Ionic Conductivity and Morphology of Semi-Interpenetrating-Type Polymer Electrolyte Entrapping Poly(siloxane-g-allyl cyanide)

Ki Hong Min,[2] Dae Beom Kim,[2] Yong Ku Kang,[1] Dong Hack Suh[2]

[1]*Advanced Materials Division, Korea Research Institution of Chemical Technology, Yusong Taejon 305-600, Korea*
[2]*School of Chemical Engineering, Hanyang University, Haengdang 1-Dong, Seongdong-Gu, Seoul 133-791, Korea*

ABSTRACT: We prepared a semi-IPN (interpenetrating network)-type solid polymer electrolyte (SPE) using poly(ethylene glycol)dimethacrylate (PEGDMA) as a polymer matrix containing a monocomb-type poly(siloxane-g-allyl cyanide) and poly(ethylene glycol)dimethylether (PEGDME) for the lithium secondary battery. The poly(siloxane-g-allyl cyanide)s were prepared by a hydrosilation reaction of poly(methyl hydrosiloxane) with allyl cyanide and characterized by ^{1}H NMR and FTIR. The semi-IPN-type electrolyte was prepared by thermal curing, and conductivities of samples were measured by impedance spectroscopy using an indium tin oxide (ITO) electrode. The ionic conductivity of the semi-IPN-polymer electrolyte was about 1.05×10^{-5} S cm^{-1} with 60 wt % of the poly(siloxane-g-allyl cyanide) and 6.96×10^{-4} S cm^{-1} with 50 wt % of the PEGDME and 10 wt % of the poly(siloxane-g-allyl cyanide) at 30°C. The SEM morphology of the cross section of the semi-IPN-polymer electrolyte film was changed from discontinuous network to continuous network as increasing the PEGDME content and decreasing the poly(siloxane-g-allyl cyanide) content. The mechanical stability was also enhanced when increasing the PEGDME content. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 1609–1615, 2008

Key words: polymer electrolyte; polysiloxane; allyl cyanide; semi-IPN

INTRODUCTION

Since Wright[1] discovered ionic conductivity in a PEO/Na+ complex in 1975, the research and development effort has become quite active on solid polymer electrolyte (SPE), in particular, for the improvement of the ionic conductivity. The principal requirements for high conductivity are ability to solvate ions and a low glass transition temperature to afford facile ion transport. The promotion of the anion–cation dissociation is desirable, because it leads to enhancement of ionic conductivity via an increase in the free ion concentration. To decrease T_g of the polymer, studies have been conducted on the preparation of oligo(ethylene oxide) grafted comb-shaped and network solid polymers using the different polymer backbone such as polyphosphazene,[2,3] polyacrylate,[4–6] and polysiloxane.[7,8] Among them, polysiloxanes are promising because they can have a wide variety of substituents bound to silicones in the backbone of the alternating silicon and oxygen atoms. Polysiloxanes are superior to polyphosphazenes with respect to their backbone flexibility,

chemical stability, thermal stability, and low toxicity. A variety of organic groups can be bound to the silicon that includes ethylene oxide containing side chains. Hooper et al.[9] have reported that the double-comb-type polysiloxane compounds prepared from the condensation of *bis*[oligo(ethylene glycol) ether propyl] dichloro silane showed conductivity of 4.5×10^{-4} S cm^{-1}. The conductivity of these polymers is very close to the conductivity of the practical use (10^{-3} S cm^{-1}). However, these materials suffer from the low mechanical strength like most low-T_g polymers. To overcome this problem, a semi-IPN system was studied.[10] A semi-IPN is a special kind of the polymer blend that swells but does not dissolve in solvents, and its creep and flow are suppressed. An IPN may be made form (i) one polymer that can complex or hold lithium salts effectively and thus exhibits high ionic conductivity or (ii) another polymer that is mechanically and electrochemically stable to lithium electrodes. Such an IPN system would, in principle, make an ideal polymer electrolyte that satisfies the dual-function requirement for its use in secondary lithium batteries. Recently, the oligomeric poly(ethylene glycol) dimethyl ether (PEGDME) was used as a plasticizer to enhance the ionic conductivity. The PEGDME was entrapped in poly(vinylidene fluoride)-hexafluoropropylene copolymers (PVdF-HFP) up to 65 wt %, and its maximum conductivity was reported

to be 2×10^{-4} S cm^{-1} at room temperature.[11] In this study, we report the synthesis of the comblike poly(siloxane-g-allyl cyanide) as a base materials for an IPN-type polymer electrolyte. The poly(siloxane-g-allyl cyanide) has an allyl cyanide pendants having the high dielectric constant to encourage the ion pair dissociation and show more enhanced ionic conductivity. The IPN-type SPE showed an ionic conductivity of 1.05×10^{-5} S cm^{-1} at 30°C higher than PEO polymers doped with lithium salts. Also, we report the additional increase of the ionic conductivity through the control of blending ratio of the PEGDME and the poly(siloxane-g-allyl cyanide). The micromorphology of cross section of semi-IPN-polymer electrolyte film and tensile strength data of the IPN-type polymer electrolyte was also presented here.

