

Effect of Salt Concentration on the Glass Transition Temperature and Ionic Conductivity of Poly(ethylene glycol)-Polyurethane/LiClO₄ Complexes

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Abstract: Solid polymer electrolytes based on poly(ethylene glycol)-polyurethane (PEG-PU) complexed with LiClO₄ salt have been prepared by the solvent casting method. A PEG-PU material (PEG:4,4'-diphenylmethane diisocyanate:1,4-butanediol = 1:2:1) was synthesized through a typical two-step condensation reaction. We investigated the effects of the salt concentration on the ionic conductivity (σ) and the glass transition temperature (T_g) of the complex electrolytes by using alternating current impedance spectroscopy, differential scanning calorimetry, and dynamic mechanical thermal analysis. The measured values of both σ and T_g exhibited similar tendencies in that they had maxima within the range studied, probably because of two opposite effects, i.e., the increased number of carrier ions and the decreased chain mobility (or increased T_g) caused by the increase in the salt concentration. The highest conductivity, on the order of $2.43 \times 10^6 \text{ Scm}^{-1}$, was obtained at an [O]/[Li⁺] ratio of ca. 16 (0.92 mol salt per kg of matrix polymer).

Keywords: thermal T_g , dynamic T_g , chain mobility, ionic conductivity.

Introduction

Since Wright's discovery of the ionic conductivity in alkali metal salt complexes of poly(ethylene oxide) (PEO),^{1,2} many studies on solid polymer electrolyte (SPE) systems of polymer/salt complex-type have attracted considerable interest because of their potential application in high-energy density batteries, sensors, electrochromic devices, light emitting diodes (LEDs), field effect transistors (FETs), etc.³⁻⁹ Various types of polyurethanes (PUs) have also been used as the matrix for SPE due to their good electrochemical stability, excellent mechanical properties and low glass transition temperature (T_g),¹⁰⁻¹² in addition to their ion solvating property. While hard segments making up the PU chain determine the inter-chain interaction and work as a supporting structure to sustain the polymer electrolyte, soft segments function as a pathway to transmit the ionic diffusion and chain motion. So the T_g characterizing the segmental mobility in the amorphous phase of a polymer matrix is an important factor in determining the ionic conductivity for polymer

electrolytes.¹³⁻¹⁵ Generally, the T_g 's of polymer-salt complexes increase with the addition of salt due to the formation of transient cross-linking between polymer chains via the coordinated interaction between polymer chains and salt. However, at high salt concentrations the decrease in T_g (or increase in chain mobility) of complexes may arise from the increased d spacing due to the electrostatic repulsion between anions, and from the decreased interaction between polymer chains and salts owing to the formation of ion pairs and/or higher order ion aggregates.^{16,17}

In this work, we studied the effects of salt content on the ionic conductivity and T_g for poly(ethylene glycol)-polyurethane (PEG-PU)/LiClO₄ complex electrolytes prepared by the solvent casting method using a.c. impedance spectroscopy, differential scanning calorimetry (DSC) and dynamic mechanical thermal analyzer (DMTA). Comparison between thermal T_g (by DSC) and dynamic T_g (by DMTA) at different salt contents was also made for reference.

Experimental

Materials. Poly(ethylene glycol) (PEG: number-average molecular weight = 1,000; Aldrich Chemical Co.) was dried

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at 65 °C in a vacuum oven for 48 h before use. 4,4'-diphenylmethane diisocyanate (MDI; Aldrich Chemical) was purified by vacuum distillation. 1,4-butanediol (BD; Aldrich Chemical) was dried by refluxing over CaH₂ for 4 h to remove the trace water and then was distilled under vacuum. The solvent *N,N*-dimethyl formamide (DMF; Junsei Chemical Co. Ltd.) was dried and distilled before use. The lithium perchlorate (LiClO₄) to be complexed with PEO was Aldrich product. It was dried under vacuum at 120 °C for 24 h prior to use.

