A new class of solid polymer electrolyte: synthesis and ionic conductivity of novel polysiloxane containing allyl cyanide groups

In Jae Lee, Gi Sang Song, Won Sil Lee, Dong Hack Suh[*]

School of Chemical Engineering, Hanyang University, Haengdang 1-dong, Seongdong-gu, Seoul 133-791, South Korea

Abstract

A monomer; (3-cyanopropyl)methylsiloxane cyclics, is prepared by a hydrosiliylation reaction of 2,4,6,8-tetramethylcyclotetrasiloxane with allyl cyanide in toluene using a platinum(0)-1,3-divinyl-1,1,3,3-tetramethyl disiloxane complex as the catalyst. The cross-linkable polysiloxane is synthesised by ring-opening polymerisation with (3-cyanopropyl) methylsiloxane cyclics using fuming sulfuric acid. The polymers, abbreviated as D_4D_2-n indicates the number of cyanide groups in the side chain), are characterised by FT-IR and ^{1}H NMR. The solid polymer electrolyte is prepared by UV irradiation in an Indium–tin oxide cell. The cyanide pendants on the network backbones make the lithium salt easy to dissolve, accelerate the migration of free lithium ions, and can lower the glass transition temperature (T_g) of the electrolyte. The maximum conductivity of the polymer with $n = 55$ is 3.38×10^{-5} S cm^{-1} at room temperature. The temperature dependence of ionic conductivity (σ) obeys the Vogel–Tammann–Fulcher relationship which implies ionic conductivity (σ) obeys the Vogel–Tammann–Fulcher relationship which implies a free-volume cation transport mechanism.
© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Polymer electrolyte; Polysiloxane; Allyl cyanide; Indium–tin oxide cell

1. Introduction

It is widely recognised that solid polymer electrolytes can be applied in many solid electrochemical devices such as high-energy batteries, electrochromic windows and light-emitting devices [1–5]. The polymer electrolytes have to satisfy several requirements which include high ambient ionic conductivity, fast charge-transfer at the electrode interface, electrochemical stability, mechanical strength, and processability.

Conventional polyether–lithium salt complexes, such as LiCF$_3$SO$_3$ in polyethylene oxide (PEO) have been investigated extensively as ionic-conducting materials [6,7]. Unfortunately however, PEO–lithium salt electrolytes exhibit very low ambient ionic conductivity, typically 10^{-7} S cm^{-1}. It has been thoroughly demonstrated that ion migration takes place mainly in the amorphous part of the polymer; the crystalline domains will impede ion mobility both by blocking the paths of ions and by reducing the overall polymer flexibility.

By contrast, polysiloxanes have highly flexible backbones with a barrier to bond rotation of only 0.8 kJ mol^{-1}, as well as very low glass transition temperatures (T_g), high free volumes and thermo-oxidative stability. These materials should therefore be good hosts for lithium-ion transport, if properly substituted [8–13]. In a previous study [14], dimethylsiloxane units were combined with short PEO segment to form a linear chain copolymer, as it was expected that dimethylsiloxane units would decrease the softening temperature of the copolymers without decreasing the solubility of the Li salts.

In addition to linear chain polymers, a variety of comb-branched polymers were investigated, in which PEO side chains were attached to a polymer backbone (which itself had a low glass transition temperature) to provide a more flexible system. Polysiloxanes with PEO side chains were first synthesised by Hall et al. [8] and Fish and co-workers [15]. Later similar systems were investigated by Spindler and Shriver [16]. The chemical stabilities were poor, however due to the Si–O–C branched side chains. Fish and co-workers [17] enhanced their chemical stability by connecting the PEO branches via a Si–C bonds.

[*] Corresponding author. Tel.: +82-2-2290-0523; fax: +82-2-2298-4101.
E-mail address: dhsuh@hanyang.ac.kr (D.H. Suh).

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 anion–cation dissociation is desirable, as it should lead to enhancement of ionic conductivity via an increase in free-ion concentration.

