

Soft Segmental Effect of Methylene Bis(*p*-cyclohexyl isocyanate) Based Thermoplastic Polyurethane Impregnated with Lithium Perchlorate/Propylene Carbonate on Ionic Conductivity

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ABSTRACT: Thermoplastic polyurethane (TPU) was employed as the polymer matrix for ion conduction as gelled electrolytes with lithium perchlorate (LiClO_4) in propylene carbonate (PC) solution. The TPU was prepared by methylene bis(*p*-cyclohexyl isocyanate) as the hard segment while employing both poly(ethylene glycol) (PEG) and poly(tetramethylene glycol) (PTMG) as the soft segments. The copolymer comprising both PEG and PTMG was prepared such that it possessed the combined characteristics of good conductivity from the former and good mechanical properties from the latter. All the polymers were characterized by gel permeation chromatography, differential scanning calorimetry, and Fourier transform IR spectroscopy. The conductivity data were obtained from alternating current impedance experiments. The results revealed that the copolymer containing both PEG and PTMG as the soft segments showed better performance than TPU containing either PEG or PTMG. The copolymer TPU(PEG/PTMG) proved to be a good gelled electrolyte from 5 to 85°C. This copolymer, impregnated with 150% LiClO_4/PC , possessed good mechanical strength and conductivity as high as 10^{-3} S/cm. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 935–942, 2001

Key words: polyurethane; ionic conductivity; gelled electrolyte

INTRODUCTION

Earlier works by Armand et al.¹ and Fenton et al.² prompted numerous investigations into the dissolution of alkali-metal salts in polyether polymers. Polymer electrolytes are ionic conductors formed by dissolving salts in suitable high molecular weight polymers, such as the polyethers, poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO),^{3,4} and so forth. Ionic transport occurs mainly through a coupling between the ions and

polymer segmental motion; hence, polymers of high flexibility are essential in order to achieve the conductivity ($>10^{-5}$ S/cm), which is necessary to be useful in various ambient temperature applications such as solid-state batteries. Harris and colleagues⁵ used PEO as the host polymer and showed that ionic conduction occurs mainly in the amorphous regions of the polymer. Considering the high tendency of PEO to crystallize at ambient temperature, some studies^{6–8} attempted to increase the amorphous phase of the polymer by extensive structural modifications.

The ionic conductivity of solid polymer electrolytes (solvent free) is related to the segmental motion in the amorphous regions of the polymer host. In recent years there were numerous studies on the electrical characteristics of such phases,

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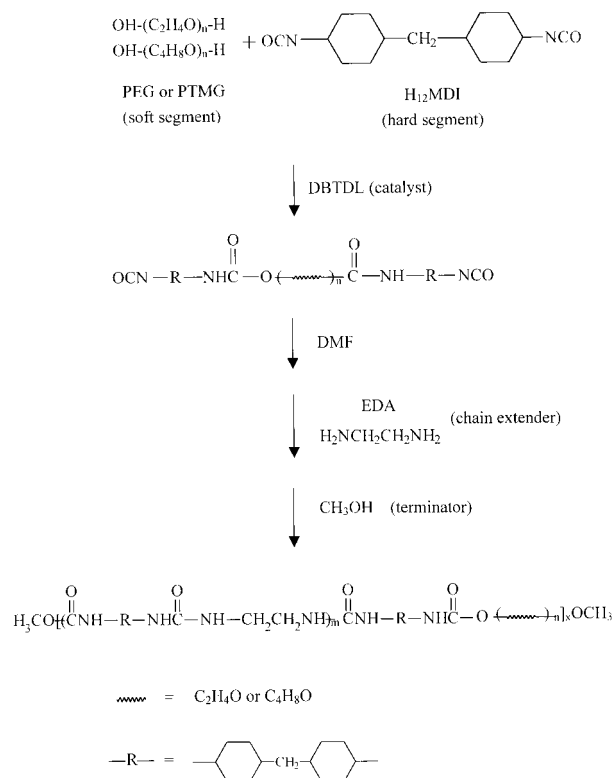
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including measurements of the conductivity as a function of the salt concentration, host molecular weight, temperature, pressure, and frequency of the electrical perturbation. Theoretical models for the conductivity mechanism were proposed.⁹