EXPERIMENTAL

Materials

Poly(methylhydrosiloxane), trimethylsilyl terminated (PMHS, $M_n = 390$), platinum (0)-1,3-divi-nyl-1,1,3,3-tetramethylldisiloxane (Pt(0)) (solution in xylene), poly (ethylene glycol) dimethyl ether (PEGDME, $M_n = 250$), poly(ethyleneglycol) dimethacrylate (PEGDMA, $M_n = 550$), N-lithiotrifluoromethane sulfonimide 97% ($LiN(CF_3SO_2)_2$, LiTFSI), benzoyl peroxide were purchased from Aldrich (St. Louis, MO). Allyl cyanide was purchased from TCI. The inhibitors (250 ppm MEHQ and 150 ppm BHT) in the PEGDMA were purified through column purification. LiTFSI and BPO were dried under vacuum before use. Toluene was stirred over calcium hydride for 24 h before use. Others were used as obtained.

Synthesis

Poly(siloxane-g-allylcyanide) was prepared by the hydrosilation reaction of poly(methyl hydrosiloxane) (10 g, 25.6 mmol) with allyl cyanide (8 g, 119 mmol) in toluene as shown in Scheme 1. The structure of poly(siloxane-g-allylcyanide) was confirmed by FTIR and ^{1}H NMR. Yield: 14.3 g, 77.04%. The data were given as follows:

FTIR (KBr), cm^{-1}: 2963 ($-CH_3$), 2881 ($-CH_2-$), 2240 ($-CN$), 1250 (Si$-$C), 1040 (Si$-$O$-$Si).

^{1}H NMR (CDCl$_3$), δ (ppm): 2.40 (m, 2H, $-CH_2$ CN), 1.71 (m, 2H, $-CH_2-$), 1.13 (d, 3H, CH_3-, α-addition), 0.74 (m, 2H, $-CH_2Si-$), 0.12–0.095 (m, 3H, $-SiCH_3$).

Electrolyte preparation

The semi-IPN-type polymer electrolytes were prepared by *in situ* radical initiated crosslinking reaction of a homogeneous solution composed of good ion-conducting materials (PEGDME or poly(siloxane-g-allyl cyanide), PEGDMA (crosslinker), lithium salt (LiTFSI), and thermal radical initiator (BPO). The homogeneous solution was filled in a small gap between ITO glasses. The thermal curing was carried out in a convection oven at 100°C for 20 min under argon atmosphere. Using this procedure, self-standing semi-IPN-polymer electrolytes with varying amount of PEGDME and poly(siloxane-g-allyl cyanide) were obtained (see Scheme 1).

Measurements

Ionic conductivity

The ionic conductivity measurement was performed by a complex-impedance measurement with ITO-blocking electrodes by using Zahner® *elektrik* model IM 6 impedance analyzer. The indium tin oxide (ITO) method was carried out with the polymer coated onto a prepatterned ITO cell that had been developed by Kang et al.[6] All procedures were carried out in a dry room (dew point: −57°C) of high purity. The polymer electrolyte was subjected to the complex-impedance measurement in the range from 30 to 80°C. An alternating current over the frequency range of 1 Hz–1 MHz was used, and the applied voltage was 0.1 V. The bulk resistance (R_b) was determined from the complex-impedance plot. Each data of the ionic conductivities performed four times, and we collected average data.

Glass transition temperature

The glass transition temperature (T_g) of the samples was measured by using an Universal V2.6D TA Instruments differential scanning calorimeter. Samples were placed in copper containers. The samples were first cooled from 30 to −110°C at the scan rate of 10°C/min and then heated to 30°C at the same scan rate. The glass transition temperature was taken at the center of the heat capacity change encountered during the transition.