This study involves the synthesis of a siloxane polymer with a 3-cyano propyl group to encourage ion-pair dissociation by virtue of the high dielectric constant and increased ion mobility. The thermal and electrical properties of the polymer when complexed with a lithium salt, like $LiClO_4$, have been measured using complex impendance spectroscopy and differential scanning calorimetry (DSC).

2. Experimental

2.1. Materials

2,4,6,8-Tetramethylcyclotetrasiloxane (D_4H) and 1,1,3,3-tetramethyldisiloxane (D_2H) were purchased from Gelest and used without further purification. Allyl alcohol, acryloyl chloride and platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane (solution in xylene) were purchased from Aldrich. Fuming sulfuric acid, sodium sulfate and magnesium sulfate were of reagent grade or were purified by standard methods. Toluene and tetrahydrofuran (THF) were stirred over calcium hydride for 24 h and distilled just prior to use. 2,2′-Dimethoxy-2-phenylacetophenone (DMPA) and lithium perchlorate ($LiClO_4$) were purchased from Aldrich and dried under a vacuum before use.

2.2. Characterisation

^{1}H NMR was carried out on a Varian Unity INOVA NMR spectrometer, using chloroform-*d* ($CDCl_3$) as a solvent and tetramethylsilane (TMS) as an internal standard FT-IR spectra were obtained on a Nicolet Magna-IR 760 spectrometer using a KBr pellet. The molecular weight ($\bar{M}_n$) was determined by a ^{1}H NMR end-group analysis (the content of a cyanide group of D_4D_2-*n* was determined by the amount of the vinyl end group).

2.3. Synthesis

2.3.1. Preparation of (3-cyanopropyl) methylsiloxane cyclics

A two-neck flask (500 ml) was equipped with a condenser and a magnetic stirring bar. The flask was charged with 50 ml (49 g, 0.2 Mol) D_4H, 80 ml (66 g, 1 mol) allyl cyanide, 0.1 wt.% platinum(0)-1,3-divinyl-1,1,3,3,-tetramethyldisiloxane, and 100 ml purified toluene [18].

After raising the temperature to 110 °C, the mixture was refluxed under a nitrogen atmosphere until the absorption band of Si–H (ca. 2165 cm^{-1}) in the infrared spectra disappeared [10]. The reaction mixture was then placed in a rotary evaporator to remove excess allyl cyanide and solvent.

To remove the Pt(0) catalyst, the crude product was stirred with activated carbon for 12 h and filtered. The viscous liquid was dried in a vacuum oven at about 40 °C. The structure of (3-cyanopropyl)methylsiloxane cyclics was confirmed by FT-IR and ^{1}H NMR; the yield was 130 g, 90%. The data were as follows. FT-IR (KBr), cm^{-1}: 2963 (–CH$_3$), 2881 (–CH$_2$–), 2240 (–CN). ^{1}H NMR ($CDCl_3$), δ (ppm): 2.40 (m, 8H, 4(CH$_2$CN)), 1.71 (m, 8H, 4(CH$_2$)), 1.13 (d, CH$_3$ of α-addition (about 13%)), 0.74 (m, 8H, 4(CH$_2$Si)), 0.15 (m, 12H, 4(CH$_3$)).