Poly(ethylene glycol) (PEG) and poly(tetramethylene glycol) (PTMG) were used as the soft segments of host waterborne polyurethane (WPU) in our earlier studies.¹⁰ The electrolyte based on WPU(PTMG) blended with PEO was previously reported to possess the dual-phase characteristics of polymer composites in which PEO absorbs LiClO₄ in propylene carbonate (PC) solution for the ion conducting phase while WPU(PTMG) only provides the mechanical strength.¹¹ A WPU-(PEG) based electrolyte was reported to contribute good conductivity, but it had very poor mechanical strength at high temperature. Thermoplastic PU (TPU) is a segmented polymer comprising alternating sequences of soft segments and hard segments, which constitute a unique microphase separated structure. When there is a high degree of phase separation, hard segments tend to generate glassy or crystalline regions and randomly arranged soft segments form the amorphous regions. In our study we used TPU made from methylene bis(*p*-cyclohexyl isocyanate) (H₁₂MDI) as the hard segment and both PEG and PTMG as soft segments in order to ascertain the efficiency of this TPU as a host material for electrolytes.

For practical use, a polymer electrolyte with high ionic conductivity combined with high durability is required. In aiming toward the high conductivity of TPU(PEG) and good mechanical properties of TPU(PTMG), we tried to blend these two systems in order to have the compromised characteristics of good conductivity and strength required for a polymer electrolyte. Unfortunately, these two TPUs are not miscible. Hence, an alternative route was attempted to get the combined characteristics by incorporating both PEG and PTMG as soft segments in a single TPU. This can result in better mixing of the PEG and PTMG units through chemical linkages of the hard segments instead of only van der Waals interaction in physical blending.

IR spectroscopy is a powerful tool and is extensively employed to identify hydrogen bonding.^{12–18} Particularly for polyether based TPUs, the fraction of the hydrogen-bonded carbonyls (NH—O=C bond) defined by a hard–hard segmented hydrogen bond was used to evaluate the extent of phase separation. On the other hand,



Scheme 1 The outline of the process for preparing the TPU.

the fraction of the hydrogen-bonded ether oxygens (NH—O bond) represented the extent of phase mixing between the hard and soft segments. Recently, several studies were made to elucidate the relationships between structure and properties within TPUs using Fourier transform IR spectroscopy (FTIR)^{12–18} and differential scanning calorimetry (DSC).^{19–22}

EXPERIMENTAL

Synthesis of TPU

A brief procedure outlining the preparation of TPU is presented in Scheme 1. The reaction was carried out in a batch reactor, which was a 2000-mL four-necked round-bottomed flask with an anchor type stirrer, a nitrogen inlet and outlet, and a thermocouple connected to the temperature controller. The raw materials employed in this study are listed in Table I. PEG and PTMG were used as the soft segments and dried in a vacuum oven at 85°C for 24 h.

Table I Raw Materials for Synthesis of TPUs

Designation	Chemical Identification	Suppliers
PEG	Poly(ethylene glycol), $M_w = 2000$	Showa Chemical Inc.
PTMG	Poly(tetramethylene glycol), $M_w = 2000$	Showa Chemical Inc.
H ₁₂ MDI	Methylene bis(<i>p</i> -cyclohexyl isocyanate)	Aldrich Chemical Inc.
DMF	Dimethylformamide	Tedia Company Inc.
EDA	Ethylene diamine	Merck Chemical Inc.
MeOH	Methyl alcohol	Tedia Company Inc.