Preparation of Polyether Polyurethane (PEG-PU). A polyether polyurethane (PEG-PU) material (PEG: MDI: BD = 1:2:1 in mole ratio) used as the matrix polymer for solid electrolyte was synthesized via the typical two-step condensation reaction. An outline of the process used in this study for preparation of PEG-PU is shown in Scheme I.¹⁸

PEG and MDI were simultaneously added to the reactor that was charged under a nitrogen gas atmosphere, to form a pre-polymer of PU where the (mol) ratio of NCO/OH was 2. The temperature was kept at 50 °C initially. After proper mixing (150~200 rpm), 0.15 wt% dibutyltin diaurate was added into the reactor to catalyze the reaction and then the temperature was raised to 70 °C. One-step reaction was stirred for 1.5 h. Then, BD was added dropwise and stirred for an additional hour. The viscosity of the reaction system was found to increase in this step. To ensure a complete reaction, the polymer solution was stirred at 80 °C for 3 h and precipitated into a large amount of distilled methyl alcohol. After filtration, the material obtained was dried in a vacuum-drying oven at 60 °C for 48 h.

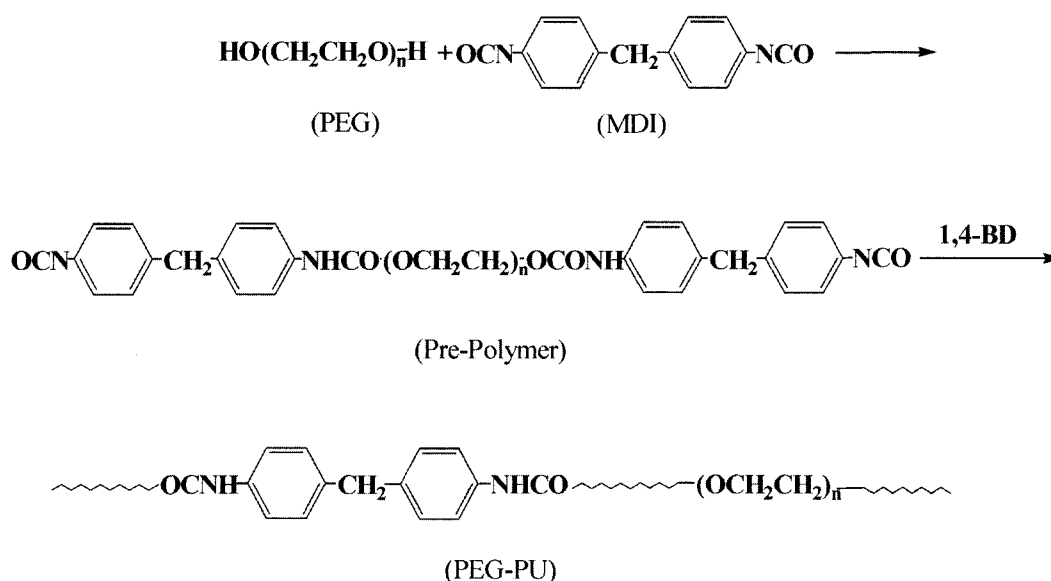
Preparation of the Complex Samples. Films of PEG-PU/LiClO₄ complexes were prepared by the solution-cast technique. The samples with different salt contents, expressed

as the ratio of ether oxygen to alkali metal cation [O]/[Li⁺], were prepared by an appropriate amount of PU and LiClO₄ being dissolved in DMF and then poured onto a Teflon plate. After the solvent was evaporated at 60 °C in an oven for 24 h, the films were transferred to a vacuum oven and further dried 60 °C for 24 h to remove the residual solvent. The formation of the bubbles could be avoided if the polymer solution in the hot crucible was vacuum-dried prior to making the film. PEG-PU/LiClO₄ complex films with diameter 15 mm and thickness 0.25~0.35 mm were finally obtained.

Characterization. The formation of complexes between polymer chain and salt was confirmed by IR spectra with Bruker IFS66 FT-IR spectrometer at a resolution of 2 cm⁻¹.¹⁸ The ionic conductivity (σ) of the electrolyte films was evaluated by a Hewlett-Packard 4192AAC impedance analyzer in the frequency (f) range 10-10⁶ Hz. The sample films were sandwiched between symmetrical cells containing blocking stainless steel (SS) electrodes. Generally, blocking electrodes (where the mobile ions from the electrolyte can not penetrate the electrode) are commonly used for the estimation of SPE bulk resistances.³ The σ was then calculated using the following equation:

$$\sigma = (1/R_b) \times (d/S) \quad (1)$$

where d is thickness of the sample, S the area of the electrode, and R_b the effective d.c. resistance of the bulk SPE determined from the complex impedance spectrum called the Cole-Cole plot.¹⁹ The thermal and dynamic T_g s of SPE samples were determined using a Perkin-Elmer Pyris 1 DSC system from -80 to 80 °C at the heating rate of 10 °C/min and DMTA MK III for the temperature range from -100



Scheme I. Synthesis of poly(ethylene glycol)-polyurethane (PEG-PU).