2.3.2. Preparation of D_2-1, 3-di(propaneacrylate)

A 500 ml flask was charged with 30 ml (22.8 g, 0.17 mol) D_2H, 29.2 ml (24.9 g, 0.43 mol) allyl alcohol, 0.1 wt.% platinum(0)-1,3-diviayl-1,1,3,3-tetramethyldisiloxane, and 100 ml purified toluene. The mixture was heated to reflux (110 °C) for 12 h. The reaction was monitored by FT-IR until the S–H stretching vibration band completely disappeared. After the reaction was completed, activated carbon was added and stirred for 12 h. The activated carbon was filtered off; evaporated, and dried in a vacuum The crude product was purified by column chromatography (ethylacetate: methanol = 10:1). The viscous product (yield: 37.4 g, 87.8%) was dried in a vacuum oven at about 40 °C. The product 40 g (0.16 mol) was placed in a two-neck 500 ml flask containing purified THF (100 ml) and fitted with a nitrogen inlet and a calcium chloride drying tube. A dry nitrogen gas was purged through the flask and a magnetic stirring bar was used to mix the solution. To the vigorously stirred solution, an equimolar amount of acryloyl chloride 25.9 ml (28.9 g, 0.32 mol) dissolved in THF (50 ml) was added dropwise at 0 °C. The mixture was stirred at this temperature for 1–2 h, and then at ambient temperature for an additional 1 h. One hundred millilitres of chloroform was added and the solvent was removed under a reduced pressure. The product was filtered and transferred to a separator funnel and then extracted with 100 ml water. The yellow oil was stirred with MgSO$_4$ for 1 h, filtered, and a hydroquinone (100 ppm) added as an inhibitor. The product was dried in a vacuum oven at room temperature. Yield: 31.8 g, 55.4%. The data were as follows: FT-IR (KBr), cm^{-1}: 2960 (–CH$_3$), 2893 (–CH$_2$–), 1724(C=O), 1634 (–CH=CH$_2$). ^{1}H NMR ($CDCl_3$), δ (ppm): 6.40 (d, 2H, 2(CH=C–)), 6.15 (m, 2H, 2(C=CH–), 5.81 (d, 2H, 2(CH=C–)), 4.12 (m, 4H, 2(OCH$_2$)), 1.68 (m, 4H, 2(CH$_2$)), 0.55 (m, 4H, 2(CH$_2$Si)), 0.07 (m, 12H, 4(CH$_3$)).

2.3.3. Polymerisation

Acrylate-ditelechelic polymers (D_4D_2-*n*, where *n*: average degree of polymerisation) were synthesised by ring-opening polymerisation of the cyclic tetramer, (3-cyanopropyl)methylsiloxane cyclics, in the presence of the corresponding chain stopper, D_2-1,3-diropaneacrylate) [19–21].

For the preparation of D_4D_2-*n*, where *n* = 10, into a 100 ml flask were placed (3-cyanopropyl)methsiloxane cyclics 2.035 g, D_2-1,3-di(propaneacrylate) 0.57 g, and 0.01 ml of fuming sulfuric acid. The mixture was stirred at 30 °C for 6 h, and then 0.01 ml of water was added and the system was

stirred for 1 h. The reaction mixture was transferred to a separation funnel, and 50 ml of chloroform was added, and the product was neutralised with the 0.1 M Na_2CO_3 aqueous solution. The product was stirred with $MgSO_4$ for 6 h, filtered, and added hydroquinone (100 ppm) as an inhibitor The viscous liquid product was dried in a vacuum oven at room temperature. Yield 2.63 g, 38%. The data were as follows: ^1H NMR ($CDCl_3$), δ (ppm): 6.40 (d, 2H, 2(CH=C–)), 6.15 (m, 2H, 2(C=CH–)), 5.81 (d, 2H, 2(CH=C–)), 2.40 (m, 2H, CH_2CN), 4.12 (m, 4H, 2(OCH_2)), 1.71 (m, 2H, CH_2), 1.68 (m, 4H, 2(CH_2)), 1.13 (d, CH_3 of α-addition), 0.74 (m, 8H, 4(CH_2Si)), 0.55 (m,4H, 2(CH_2Si)), 0.18–0.07 (m, 3H, CH_3).

2.4. Ionic conductivity

2.4.1. Film preparation

A solid polymer electrolyte was prepared by UV (Spectroline® model ENF-280C, 365 nm) radiation curing of a homogeneous mixture solution of D_4D_2-*n* and lithium salt. 2,2′-Dimethoxy-2-phenyl acetophenone (3 wt.% based on the macromonomers) as a photo-occurring agent was dissolved in the macromonomers and stirred to form a homogeneous viscous solution [22]. The typical method of preparation of the polymer electrolyte is shown in Fig. 1.