The PEG ($M_w = 2000$, 50 g, 0.025 mol), PTMG ($M_w = 2000$, 50 g, 0.025 mol), and H₁₂MDI ($M_w = 262.35$, 26.235 g, 0.1 mol) were added into the reactor at the same time to make a prepolymer of TPU by maintaining the NCO/OH as 2. The temperature was initially kept at 50°C. After completely mixing the reactants by stirring (100 rpm), 0.05 g of the 10 wt % catalyst dibutyltin dilaurate was added into the batch to catalyze the reaction and then the temperature of the batch was set at 85°C. After a 6-h reaction, 600 g of dimethylformamide (DMF) was added to completely dissolve the prepolymer; and then the chain extender, a 10 wt % solution of ethylene diamine (3 g, 0.05 mol) in DMF, was added to complete the polymerization reaction. The viscosity was found to increase in this step. After an hour of reaction, a few drops of methyl alcohol were added to terminate the reaction. In order to make comparisons, the PEG and PTMG were polymerized separately with H₁₂MDI to make two other TPUs. The NCO/OH ratio for these two TPUs was also maintained as 2. In this study, TPU(PEG), TPU(PEG/PTMG), and TPU(PTMG) were assigned to be P1, P2, and P3, respectively, and the gel polymer electrolytes that intake LiClO₄/PC were referred to as G1, G2, and G3. The descriptions of the different components of these three TPUs are presented in Table II.

Gel Permeation Chromatography Measurements

The number-average molecular weight (M_n) and weight-average molecular weight (M_w) of the syn-

Table II Components of Synthesized TPUs

TPU Code	Hard Segment	Soft Segment	NCO/OH Molar Ratio
P1	H ₁₂ MDI	PEG	2
P2	H ₁₂ MDI	PEG/PTMG	2
P3	H ₁₂ MDI	PTMG	2

thesized polymers were measured with a Shimadzu gel permeation chromatography instrument fitted with a Shimadzu HPLC pump and a differential refractometer.

These polymers were dissolved in DMF at a concentration of 1 wt %. The solutions were then injected into the Jordi gel divinyl benzene mixed bed with a 10-mm i.d. and 250-mm length at a flow rate of 2.0 mL/min. The system was calibrated by 10 polystyrene standards. The molecular weight and molecular weight distribution of the synthesized TPUs are listed in Table III.

DSC Analysis

The thermal analysis of the TPU films were performed by TA DSC 2010 DS calorimeter with a heating rate of 10°C/min. The temperature was equilibrated at -100°C and then scanned from -100 to -20°C. About 3 mg of the dried TPU samples were preweighed and then put on the aluminum capsules for analysis.

FTIR Investigation

FTIR was used to investigate the functional groups of the PUs. For comparison of P1, P2, and P3, three TPUs were independently dissolved in DMF to make dilute solutions and then dropped on KBr pellets. The samples were placed in a vacuum oven at 120°C for 24 h to remove residual solvent and moisture. The IR spectra were recorded with a Nicolet 550 system.

Table III Molecular Weights and Distributions of Synthesized TPUs

TPU Code	P1	P2	P3
M_n	70200	45700	54300
M_w	173000	110300	101500
M_w/M_n	2.47	2.41	1.87

M_w/M_n , polydispersity index.

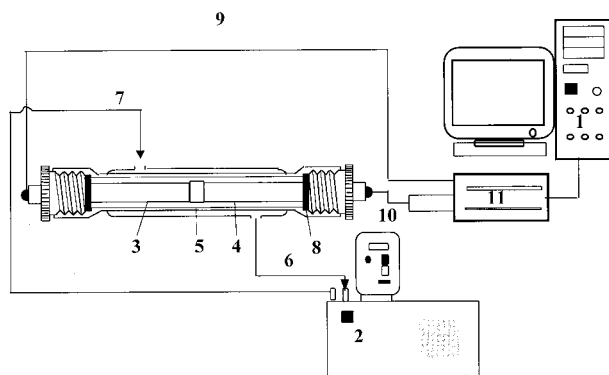


Figure 1 The construction of the test cell and circuit diagram for electrochemical analysis: 1. personal computer; 2. thermostat circulator; 3, 4. Stainless steel ($D = 1\text{-cm}$ diameter); 5. polymer electrolytes ($D = 1\text{-cm}$ diameter); 6, 7. inlet and outlet of circulating fluid; 8. o-ring; 9. working electrode; 10. reference and counter electrode; 11. CMS300 EIS system or PGSTAT20.

