ and $\text{C}=\text{O}$ group stretching modes and their associated band areas would provide better insight about the variations in molecular interactions in the doped and undoped states as a result of the presence of two different soft segments. Such variations could cause the changes in thermal characteristics seen in the DSC results.

FTIR Spectroscopy

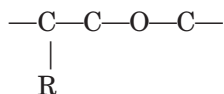
In this study, FTIR was used to study the effect of structural changes in the soft segment of TPU on altering the phase morphology and associated thermal transitions of the soft segment. The presence of $(-\text{CH}_2-\text{CH}_2-\text{O}-)$ and





Scheme 1 Schematics for the suggested interactions in TPU.

as soft segments in E0 and P0, respectively, were envisaged to alter the extent of hydrogen bonding between these groups and the hard segment (N—H group) of TPU. Also, this may have an induced effect of altering the hydrogen bonding between hard-segment (N—H) and C=O groups [Scheme 1(a)]. To bring out these changes in hydrogen-bonding characteristics, three IR regions were examined: (1) 3650–3200 cm^{-1} , which includes the hydrogen-bonded N—H stretching mode and free N—H stretch; (2) 1750–1650 cm^{-1} , which includes the stretching of urethane carbonyl groups; and (3) 1150–1000 cm^{-1} , which includes the (—C(O)—O—C—) stretch of ether band phase and the



of the soft segment of PPG or PEG (where —R = —CH₃ for PPG and —R = —H for PEG). These spectral regions were analyzed to examine the H—S and H—H group interactions in the undoped E0, P0, and C0 samples. Also, the FTIR data were used to make similar comparisons with doped (in the presence of LiClO₄) E1, E2, P1, P2, C1, and C2 samples.

Figure 4 represents the IR spectra of the N—H stretching region for the undoped E0, P0, and C0. On analysis of these spectra, the phase mixed state between hard and soft segments through hydrogen-bonding formation was evident. The N—H stretching region was deconvoluted (Fig. 4) by fitting through the Gaussian–Lorentzian sum.³⁰ A close examination of N—H stretching region revealed the presence of at least three contributing bands (Table IV). The bands at 3499–

3510 cm^{-1} and 3251–3329 cm^{-1} are assigned to N—H stretching modes of free and hydrogen-bonded N—H groups, respectively, of the polyurethane. The band around 3350–3422 cm^{-1} can be assigned as an overtone of the fundamental free

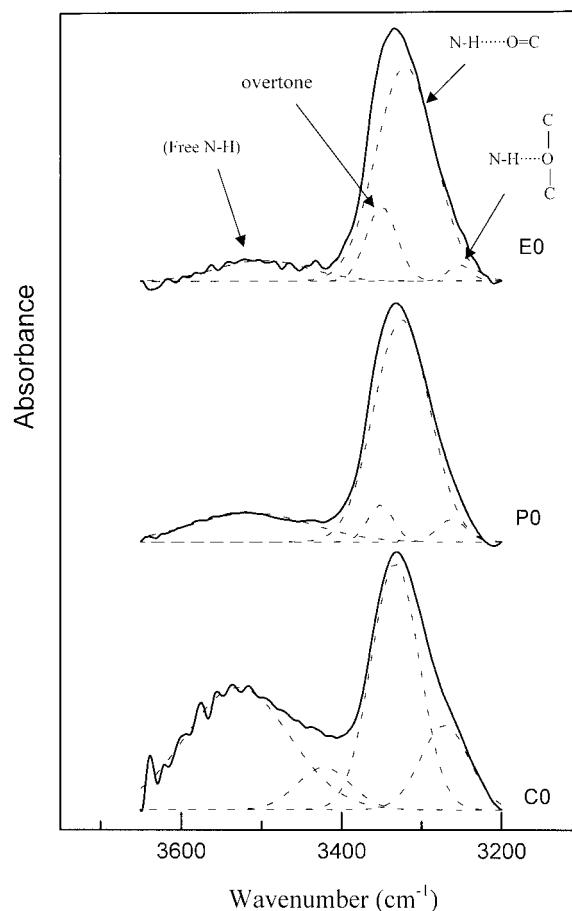


Figure 4 The deconvolution of N—H stretching for E0, P0, and C0.