2.4.2. Measurements

The glass transition temperature (T_g) of the samples was measured by means of a differential scanning calorimetry

Universal V2.6D TA Instruments. The scanning rate was 10 °C min^{-1} and the temperature was in the range −120 to 120 °C. The T_g was taken at the center of the heat capacity change encountered during the transition. Ionic conductivity measurements were performed according to the methods described in previous studies [23–25]. The indium–tin oxide (ITO) method was carried out with the polymer coated on to a pre-patterned ITO cell that had been developed by Kang et al. [22]. The thickness of the polymer was about 100 μm. The complex impendance of the samples was measured by using a Zahner® *elektrik* model IM 6 with an alternating current frequency range of 100 Hz to 1 MHz between 20 and 80 °C.

3. Results and discussion

3.1. Synthesis and characteristics

3.1.1. (3-Cyanopropyl) methylsiloxane cyclics

The reaction between 2,4,6,8-tetramethylcyclotetrasiloxane (D_4H) and allyl cyanid with platinum(0) as a catalyst resulted in a monomer; the expected structure of which is depicted in Fig. 2.

The hydrosilylation of the allyl cyanide with D_4H was quantitative. The subsequent reaction with excess allyl cyanide completed the hydrosilylation of the remaining Si–H groups of D_4H. In toluene, about 20% α-addition has been reported for the reaction with the D_4H [26,27].
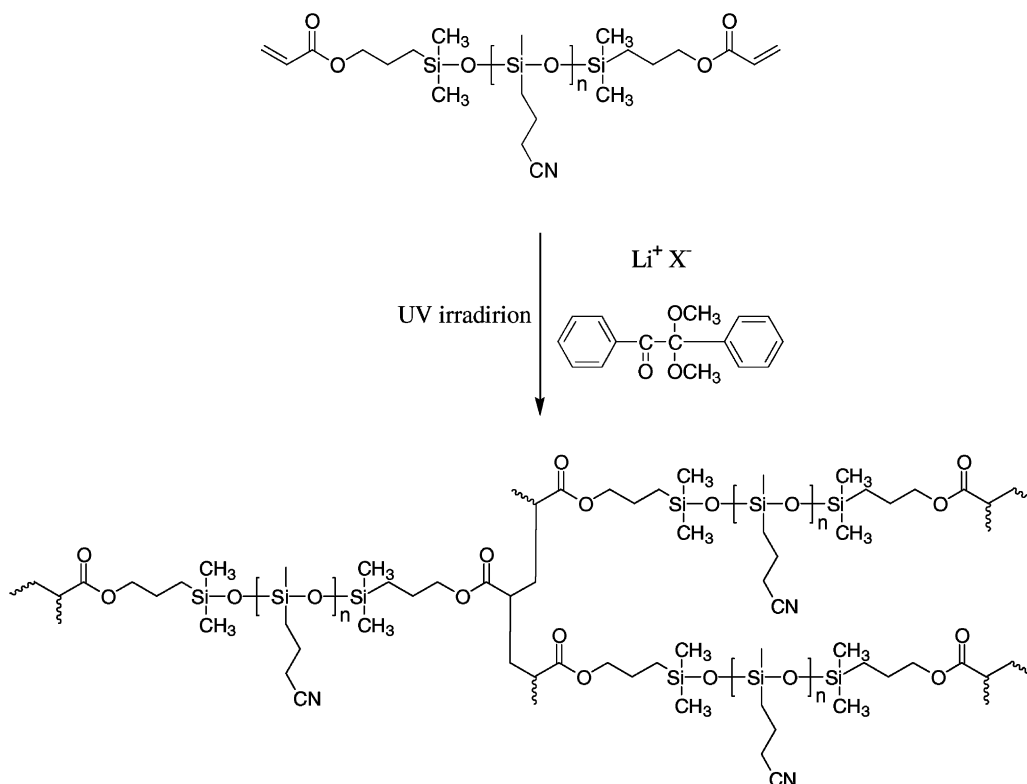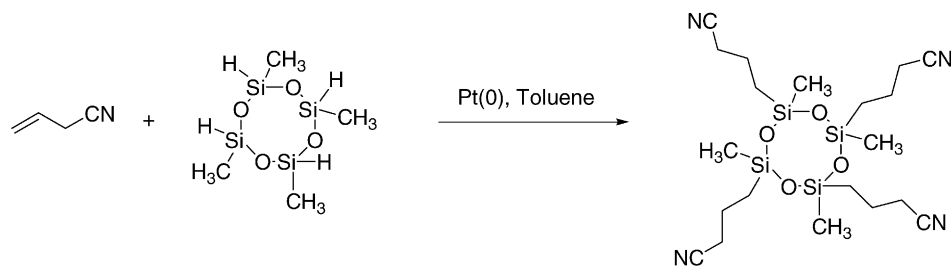

Fig. 1. Synthesis of network polymer electrolyte.