Preparation of Electrolytes

Polymers P1, P2, and P3, which contained 14.0, 14.0, and 13.6 wt % solids, respectively, were dissolved in DMF to get dilute solutions. The solutions were cast onto glass petri dishes and dried in a vacuum oven at 50°C for several days to make polymer films with $150\text{--}200\ \mu\text{m}$ thickness.

The LiClO_4 (anhydrous, Anderson Phys. Lab.) was dissolved in PC (anhydrous, 99.7%, Aldrich) to make 1M LiClO_4/PC solution inside the glove box. The electrolytes were prepared by dipping dried TPU films into 1M LiClO_4/PC solution until the swelling percentage reached the required values. The extent of the swelling weight ($\text{Sw}\%$) was defined by the following equation:

$$\text{Sw} = (w - w_0)/w_0 \times 100\% \quad (1)$$

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

The gelled electrolytes prepared from P1, P2, and P3 were assigned as G1, G2, and G3, respectively.

On the other hand, $\text{LiClO}_4/\text{DMF}$ solution was also mixed with TPU/DMF solution to make a dry film with a constant amount of lithium salt ($0.5\ \text{mmol/g}$ TPU). This was followed by the dropwise addition of different amounts of PC to the film to change the ratio of PC/LiClO_4 .

Conductivity Measurement

The conductivity of the gelled electrolytes was measured via impedance analysis with electro-

chemical cells consisting of the electrolyte film sandwiched between two blocks of stainless steel, which was sealed with an o-ring in a jacketed glass tube where heating/cooling water circulation was made through the outer jacket. Figure 1 is the outline of the cell described above. The impedance analysis was performed by using a CMS300 EIS system (Gamry Instruments, Inc.) with an SR810 DSP lock-in amplifier (Standford Research Systems, Inc.) under an oscillation potential of $10\ \text{mV}$ from 100 to $1\ \text{kHz}$.

RESULTS AND DISCUSSION

DSC Analysis

Figure 2 indicates the DSC thermograms of the three TPUs. As expected from the nature of the soft segments, the glass-transition temperatures (T_g) of the TPUs were in the order $\text{P1} > \text{P2} > \text{P3}$. The T_g values were -42 ± 1 , -59 ± 1 , and $-79 \pm 1^\circ\text{C}$ for P1, P2, and P3, respectively. The soft segment of P1 was PEG, which has a shorter chain length than that of P3 where the soft segment was PTMG. The shorter chain length of the segment in P1 made the soft segment more rigid and provided a higher T_g than that of P3. Because P2 contains both PEG and PTMG as soft seg-

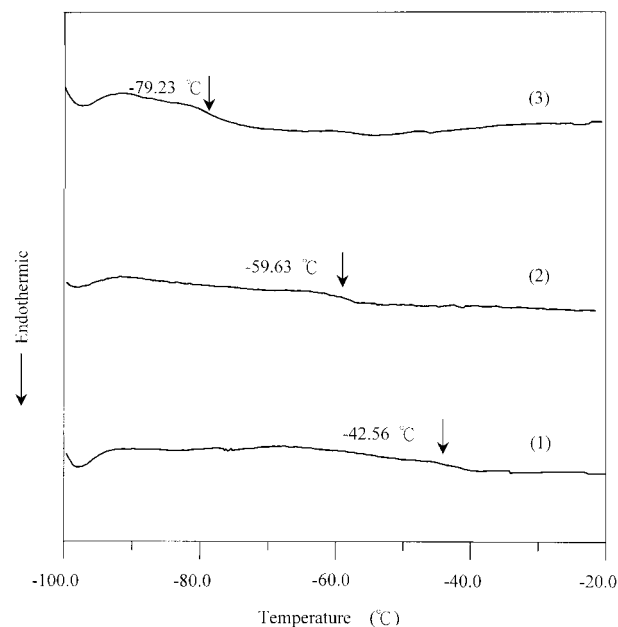


Figure 2 DSC thermograms of P1 (curve 1), P2 (curve 2), and P3 (curve 3).