Table IV Deconvolution Results of the N—H Region for E0, P0, and C0

Polymer	Peak Position (Frequency)				Peak Area ^a (%)			
	Free	Overtone	H—H	H—S	Free	Overtone	H—H	H—S
E0	3499	3350	3320	3251	11.2	13.3	73.5	2
P0	3512	3352	3325	3262	19.6	5.4	71.3	3.7
C0	3510	3422	3329	3279	41.4	6.7	35.9	11.7

Free = free N—H bonding; overtone = overtone of C=O.

^a Peak areas are based on total N—H stretching band area.

carbonyl³⁰ of E0, P0, and C0. Also, the bands at 3251–3329 cm^{-1} could be resolved into the 3251–3279 cm^{-1} N—H stretching mode, which corresponds to H—S hydrogen bond [Scheme 1(c)] and 3320–3329 cm^{-1} for H—H hydrogen bonds [Scheme 1(b)]. These results are attributed to the phase mixed state between hard and soft segments via hydrogen bonding in all of the three TPU systems however to a different extent. The H—H hydrogen-bonding N—H stretching frequency of P0 was found to be higher (3325 cm^{-1}) compared to that of E0 (3320 cm^{-1}). Given the fact that band position is a function of the strength of the N—H bonds, we presumed that the strength of N—H bond was more for P0 than for E0. The increase in the strength of the N—H band can cause weakening of the extent of hydrogen bonds.

The analysis of band areas associated with H—H segments of hydrogen-bonded N—H stretching bands demonstrated that H—H hydrogen-bonded areas for P0 were fewer in comparison with E0. This is consistent with the higher frequency of N—H bands (H—H hydrogen bonded), which would result in the weakening of hydrogen bonding. Also, this would cause more free N—H groups in P0. The observed increase in free N—H band areas justifies this. The deconvolution of the C=O stretching mode (not shown) also increased the free carbonyl group band area for P0, which supports this supposition. The observed lower value of T_g than the expected increase for P0 (as observed through the DSC results) in comparison with E0 (Table III) could, therefore, be taken as clue that decrease in H—H hydrogen bonds between H—H segments in P0 did not cause any phase mixing.

Now, it is interesting to consider the band areas of the H—H hydrogen bonds and the strength of N—H bands in the copolymer in which both PEG and PPG units were present together. The N—H bond stretching frequency of H—H hydro-

gen-bonded segments was found to be higher for C0 than for E0 and P0. The consequent weakening of hydrogen-bond strength was clearly evident from the low band areas for this. The observed decrease in T_g for the copolymer was, therefore, arising from the reduced hydrogen bonding between C=O and N—H groups of hard segments. The release of H—H segment hydrogen bonds made the soft-segment units more flexible and resulted in a decrease in T_g for the soft segment (Table III).

The deconvolution of the H—S hydrogen-bonded N—H stretching region (Fig. 4) showed two bands that corresponded to PPG (3279 cm^{-1} assigned from the observed higher frequency N—H stretching for P0) and PEG (3251 cm^{-1}) soft segments. The band areas of these regions showed that the ether oxygen of PPG units were involved more in hydrogen bonding than was PEG.

The effect of added lithium salt concentration on the N—H stretching band (free and hydrogen bonded) for the three TPU systems were analyzed through FTIR spectroscopy (Fig. 5). In the presence of Li^+ ion, the band corresponding to N—H stretching caused by hydrogen bonding between N—H and carbonyl shifted to a higher frequency for TPU-E, TPU-P, and TPU-C. The strength of the hydrogen-bonded N—H bond increased in all the three cases. Weakening of hydrogen bonds between the C=O and N—H groups was, therefore, evident. This might have been caused by the localization of electron-rich oxygen, which coordinated with Li^+ ion through hydrogen-bonded species (Scheme 1b). The weakening of hydrogen bonding resulted a decrease in H—H N—H stretch band areas (Table IV) for the three TPU systems. The relative variations in band areas between E0 and E1, P0 and P1, and C0 and C1 indicated that different extents of interactions of Li^+ ion with carbonyl—NH hydrogen-bonded species were present.