SEM morphology of the cross section of the semi-IPN-polymer electrolyte

Scanning electron microscopy (SEM) was employed to study the morphology of the cross section of semi-IPN-polymer electrolyte. The semi-IPN-polymer electrolyte was attached on the scratched slide glass and divided into two parts after being merged in liquid nitrogen. After subsequent drying, the samples were sputter coated with a 15-nm thick layer of Pt. The study was performed using a JSM-6330F scanning electron microscope.
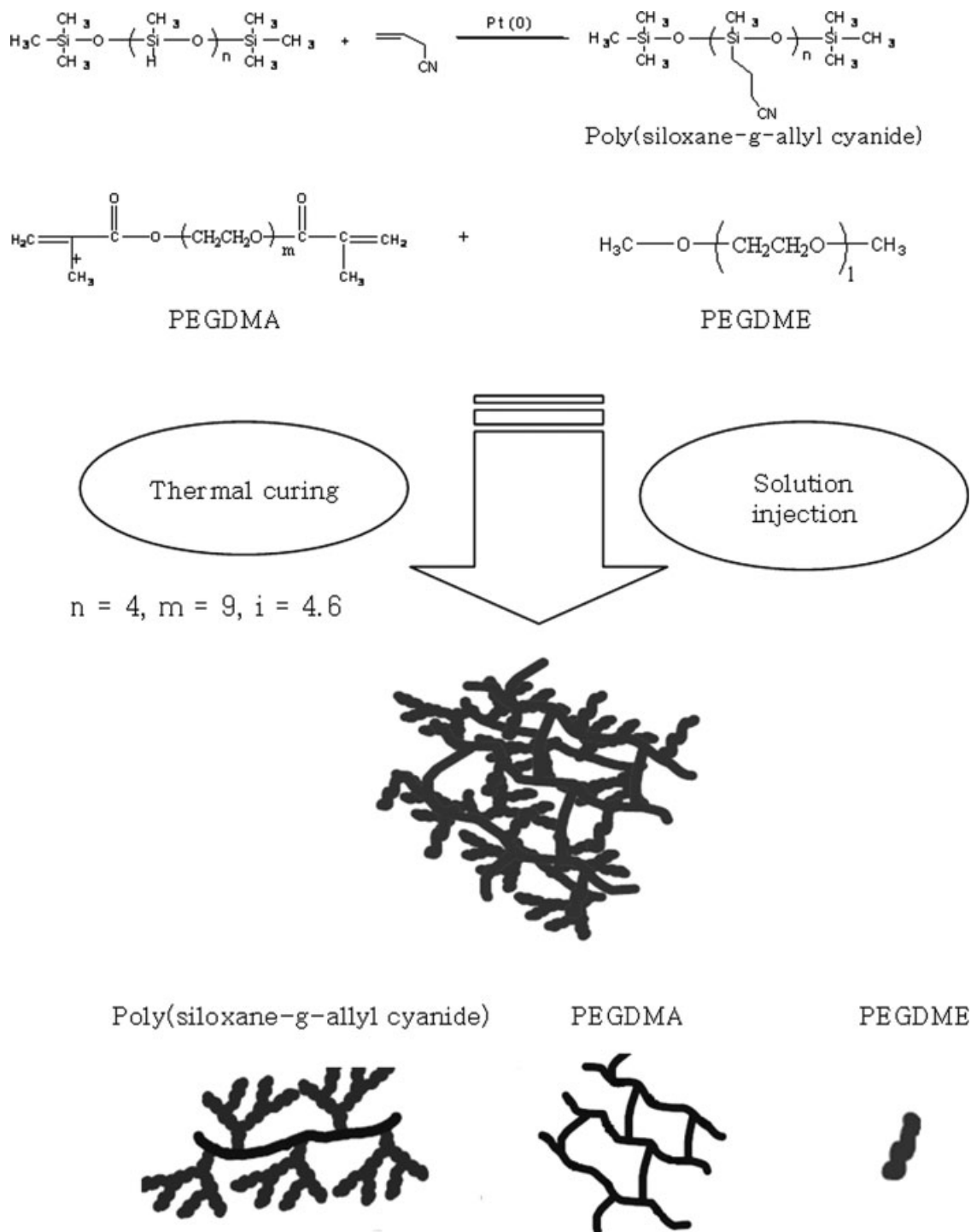
Scheme 1 Preparation of SPE films.

Mechanical analysis

Mechanical analysis was performed on the semi-IPN-polymer electrolytes films by using an Instron Tensile Machine mod 4301. The used machine parameters were set as follows: sample rate 10,000 pts/s, crosshead speed 7500 mm/mn F 1 kN. The mechanical test was carried out at 22°C.

RESULTS AND DISCUSSION

Synthesis

The monocomb poly(siloxane-g-alkyl cyanide) was synthesized from commercially available PMHS. The PMHS is a trimethylsilyl-terminated type and has low molecular weight ($M_n = 390$). The hydrosilation of allyl cyanide with PMHS was carried out using

the previously reported method.[10,12,13] The reaction was monitored by FTIR until Si—H stretching vibration band at 2165 cm^{-1} completely disappeared. The hydrosilation of allyl cyanide with PHMS gave a mixture of α- and β-addition isomers. In toluene, about 20% α-addition has been reported for the reaction with the D$_4$H.[14,15] Under the present experiment condition, the side reaction (α-addition) was conformed to be about 12% by ratio of —CH$_2$CN (δ = 2.40) to CH$_3$— (δ = 1.13) in ^{1}H NMR.