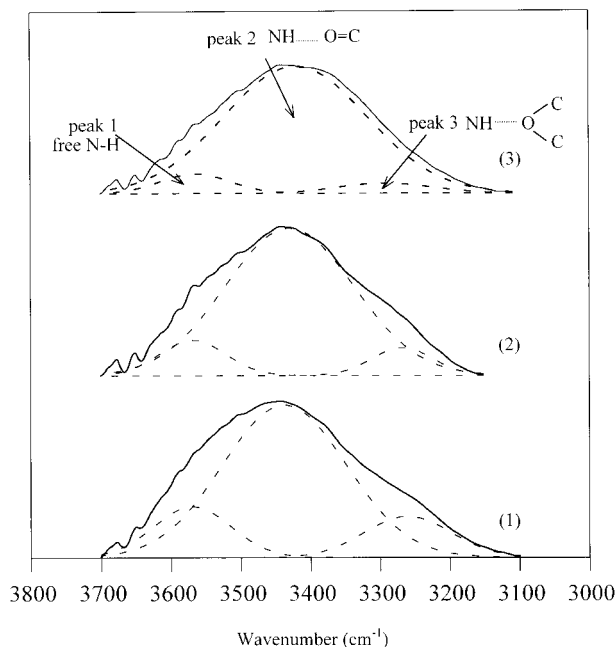


Figure 3 The deconvolution of N—H stretching for TPUs with different soft segments: P1 (curve 1), P2 (curve 2), and P3 (curve 3).

ments, it showed an intermediate T_g between P1 and P3.

IR Analysis

FTIR recorded at ambient temperature was used to get an idea about the phase morphology of the TPUs. The main spectrum region in this study was the N—H stretching vibration in the region of $3000\text{--}3700\text{ cm}^{-1}$. The deconvolution of the N—H stretching region was done to the best fit by a Gaussian-Lorentzian sum. Figure 3 is the deconvolution of the N—H stretching for the TPUs and the results are listed in Table IV. The three peaks representing the free —NH stretching vibration (peak 1), the —NH stretching vibration where —NH is H bonded with the urethane carbonyl oxygen of the hard segment (peak 2), and the

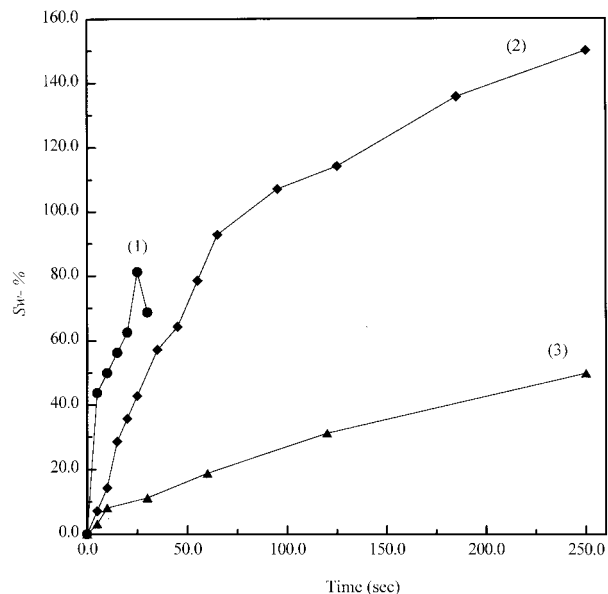


Figure 4 The swelling rate of P1 (curve 1), P2 (curve 2), and P3 (curve 3).

same where —NH is H bonded to the ether oxygen of the soft segment are considered here for discussion (peak 3). Peak 2 can consequently be taken as a measure of the extent of phase separation and peak 3 as phase mixing. From the results in Table IV, P1 possesses the highest extent of phase mixing as a consequence of the soft segment (PEG) with a short chain length (—C—C—O—) and P3 shows a high extent of phase separation because of its longer main chain length (—C—C—C—C—O—). However, the behavior of P2 was found to be in between P1 and P3. The higher extent of phase separation resulted in the lower swelling rate of the TPU, and at the same time, a higher extent of phase mixing resulted in a higher swelling rate.