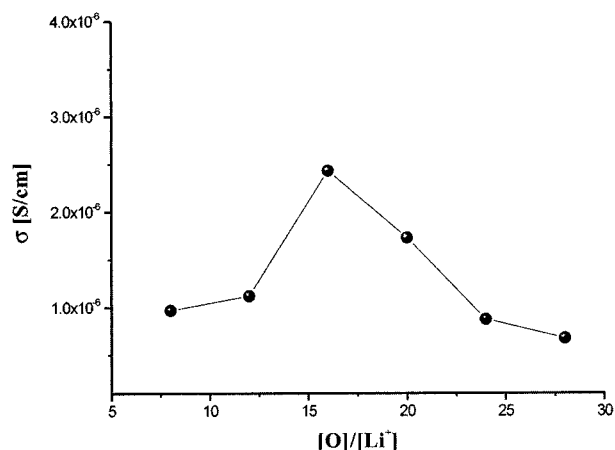


Figure 1. Ionic conductivity (σ) at room temperature as a function of $[O]/[Li^+]$ ratio for the PEG-PU polymer electrolyte complexed with $LiClO_4$.

to 100 °C, respectively.

Results and Discussion

The values of ionic conductivity (σ) for complex electrolytes as determined from the diameters (or intersections with the Z' axis) of semi-circles shown in the a.c. impedance spectra using eq. (1) are plotted as a function of salt contents (expressed as the $[O]/[Li^+]$ ratio) in Figure 1 at room temperature. In polymer/salt complex-type electrolytes, the dependence of conductivity on salt concentration generally reveals a maximum due to two opposing combined effects, i.e., the increased number of charge carrier (or carrier ions) dissociated and decreased segmental mobility in the amorphous chain (or increased T_g) caused by the addition of salt.³

As shown in Figure 1, the initial increase in conductivity upon the addition of salt in the polymer matrix is presumably due to an increase in the number of charge carriers in the matrix. For larger salt concentrations, the build-up of charge carriers will be offset by the retarding effect of ion aggregates (such as ion pairs) acting as the barrier for the ionic movement. Accordingly, the ionic conductivity reaches the maximum value of ca. $2.43 \times 10^{-6} \text{ Scm}^{-1}$ near the salt content $[O]/[Li^+] = 16$ (corresponding to 0.92 mol per kg matrix polymer) for PEG-PU/ $LiClO_4$ complex, which is much larger than that ($\sigma \approx 10^{-7} \text{ Scm}^{-1}$) for PEG-PU/ $NaSCN$ complex.¹⁸ This difference may arise because $NaSCN$ resulted in a higher degree of ion-pairing due to lower complexing ability with PEO-based polymer matrix of lower dielectric constant compared to $LiClO_4$.³

DSC measurements were carried out on quenched pure PEG-PU and PEG-PU/ $LiClO_4$ complex samples at a heating rate of 10 °C/min to determine thermal T_g values of complexes at different salt contents, whose results are displayed in Figure 2, and summarized in Table I.

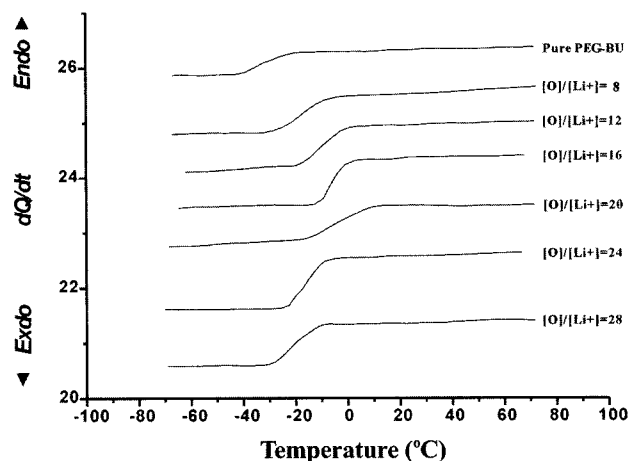


Figure 2. DSC thermograms of PEG-PU/ $LiClO_4$ complexes at different $[O]/[Li^+]$ ratios.