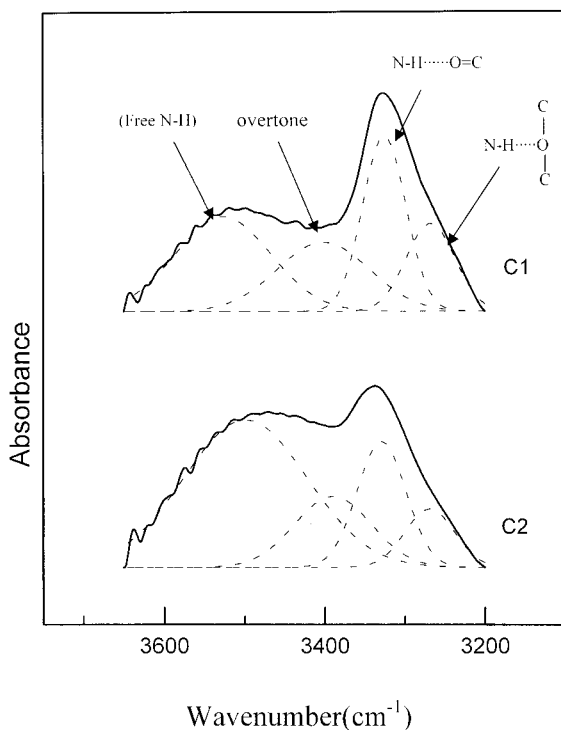
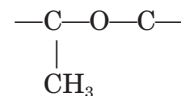


Figure 5 The deconvolution of N—H stretching for TPU-C doped with various LiClO_4 concentrations: (C1) 0.20 and (C2) 0.70 mmol/g TPU.

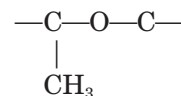
Also, the band positions of hydrogen-bonded N—H to ether oxygen shifted to a different extent for the homopolymers in the presence of Li^+ ion (Table V). The shift to a higher frequency indicated the increase in bond strength of N—H. This arose from the coordination of nonbonded electron-rich ether oxygen with Li^+ ion [Scheme 1(c)], which resulted in the weakening of hydrogen bonding. However, an increase in band areas of

this region was attributed to the inductive increase in hydrogen bonding.

In the case of the copolymer, the deconvolution of N—H stretching region $3250\text{--}3290\text{ cm}^{-1}$ resulted in two bands. The lower frequency (3251 cm^{-1}) and higher frequency (3279 cm^{-1}) bands were assigned to (—C—O—C—) and



soft-segment interactions with N—H groups, respectively. The observed increase in the band areas of the regions in comparison with the homopolymers E0 and P0 indicated that the interactions of these soft segments in the copolymer were different. The changed morphology may be the reason for the observed low T_g for C0 in comparison with E0 and P0. When Li^+ ion was added to C0, both bands were shifted to the higher frequency. This obviously means that Li^+ ion coordinated with the ether oxygen of PEG and PPG segments in the copolymer. The observed increases in band areas for both the band were also consistent with the involvement of (—C—O—C—) and



coordinating with Li^+ ion in the copolymer. The higher $\Delta T_g/\Delta C$ value for the copolymer as noticed in DSC by the addition of Li^+ ion could now be hypothesized to be caused by the previous combined interactions in the copolymer.

Table V Deconvolution Results of the N—H Region for the TPU-E, TPU-P, and TPU-C Systems

Polymer	Peak Position (Frequency)				Peak Area ^a (%)			
	Free	Overtone	H—H	H—S	Free	Overtone	H—H	H—S
E1	3503	3395	3323	3258	40.3	15.1	37.4	7.2
E2	3508	3406	3326	3258	48.9	24.0	19.7	7.3
P1	3500	3395	3329	3267	49.6	10.2	32.1	8.1
P2	3495	3386	3329	3269	61.1	12.1	17.8	9.0
C1	3512	3410	3335	3286 ^b 3254 ^c	46.5	13.0	22.3	12.4 ^b 5.7 ^c
C2	3510	3417	3343	3290 ^b 3258 ^c	52.9	9.9	19.3	14.8 ^b 7.1 ^c

Free = free N—H bonding; overtone = overtone of C=O.