Preparation of polymer electrolyte

To prepare the SPE, the semi-IPN method was used. Semi-IPN method is very useful for fabricating SPE that can be processed as a film.[10] The PEGDMA as a polymer matrix was blended in any portions with PEGDME and poly(siloxane-g-allyl cyanide) without phase separation in liquid state. The percentages of the PEGDME and the poly(siloxane-g-allyl cyanide) varied [0 wt %/60 wt %; 10 wt %/50 wt %; 30 wt %/ 30 wt %; and 50 wt %/10 wt %], and the PEGDMA content was fixed 40 wt %. Every polymer was doped with the lithium salt.[16] After crosslinking, the crosslinked SPE showed a phase separation up to 30 wt % of the poly(siloxane-g-allyl cyanide) and 30 wt % of the PEGDME. Every semi-IPN-polymer electrolyte showed free-standing film as shown in Figure 1. The transparent free-standing film was obtained with 50 wt % PEGDME and 10 wt % poly(siloxane-g-allyl cyanide). Final thickness of the SPEs was controlled to <100 μm. The SPE film was monitored by IR spectroscopy. Figure 2(d) represents the crosslinked polymer electrolytes by using semi-IPN method. The absence of the (C=C) conjugation stretch absorption band at 1640 cm^{-1} indicates the
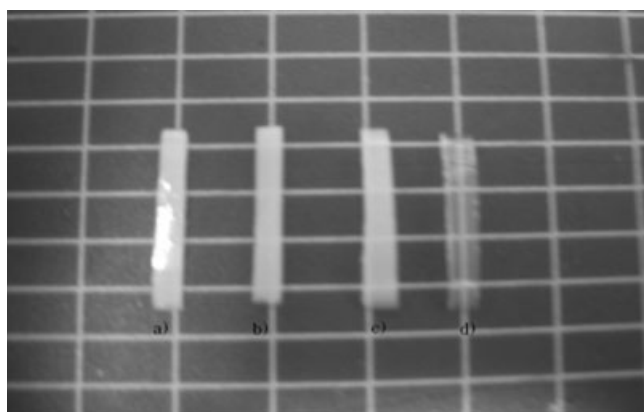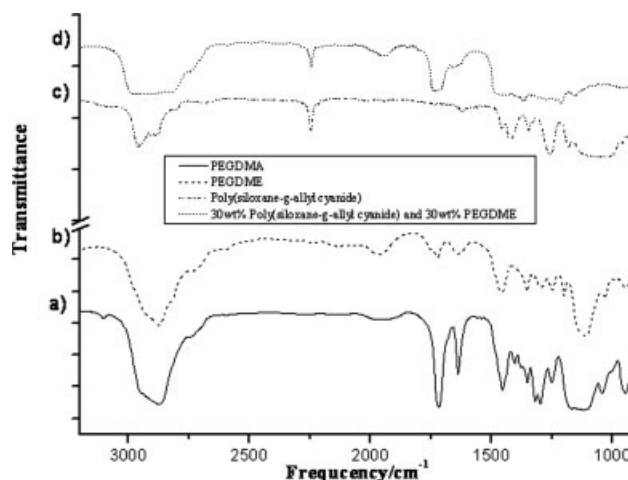

Figure 2 FTIR spectra of (a) PEGDMA, (b) PEGDME, (c) poly(siloxane-g-allyl cyanide), and (d) the semi-IPN-polymer electrolyte, 30 wt % PEGDME and 30 wt % poly(siloxane-g-allyl cyanide).

formation of the PEGDMA polymer matrix. In Figure2(c,d), the absorption band at 2240 cm^{-1} indicates —CN group, and no Si—H stretch absorption band at 2165 cm^{-1} was observed.