Table I. DSC Glass Transition Temperature (T_g) and Specific Heat Difference (ΔC_p) at the Transition Interval as a Function of $[O]/[Li^+]$

| $[O]/[Li^+]$ | Onset (K) | Endpoint (K) | T_g^a (K) | ΔC_p (kJ/mol) |
|--------------|-----------|--------------|-------------|-----------------------|
| Pure PEG-PU | 233.6 | 247.0 | 239.8 | 0.31 |
| 8 | 248.4 | 258.2 | 253.3 | 0.32 |
| 12 | 257.6 | 274.7 | 266.1 | 0.62 |
| 16 | 264.0 | 272.4 | 268.2 | 0.62 |
| 20 | 261.7 | 283.1 | 272.4 | 0.49 |
| 24 | 254.7 | 266.4 | 260.5 | 0.72 |
| 28 | 245.6 | 260.7 | 253.1 | 0.60 |

^a T_g was taken as the midpoint at the transition interval in DSC thermogram.

As can be seen from this Table, the DSC T_g initially increases with increasing salt content (or decreasing $[O]/[Li^+]$ ratio), similar to the case of Figure 1. This tendency is in accord with the general expectation that T_g will increase owing to the formation of transient cross-linking points between PU chain segments via the coordinated interaction between ether oxygen and lithium cations caused by the addition of salt. However, at higher salt contents beyond $[O]/[Li^+] = 20$ the T_g value gradually decreases. A possible explanation for this would be as follows. When lithium cations are present as free ions, they can act as transient cross-linkers between polymer chains, resulting in an increase in T_g . However, once ion pairs and/or higher-order ionic aggregates start to form at high concentrations of the salt, lithium ions may no longer act as transient cross-linkers. Accordingly, the interaction between polymer chains and salt may be weakened, thereby yielding the decrease in T_g (or increases in chain mobility) of polymer-salt complexes at

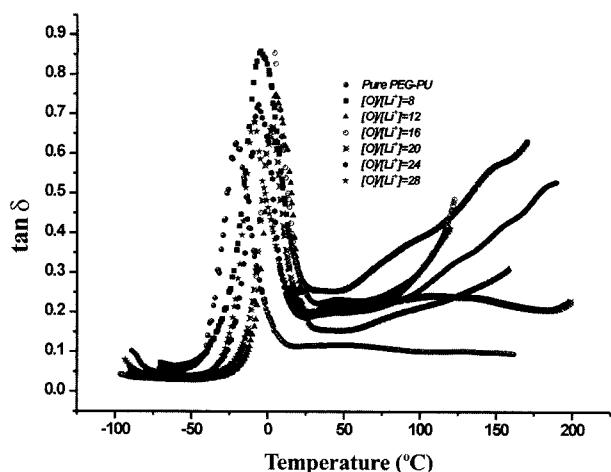


Figure 3. Tan δ curves as a function of temperature for PEG-PU/LiClO₄ complexes at a frequency of 1 Hz.

high salt concentrations.^{16,17}

On the other hand, as a preliminary step for the ensuing rheological study on polymer/salt complex electrolytes, dynamic T_g 's were measured on pure PEG-PU and PEG-PU/LiClO₄ complex samples under the condition of small oscillatory strain amplitudes by using DMTA. Figure 3 shows the temperature dispersions of loss tangent, $\tan \delta = E''/E'$ (where E' and E'' are storage and loss tensile moduli, respectively), for PEG-PU/LiClO₄ complexes of different salt contents at a frequency of 1 Hz.

All dynamic T_g points for complex samples were identified with the maxima of the $\tan \delta$ absorption spectra. The dynamic T_g values obtained from Figure 3 reveal a similar salt content dependence to that of Figure 2 or Table I, although there exist some definite differences in magnitude. In fact, there is usually a difference of 10°C or so between the values of T_g determined by the DSC and DMTA techniques.^{20,21} For DSC, T_g is a weak (secondary) relaxation associated with the thermal transition between chain segments in the amorphous region. For DMTA, by contrast, T_g is a prominent relaxation between chain segments. Furthermore, measurements of dynamic viscoelastic properties by DMTA can also give important information on chain motion in polymer/salt complexes. Typically, the peak intensity at dynamic T_g may represent the relaxation strength of the α_a -absorption arising from the onset of micro-Brown motion of main chain segments in the amorphous region. In this regard, we can see from Figure 3 that the peak intensity for the sample with $[O]/[Li^+] = 16$ is relatively large, which seems to be closely related with the higher ionic conductivity at this salt content.