Impregnation with LiClO_4/PC

The effect of time on the extent of swelling weight for P1, P2, and P3 is given in Figure 4. The pre-

Table IV Deconvolution Results of N—H Stretching

TPU Code	Peak Position			Peak Area (%)		
	1	2	3	1	2	3
P1	3570.1	3437.8	3260.8	14.9	71.6	13.5
P2	3569.1	3429.9	3268.0	10.2	82.5	7.3
P3	3564.2	3420.4	3292.6	6.8	88.6	4.6

pared polymer films with about 150–200 μm thickness were dipped into 1M LiClO_4/PC solution and the weights of the wet films were measured after an interval of time. The swelling weight percentage (as defined in the experimental section) was calculated using eq. (1). Figure 4 shows the order of the swelling rate, which shows that $\text{P1} > \text{P2} > \text{P3}$. It can be expected that the Li^+ salt would get into the P1 structure more easily because of the softer nature of P1. But after 81% swelling, there was a decrease in the swelling rate. This may have been due to the dissolution of a part of the P1 in DMF when kept immersed for a long time. This phenomenon also revealed that the strength of P1 was very weak. On the other hand, the strengths of P2 and P3 were better than that of P1 by using the swelling values. As evident from Figure 4 and P2, the swelling weight percentage for P2 was higher than P1, and it did not show any decreasing tendency. The P2 and P3 films both showed better stability when kept immersed in the solution throughout the day. Because P3 only contained more rigid PTMG in the soft segment, the swelling weight percentage of P3 was lower than that of P2 when swelled for an identical period of time.

Conductivity Measurement

Figure 5 is the Arrhenius plot of the conductivity of these three TPUs with the same content (50%) of 1M LiClO_4/PC solution. The conductivity of the gelled electrolytes under any specific temperature showed the same trend as noticed with the swelling rates of the TPUs (i.e., $\text{G1} > \text{G2} > \text{G3}$). We could not get the conductivity data for G1 above 55°C. The presence of a very soft nature in the P1 may have resulted in flow at high temperature, which might have led to a short circuit of the cell at the time of the conductivity measurement. This fact also revealed the earlier information that the strength of P1 is much lower than the other two TPUs. From the results of Figure 4 and Figure 5 it is evident that P1 contributed good conductivity but low strength, and P3 had the opposite trend with good strength but low conductivity. However, P2 had a favorable balance of P1 and P3 with sufficient conductivity and strength to be used as a polymer electrolyte. As can be seen from Figure 5, the conductivity of each TPU increased with the increasing temperature. This can arise because of the higher mobility of Li^+ at higher temperatures. Because all three TPUs were made with the same hard segment, H_{12}MDI , and the

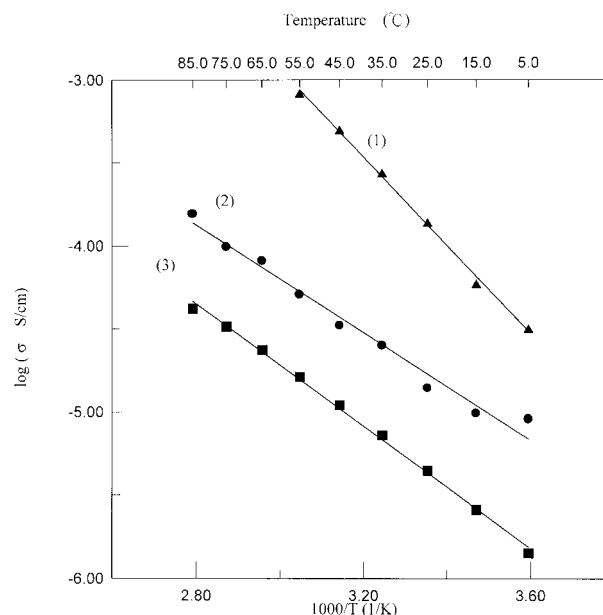


Figure 5 An Arrhenius plot of G1 (curve 1), G2 (curve 2), and G3 (curve 3) with 50% 1M LiClO_4/PC solution.

only difference between them was their soft segment, the difference in conductivity data can be explained by the soft segment characteristics. The higher conductivity of G1 at any temperature may be due to the higher polarity of the PEG, which facilitates easier dissociation of the Li salt and hence a higher number of charge carriers. In TPUs the polarity of the PTMG is lower than PEG and hence the dissociation of Li salt is less facilitated in comparison with PEG. The conductivity of G2 was found to be in between G1 and G3.