^a The peak areas are based on total N—H stretching band area.

^b PPG based TPU.

^c PEG based TPU.

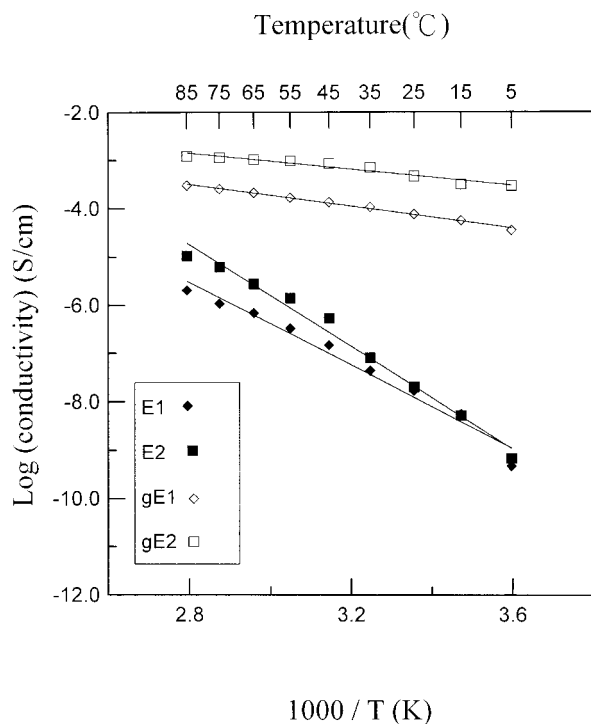


Figure 6 Temperature dependence of conductivity for TPU-E-LiClO₄ complexes containing 50% PC (gel type).

Conductivity

The temperature dependence of ionic conductivity of the homopolymers and copolymer were determined for additions of different lithium salt concentrations. Figures 6 and 7 show the temperature dependence of conductivity for TPU-E and TPU-P, respectively. The conductivity increased with temperature for both the homopolymers. At all temperatures, the conductivity of TPU-E was found to be higher than TPU-P. An increase in the concentration of LiClO₄ did not affect the conductivity much for TPU-E or TPU-P. It was observed by DSC measurement that the added Li⁺ ion coordinated with ether soft segment of E0 and P0, which caused an increase in T_g of the soft segment. In fact, $\Delta T_g/\Delta C$ of TPU-E was found to be higher than that of TPU-P. This would have made the conductivity of TPU-E much lower than TPU-P if the ionic conductivity was coupled with segmental motion of polymer matrix. The observed high conductivity for TPU-E compared to TPU-P could, therefore, be viewed as a result of the mobility of the Li⁺ ion in a decoupled way to the segmental motion of the polymer matrix.

For TPU-P, because $\Delta T_g/\Delta C$ was found to be low (seen in DSC results), the possibility of the

existence of a Li⁺ ion pair became dominant with high lithium salt concentrations, which caused the conductivity to decrease much in comparison with TPU-E. However, at temperatures higher than 65°C, TPU-P with high Li⁺ ion concentration showed a higher conductivity, and an associated high slope value for the Arrhenius plot was also noticed. The disassociation of ion pairs can explain such observations. Also, for the sample E₂, a slight deviation was observed from the linear Arrhenius plot at higher temperatures. This can be explained as caused by the coupling of conductivity to segmented motion in line with observations made by earlier workers.³⁷

TPU-C was found to have a higher conductivity (Fig. 8) than TPU-P at all temperatures. These observations were noticed for the addition of 0.2 and 0.7 mmol/g of LiClO₄. However, the conductivities of C1 and C2 were found to be lower than those of E1 and E2. FTIR results indicated that the added Li⁺ ion coordinated to both PEG and PPG soft-segment units of the copolymer. For the copolymer, DSC results also showed higher $\Delta T_g/\Delta C$ values for the addition of Li⁺ ion in comparison with TPU-P. Hence, the observed higher conductivities for C1 and C2 compared to P1 and