Conclusions

To gain a more insight into the ionic conduction mecha-

nism, solid polymer electrolytes based on poly(ethylene glycol)-polyurethane (PEG-PU) complexed with LiClO₄ salt have been prepared by the solvent casting method in this study. Effects of the salt concentration on the ionic conductivity (σ) and glass transition temperature (T_g) of the complex electrolytes thus prepared were investigated by using the alternating current (a.c.) impedance spectroscopy, differential scanning calorimetry (DSC), and dynamic mechanical thermal analyzer (DMTA). Both σ and T_g values measured exhibited similar tendencies to possess a maximum point within the range studied, probably due to two competing effects caused by the increase in salt concentration: the increased number of carrier ions dissociated and decreased chain mobility (or increased T_g). The highest conductivity on the order of $2.43 \times 10^{-6} \text{ Scm}^{-1}$ was obtained near the ether oxygen-to-sodium cation mole ratio $[O]/[Li^+] = 16$ (corresponding to 0.92 mol salt per kg matrix polymer). The salt content dependences of thermal (DSC) and dynamic (DMTA) T_g 's showed similar tendencies with a maximum point near $[O]/[Li^+] = 20$, although there existed some definite differences between the two values (DMTA T_g being higher by 10°C or so).

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References

- (1) D. E. Fenton, J. M. Parker, and P. V. Wright, *Polymer*, **14**, 589 (1973).
- (2) P. V. Wright, *Br. Polym. J.*, **7**, 319 (1975).
- (3) J. R. MacCallum, and C. A. Vincent, *Polymer Electrolyte Reviews*, Elsevier Applied Science Edition, London, UK, 1987, Vol. 1, Chapters 1 and 8.
- (4) A. Eisenberg, K. Ovans, and H. N. Yoon, *The Viscosity Enhancement of Polyethers by Salts. In Ions in Polymers*, A. Eisenberg, Ed., Advances in Chemistry Series 187, ACS, Washington, DC, 1980, pp 267-282.
- (5) M. B. Armand, J. M. Chabagano, and M. J. Duclot, *Polyethers as Solid Electrolytes. In Fast Ion Transport in Solids: Electrodes Electrolytes*, Proc. Int. Conf., P. Vashishta, J. N. Mundy, and G.K., Shenoy, Eds., North Holland, New York, 1979, pp 131-136.
- (6) *Chemical and Engineering News*, Nov. 25, pp 28 (1985).
- (7) S. Chao and M. S. Wrighton, *J. Am. Chem. Soc.*, **109**, 2197 (1987).
- (8) E. Tsuchida, *J. Mac. Sci. Chem.*, **A25 (5-7)**, 687 (1988).
- (9) J. H. Burroughes, C. A. Jones, and R. H. Friend, *Nature*, **335 (6186)**, 137 (1988).
- (10) G. Robila, M. Ivanoin, and E. C. Buruiana, *J. Appl. Polym. Sci.*, **49**, 2025 (1993).
- (11) V. Okamoto, T. F. Yeh, H. S. Lee, and T. A. Skotheimic, *J. Polym. Sci.; Part A: Polym. Chem.*, **31**, 2573 (1993).
- (12) T. C. Wen, S. S. Luo, and C. H. Yang, *Polymer*, **41**, 6755 (2000).

- (13) J. P. Donoso, T. J. Bonagamba, P. L. Frare, and H. Panepucci, *Electrochim Acta*, **40**, 2361 (1995).
- (14) J. L. Acosta and E. Morales, *Solid State Ionics*, **85**, 85 (1996).
- (15) E. Strauss, D. Golodnitsky, G. Ardel, and E. Peled, *Electrochim. Acta*, **43**, 1315 (1998).
- (16) J. Y. Kim, S. U. Hong, J. Won, and Y. S. Kang, *Macromolecules*, **33**, 3165 (2000).
- (17) J. H. Kim, B. R. Min, J. Won, and Y. S. Kang, *J. Phys. Chem. B*, **107**, 5901 (2003).
- (18) P. H. Huh, M. S. Thesis, Pusan National University, Kr, 2002.
- (19) K. S. Cole and S. Cole, *J. Chem. Phys.*, **9**, 341 (1941).
- (20) L. H. Sperling, in *Sound and Vibration Damping with Polymers*, R. D. Corsaro and L. H. Sperling, Eds., ACS Books Symp. Ser. 424, American Chemical Society, Washington, DC, 1990.
- (21) E. Catsiff and A. V. Tobolsky, *J. Polym. Sci.*, **19**, 111 (1956).