Figure 6 is the Arrhenius plot of G2 with 50% 1M LiClO_4/PC solution. The conductivity determined during the heating scan almost overlap with those found in the following cooling scan. This is a convincing indication that, in the temperature range examined, no chemical changes or partial crystallization phenomena occur in the electrolyte. In other words, the thermal stability of G2 as an electrolyte can be taken as good.

Figure 7 is the Arrhenius plot of G2 with different electrolyte contents. It is reasonable that the conductivity increased with the content of Li^+ ions. The curves can be fitted into straight lines with nearly the same slopes except for curve 4, which is slightly less than the others. All of these conductivity data can be analyzed by the Arrhenius phenomenological relationship as follows:

$$T = A \exp\left[-\frac{E_{\alpha/h_n T}}{R}\right] \quad (2)$$

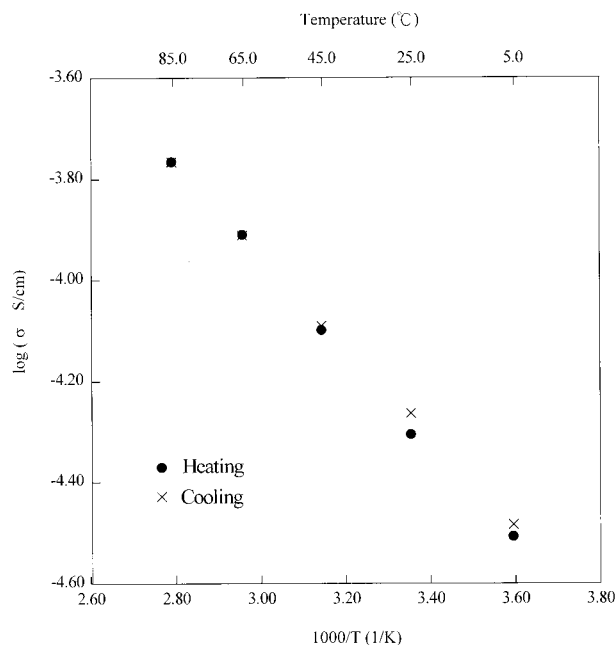


Figure 6 An Arrhenius plot of G2 with 50% 1M LiClO₄/PC solution.

The Arrhenius form is used when the ions are decoupled from the polymer host and activated hopping is dominant for ionic transport.

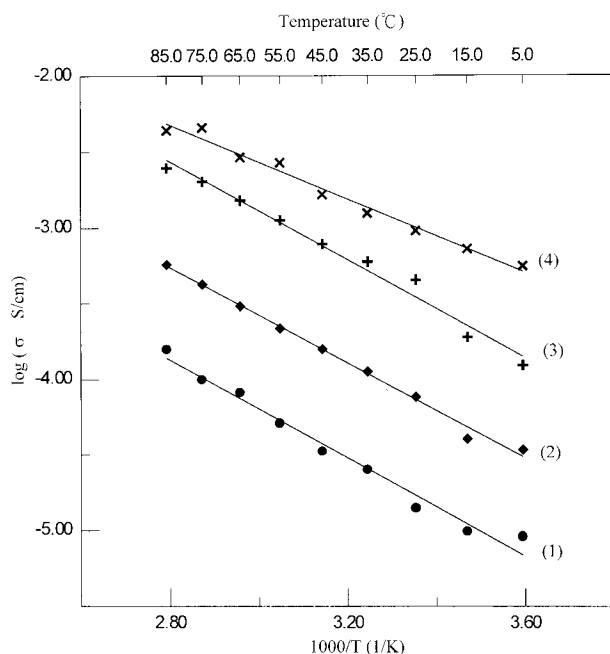


Figure 7 An Arrhenius plot of G2 with different contents of 1M LiClO₄/PC solution (%): 50 (curve 1), 70 (curve 2), 100 (curve 3), and 150 (curve 4).