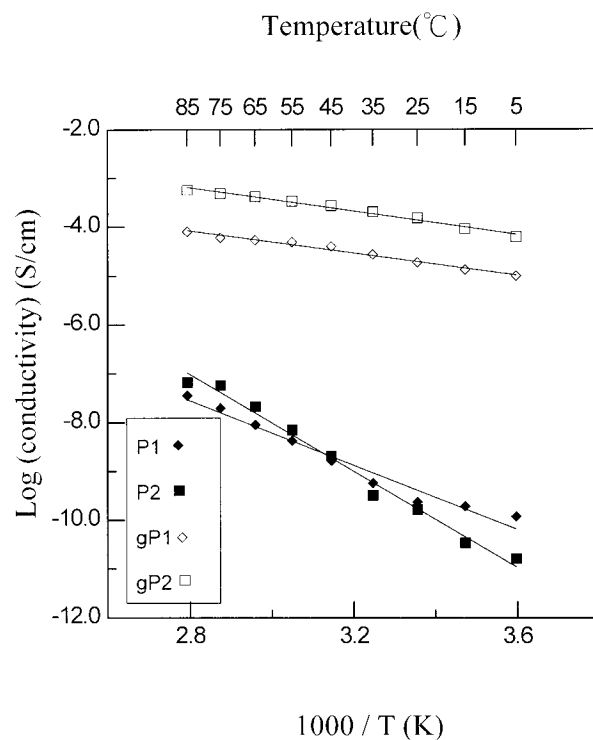


Figure 7 Temperature dependence of conductivity for TPU-P-LiClO₄ complexes containing 50% PC (gel type).

P2 might be explained as caused by the mobility of the Li^+ ion in a decoupled way to the segmental motion of the polymer. The existence of uncoordinated LiClO_4 contributed to the lower conductivity. As the temperature increased, part of the ion pair also dissociated, which resulted in the higher conductivity.

To improve the conductivity in the three TPU systems, gel-type electrolytes were prepared through impregnation with PC. The conductivity was found, strikingly, to increase with PC addition in all the three polymer systems for a constant addition of LiClO_4 . The results suggested that the addition of PC might have disturbed the hydrogen bonds in all three of the TPU systems and made the environment better for mobility of the Li^+ ions. Also, the higher dielectric medium (PC) made the dissociation of Li^+ salt greater. For all TPU systems, an increase in Li^+ salt concentration increased conductivity at all temperatures. The effect of temperature on conductivity was dominant with 0.20 mmol/g of LiClO_4 in all the three TPU systems. However, with an addition of a higher LiClO_4 concentration (0.70 mmol/g TPU), the difference in conductivity was insignificant. These observations indicate that for

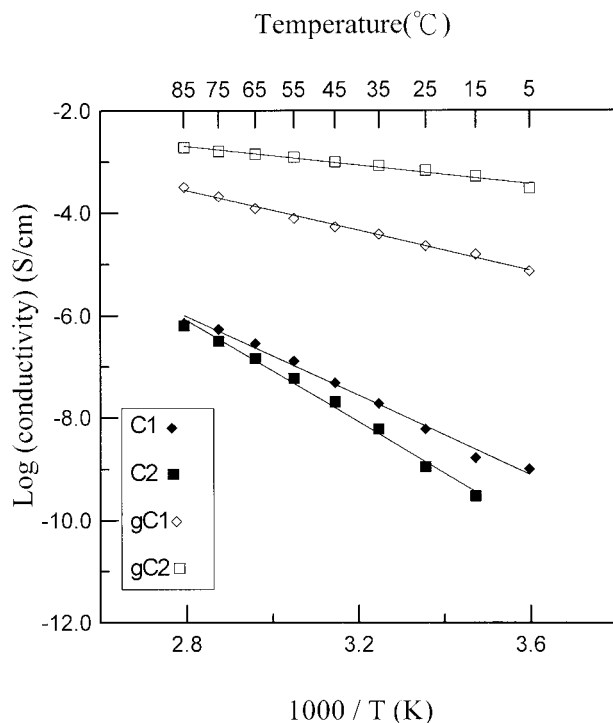


Figure 8 Temperature dependence of conductivity for TPU-C- LiClO_4 complexes containing 50% PC (gel type).