Cross section micrograph and DSC of semi-IPN-polymer electrolyte

The micrograph of cross section of SPE film was investigated by scanning electron microscopy (SEM). Electron micrographs of cross section with 60 wt % poly(siloxane-g-allyl cyanide) SPE film, and some plasticized SPE films are displayed in Figure 3. The cross section micrograph with 60 wt % poly(siloxane-g-allyl cyanide) SPE film shows discontinuous phase that consists of 200–300-nm diameter particles. It is considered poor miscibility between the PEGDMA and the poly(siloxane-g-allyl cyanide) when the thermal crosslinking was advanced. Some authors describe IPNs that exhibit varying degrees of phase separation depending principally on the miscibility of the polymers.[17] The cross section micrograph of SPE film changes with the increase in the PEGDME content. The particles gradually aggregated and formed more large diameter particles by increasing the PEGDME content. The particle diameter is up to 1 μm when the composition of the SPE is up to 30 wt % PEGDME and 30 wt % poly(siloxane-g-allyl cyanide), and the cross section micrograph showed homogeneous and continuous phase when the composition of the SPE is 50 wt % PEGDME and 10 wt % poly(siloxane-g-allyl cyanide). Figure 4 shows that the glass transition temperature decreased with the increasing PEGDME content. These values are well below the room temperature, and the low values reflect the good flexibility of the SPE.
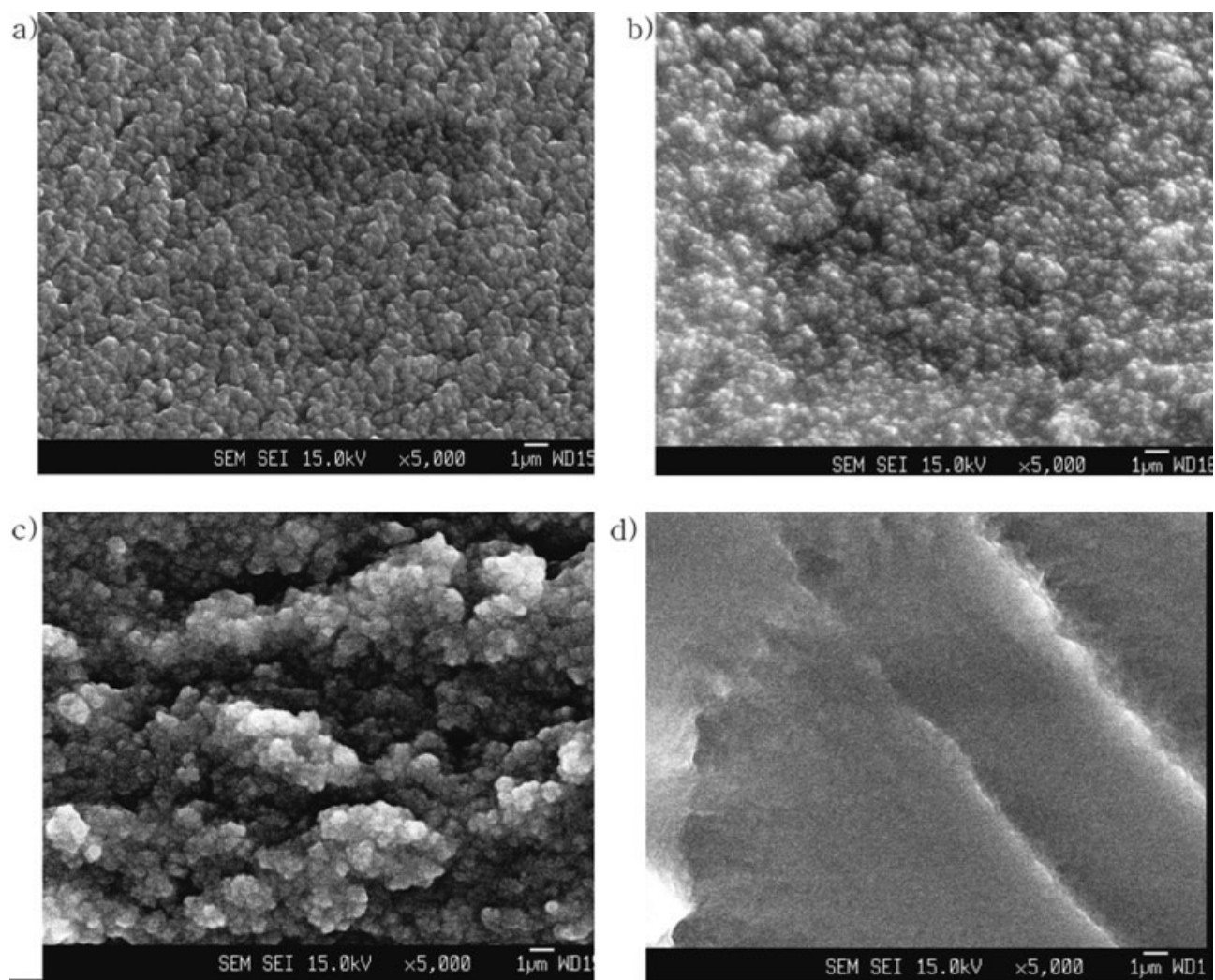

Figure 1 Photograph of SPE films: (a) 60 wt % poly(siloxane-g-allyl cyanide) contained; (b) 50 wt % poly(siloxane-g-allyl cyanide) and 10 wt % PEGDME contained; (c) 30 wt % poly(siloxane-g-allyl cyanide) and 30 wt % PEGDME contained; and (d) 10 wt % poly(siloxane-g-allyl cyanide) and 50 wt % PEGDME contained.

Figure 3 SEM micrographs of SPE films: (a) 60 wt % poly(siloxane-*g*-allyl cyanide) contained; (b) 50 wt % poly(siloxane-*g*-allyl cyanide) and 10 wt % PEGDME contained; (c) 30 wt % poly(siloxane-*g*-allyl cyanide) and 30 wt % PEGDME contained; and (d) 10 wt % poly(siloxane-*g*-allyl cyanide) and 50 wt % PEGDME contained.