Fig. 2. Synthesis of (3-cyanopropyl)methylsiloxane cyclics.

Under the present experimental conditions, the side reaction (α-addition) was confirmed to be about 13%.

The sensitive Si–H absorption band of FT-IR at about 2165 cm^{-1} monitored (Fig. 3a). This band was absent in the product monomer (Fig. 3(b)), which indicates an essentially quantitative substitution. Alternatively, the progress of the reaction could be monitored by ^{1}H NMR (4.72 ppm of a Si–H peak; Fig. 4).
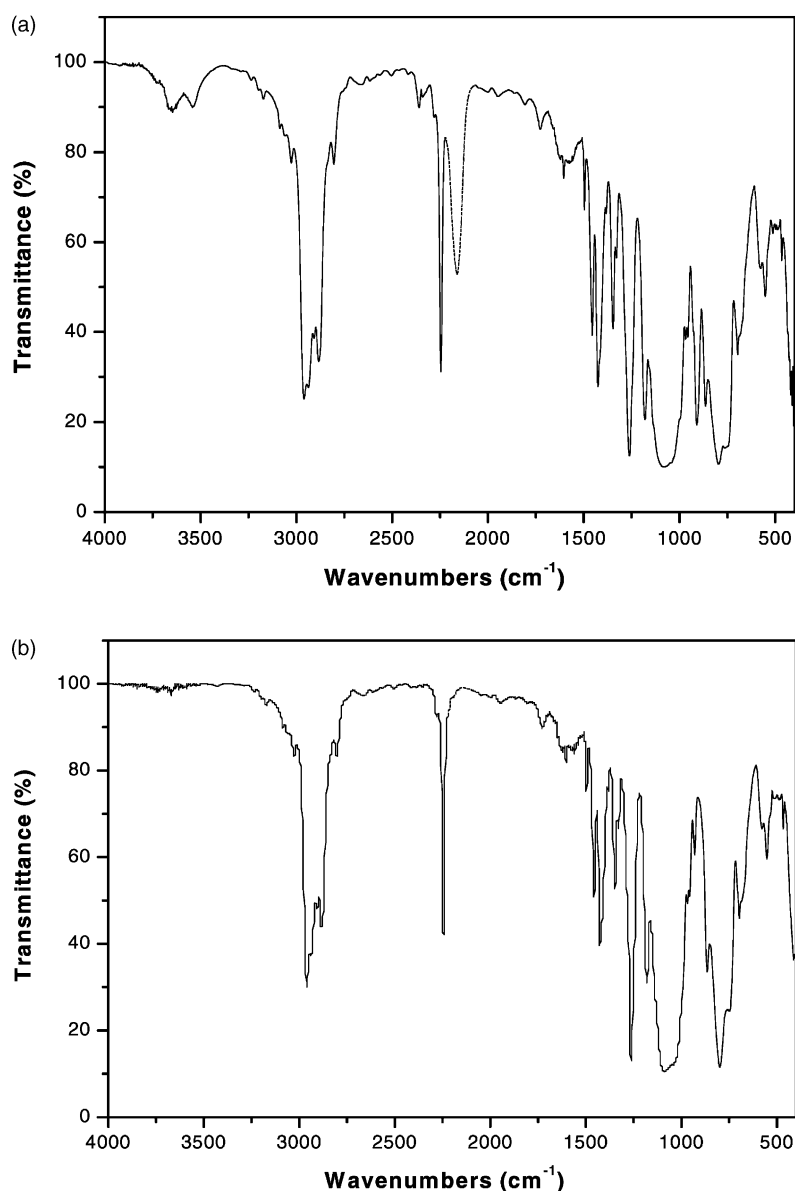

Fig. 3. Disappearance of Si-H band (2165 cm^{-1}) of monomer: (a) before reaction; (b) after reaction.