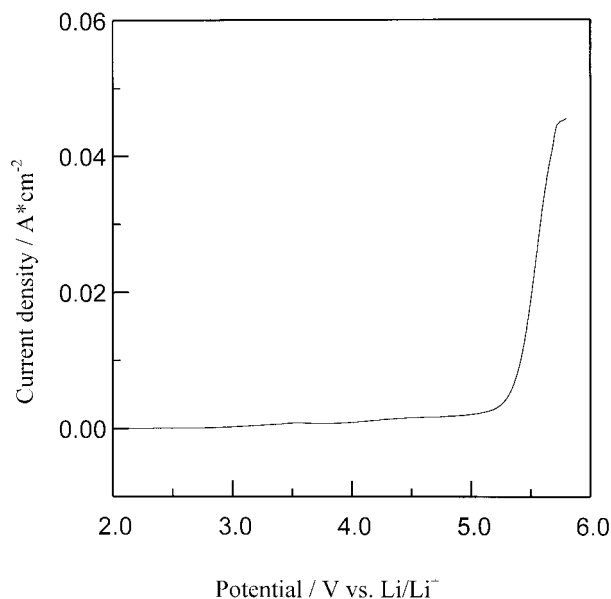


Figure 9 Linear sweep voltammogram for the laminated Li/GPE/SS cell.

the 0.20 mmol/g LiClO_4 addition (gE1, gP1 and gC1), PC improved the dissociation of LiClO_4 ; as a result, Li^+ ion and the dissociated Li^+ ion contributed to conductivity. The increase in this trend existed up to the addition of 0.7 mmol/g LiClO_4 (gE2, gP2 and gC2). Beyond that, the dissociated Li^+ ion concentration did not change much, which made the conductivity remain constant. The difference extent of the association of Li^+ ion with soft-segment groups in the three TPU systems made the free Li^+ ions available for ionic transport vary in the these three matrixes. The ionic conductivity for the three TPU systems was, thus, in the following order: TPU-E > TPU-C > TPU-P.

Electrochemical Stability

To ascertain the electrochemical stability potential window for the gel-type TPU-C, LSV was performed by the fabrication of a laminated electrode cell at ambient temperature in the glove box. The LSV of sample C0 is presented in Figure 9. The potential was scanned from 2.0 to 6.0 V (vs. Li/Li^+) at a sweep rate of 1 mV/sec. Figure 9 reveals that there is no evidence for any electrochemical reaction in the potential range 2.0–5.4 V. The oxidation peak appeared at 5.5 V. The result indicates that TPU-C-based gelled electrolyte has good electrochemical stability suited for applications in rechargeable lithium polymer batteries.

CONCLUSIONS

Changes in the morphology and ionic conductivity were evident between the TPU–LiClO₄ complexes based on PEG, PPG, and a mixture of PEG and PPG as soft segments. The dissolution of LiClO₄ increased the T_g of the soft segment but to different extents in the three TPU systems. There existed an interaction between the Li⁺ ion and the electron-rich components of the urethane moiety. The observed variations in T_g for the three TPUs in the presence of added lithium salt arose from the differences in molecular interactions between hard and soft segments of TPUs as a result of alterations in hydrogen-bonding characteristics. The thermal stability of the copolymer-based TPU was found to be better than the other two TPUs. FTIR and conductivity results provided evidence for the involvement of a combined interaction of both PEG and PPG soft segments with lithium ions for the copolymer. The fabricated laminated cell with gelled TPU-C electrolyte possessed good electrochemical stability in a wider potential window (2.0–5.4 V). We, therefore, conclude that the characteristics of TPU-C show its suitability for use as a gelled polymer electrolyte in lithium batteries.

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