Ionic conductivity

The polysiloxanes were mixed with LITFSI, and the ionic conductivities were measured. Figure 4 shows the conductivity data of the monocomb poly(siloxane-*g*-allyl cyanide) electrolyte. The lithium salt molar ratio was optimized to $[CN]/[Li^+] = 20$, and then the poly(siloxane-*g*-allyl cyanide) showed the highest ionic conductivity above 10^{-4} S cm^{-1} at 30°C. These values are higher than the polyethylene oxide electrolytes complexed with lithium salts by one to two orders of magnitude. Such an improvement of the conductivity may be attributed to the increase in ion salvation.[12,18] And the low glass transition temperature of the poly(siloxane-*g*-ally cyanide) is advantage for higher ionic conductivity. The LiTFSI was studied by Armand et al.[19] The presence
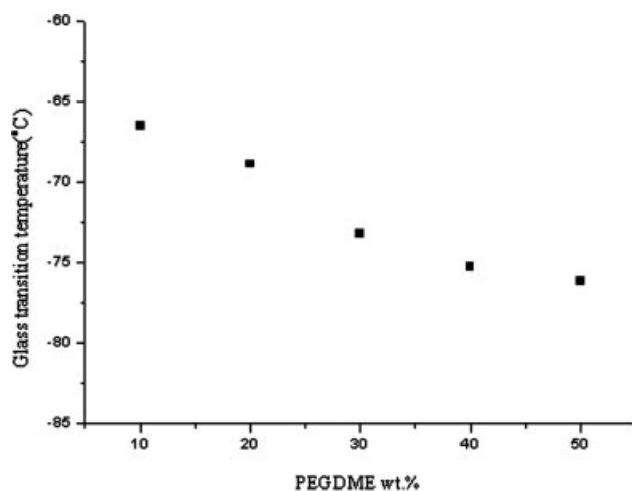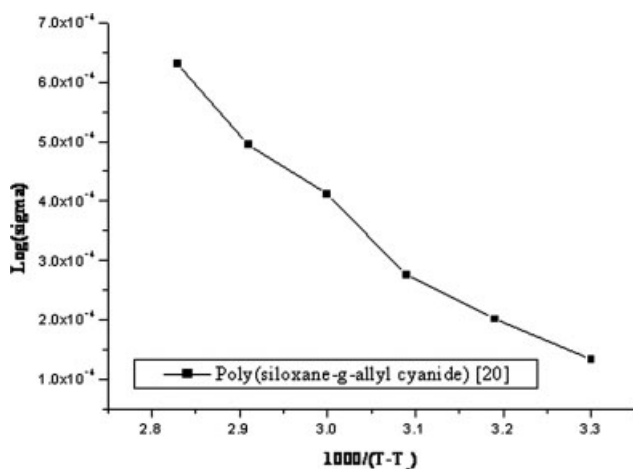

Figure 4 Change of the glass transition temperature.

Figure 5 The temperature dependence on conductivity of the lithium salt-dopped poly(siloxane-*g*-allyl cyanide).

Figure 6 Impedance spectroscopy analysis of the lithium salt-dopped poly(siloxane-*g*-allyl cyanide).

of the highly electron-delocating anion in these salt was thought to plasticize the polymer chain, making it more flexible. The polymer electrolytes containing these novel salts have shown much lower crystallinity, higher conductivity, and low-anion transference number.[20] Figure 5 exhibits the VTF behavior throughout the available thermal range. The conduction activation energy of the poly(siloxane-*g*-allyl cyanide) was 8.13 kJ/mol, and A was 2.76 S cm^{-1} K$^{0.5}$.