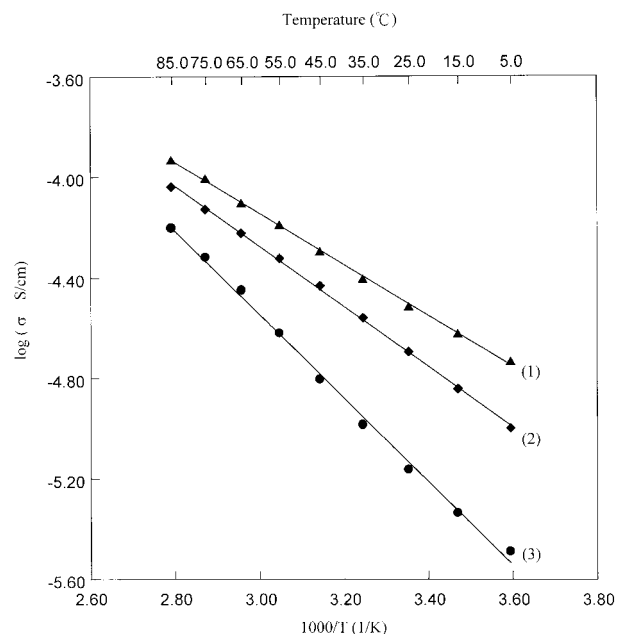


Figure 8 An Arrhenius plot of G2 with different PC/LiClO₄ ratios (g/mol): 1085/1 (curve 1), 862/1 (curve 2), and 592/1 (curve 3).

The slope of the straight line in the Arrhenius plot is $-E_a/2303 k_B$ where E_a is the activation energy for transportation of Li⁺ in the polymer host. The smaller the slope, the smaller is the E_a and hence the easier is the movement of the Li⁺ ions. The lower slope of G2 with 150% LiClO₄/PC can be explained as a result of the transition from a gelled electrolyte to a liquid electrolyte. When the PC content in the system is very high (here it is ~150%), the electrolytes may find themselves in a liquid environment rather than in a polymer gel matrix, making the energy for movement of Li⁺ ions in a liquid-like environment less. In the case of TPU with 150% LiClO₄/PC, the transformation into a liquid-like environment is certainly possible. On the other hand, a comparison between Figure 5 and Figure 7, when the content of LiClO₄/PC is 100%, shows that the conductivity of G2 is higher than that of G1. Because the strength of P2 is higher than P1, this polymer is a better choice for use as a gelled electrolyte.

Figure 8 illustrates the effect of PC on the conductivity. Here the amount of LiClO₄ was kept constant while the PC in the polymer films was changed. As the amount of PC increased, the conductivity increased. PC acts as a plasticizer in the electrolyte to dissociate LiClO₄ and increase the mobility of ion carriers (Li⁺). It can also be seen from Figure 8 that the slopes of the straight lines

with higher content of PC are smaller. The same reason as given earlier may be applied for this also. The increased PC content in the polymer host would make the polymer film close to a liquid type, making the energy required for Li^+ to move relatively low.

CONCLUSION

TPU(PEG/PTMG) was used as a gelled electrolyte. The characteristics were compared with its two parent systems, TPU(PEG) and TPU(PTMG). It was found that TPU(PEG/PTMG) possessed characteristics intermediate between TPU(PEG) and TPU(PTMG) when compared by the swelling rate, strength, T_g , phase separation, and conductivity. TPU(PEG/PTMG) showed an excellent combination of conductivity and mechanical properties arising from the combined presence of PEG and PTMG, which were better than the parent systems TPU(PEG) and TPU(PTMG), respectively. The results also showed that the thermal stability of the polymer electrolyte was good, resulting in a high conductivity of about 10^{-3} S/cm at room temperature. From these results it can be concluded that copolymerization of PEG and PTMG as soft segments to produce a TPU is a good way to make a well-behaved polymer gelled electrolyte.

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