The ionic conductivity of semi-IPN-polymer electrolyte was 1.05×10^{-5} S cm^{-1} at 30°C when the poly(siloxane-*g*-allyl cyanide) was 60 wt %. This result is higher 1/2 orders than the branched and crosslinked PEO polymer electrolytes.[2–6] To increase the ionic conductivity of the semi-IPN-polymer electrolyte, the PEGDME was added, and the blending ratio between the poly(siloxane-*g*-allyl cyanide) and PEGDME was controlled. The weight percentage of the PEGDMA was fixed at 40 wt % to maintain the free-standing film. Figure 6 illustrates the complex plane impedance spectrum of the synthesized polymer electrolyte. A straight line appears at low frequency due to diffusion impedance at the electrode. From the polt of Z'' versus Z' plot, ionic conductivity values were calculated from the intercept of the curve with real axis. The conductivity of the poly(siloxane-*g*-allyl cyanide) doped with the lithium salt ($[CN]/[Li^+] = 20$) gradually increased with the increasing temperature. The ionic conductivity mechanism of the poly(siloxane-*g*-allyl cyanide) doped with the lithium salt ($[CN]/[Li^+] = 20$) follows the Vogel-Tamman-Fulcher (VTF)-like relationship ($\sigma = AT^{-1/2} \exp[-B/K_B(T - T_0)]$) where A is a constant, which is proportional to the number carrier ions, and B denotes the pseduoactivation energy associated with the motion of the polymer segment, K_B represents the Boltzmann constant, E the activation energy, and T_o is a reference temperature (normally
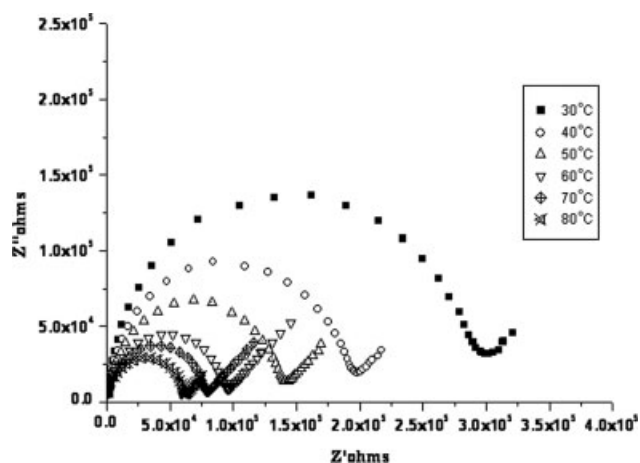
associated with the ideal T_g at which the free volume is zero, or the temperature at which the configuration entropy becomes zero). Figure 7 shows the conductivity data of the semi-IPN-polymer electrolyte with varying the PEGDME content. As increasing the PEGDME from 10 to 50 wt % and as decreasing the poly(siloxane-*g*-allyl cyanide) from 50 wt % to 10 wt %, the ionic conductivity of the semi-IPN-polymer electrolyte was increased from 1.15×10^{-4} S cm^{-1} to 6.96×10^{-4} S cm^{-1} at 30°C. The improved conductivity may be explained by the changing of the cross section micrograph. The cross section micrograph was changed from the discontinuous phase to continuous and homogeneous phase. The ionic conductivity mechanism of semi-IPN-polymer electrolytes follows the Vogel-Tamman-Fulcher (VTF)-like relationship. The VTF expression implies that the main mechanism of ion conduction may be related to the
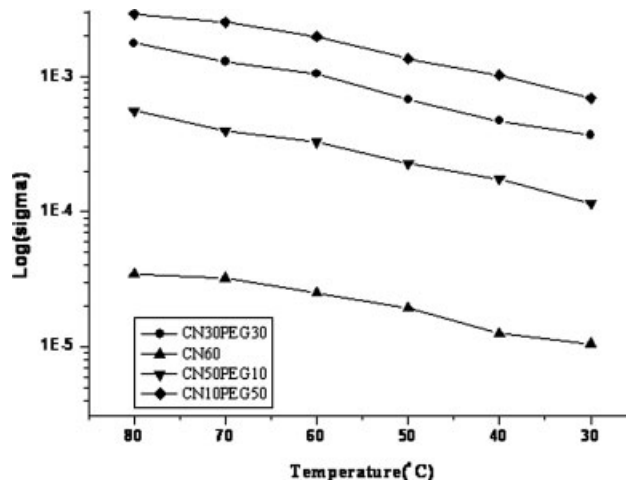

Figure 7 The temperature dependence on conductivity of the SPEa doped with the lithium salt-dopped SPEs.
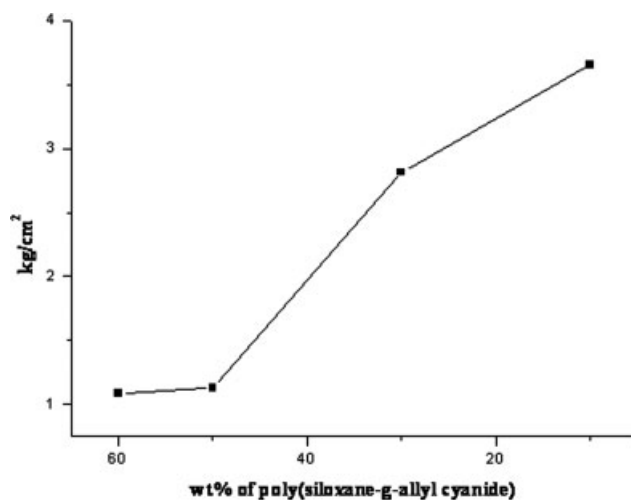
Figure 8 The tensile strength increases with the decrease in the poly(siloxane-g-allyl cyanide) contents.

free-volume theory; a curved log σ versus $1/T$ plot is generally exhibited in the amorphous polymer electrolyte.[16]

Mechanical analysis

The tensile properties, such as Young's modulus, strength at break, and strain at break, have been evaluated for all prepared SPE films from the experimental stress–strain curves. Figure 8 shows the relationship between the weight percentage of the poly(siloxane-g-allyl cyanide) and the tensile strength. The tensile strength increased with the increase in the contents of the PEGDEM. When the composition of SPE was 10 wt % poly(siloxane-g-allyl cyanide) and 50 wt % PEGDME, the tensile strength of the film was 3.65 kg/cm^2 at 22°C. It is considered that the continuous phase of the semi-IPN-polymer electrolyte film increased the tensile strength. However, these results are very low for the SPE and require improved mechanical strength for practical application.

CONCLUSIONS

Polysiloxanes with allyl cyanide pendants (poly(siloxane-g-allyl cyanide)) were synthesized. When dopped with lithium salt, LiTFSI, the poly(siloxane-g-allyl cyanide) showed ionic conductivity 1.35×10^{-4} S cm^{-1} at 30°C and 6.31×10^{-4} S cm^{-1} at 80°C. The SPE-containing 60 wt % poly(siloxane-g-allyl cyanide) was 1.05×10^{-5} S cm^{-1} at 30°C, and

the ionic conductivity of SPE enhanced with the increase in the PEGDME content. The improved ionic conductivity was explained by the miscibility of polymers, PEGDMA, PEGDME, and poly(siloxane-g-allyl cyanide). When increasing the PEGDME content, the cross section micrograph changed from discontinuous phase to continuous and homogeneous phase. And the tensile strength of the SPE film increased as the cross section micrograph changed to continuous phase. The ionic conductivity is 6.96×10^{-4} S cm^{-1} at 30°C and 2.83×10^{-3} S cm^{-1} at 80°C when the composition of SPE was 50 wt % PEGDME and 10 wt % poly(siloxane-g-allyl cyanide). Finally, the tensile strength of the film was 3.65 kg/cm^2.

References

1. Wright, P. V. Brit Polym J 1975, 7, 319.
2. Allcock, H. R.; Kuharick, S. E.; Reed, C. S.; Napierala, M. E. Macromolecules 1996, 29, 3384.
3. Allcock, H. R.; Ravikiran, R.; O'Connor, S. J. M. Macromolecules 1997, 30, 3184.
4. Kono, M.; Hayashi, E.; Watanabe, M. J Electrochem Soc 1998, 145, 1521.
5. Choi, Y.; Kim, S. K.; Chang, K. H.; Lee, M. H. J Appl Electrochem 1997, 27, 1118.
6. Kang, Y.; Kim, H. J.; Kim, E.; Oh, B.; Cho, J. H. J Power Sour 2001, 92, 255.
7. Fish, D.; Khan, I. M.; Wu, E.; Smid, J. Brit Polym J 1998, 20, 281.
8. Tsutsumi, H.; Yamamoto, M.; Morita, M.; Matsuda, Y.; Nakamura, T.; Asai, H. Electrochim Acta 1990, 191, 2195.
9. Hooper, R.; Lyons, L. J.; Mapes, M. K.; Schumacher, D.; Moline, D. A.; West, R. Macromolecules 2001, 34, 931.
10. Oh, B.; Vissers, D.; Zhang, Z.; West, R.; Tsukamoto, H.; Amine, K. J Power Sour 2003, 119, 442.
11. Abraham, K. M.; Jiamg, Z.; Carrol, B. Chem Mater 1997, 9, 1978.
12. Lee, Y. S.; Song, G. S.; Kang, Y.; Suh, D. H. Electrochim Acta 2004, 50, 311.
13. Kang, Y.; Lee, W.; Suh, D. H.; Lee, C. J Power Sour 2003, 119–121, 448.
14. Lestel, L.; Boileau, S.; Cheradame, H. Polym Prepr (Am Chem Soc, Div Polym Chem) 1989, 30, 133.
15. Kricheldorf Silicon in Polymer Synthesis; Springer: Germany, 1996.
16. Maccallum, J. R.; Vincent, C. A. Polymer Electrolyte Review; Elsevier: London, 1987; Chapter 8.
17. Klempner, D.; Wang, C. L.; Ashtiani, M.; Frisch, K. C. J Appl Polym Sci 1986, 32, 4197.
18. Lee, I. J.; Song, G. S.; Lee, W. S.; Suh, D. H. J Power Sour 2003, 114, 320.
19. Armand, M.; Georecki, W.; Andreani, R. In Proceedings in the Second International Meeting on Polymer Electrolytes; Scrosati, B., Ed.; Elsevier: New York, 1990, p 91.
20. Benrabah, D.; Baril, D.; Sanchez, J. Y.; Armand, M. J Chem Soc Faraday Trans 1993, 89, 355.