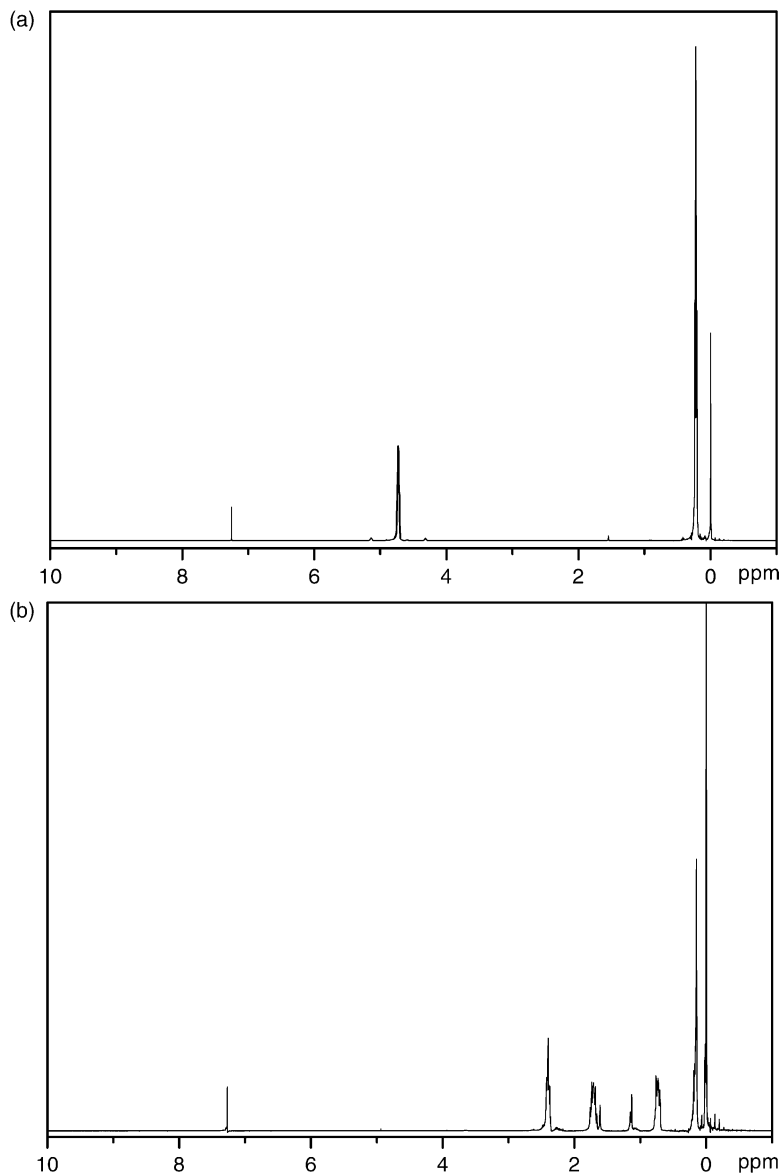Fig. 4. Disappearance of Si-H peak (4.72 ppm) of monomer: (a) before reaction; (b) after reaction.

3.1.2. D_2-1, 3-di(propaneacrylate)

The D_2-1,3-diropaneacrylate) as a cross-linkable ending group was synthesised according to a previous method (Fig. 5).

The FT-IR (KBr) and ^1H NMR (CDCl$_3$) spectra are shown in Fig. 6(a) and (b) and respectively. All spectra show a peak at 5.80–6.40 ppm assigned to the vinyl protons of acrylate. The methylene protons of the product resonate at about 0.55, 1.68 and 4.12 ppm, respectively.

3.1.3. Cross-linkable siloxane polymer

The cross-linkable polysiloxane was synthesised by ring-opening polymerisation with (3-cyanopropyl)methylsilox-ane cyclics using fuming sulfuric acid in Fig. 7.
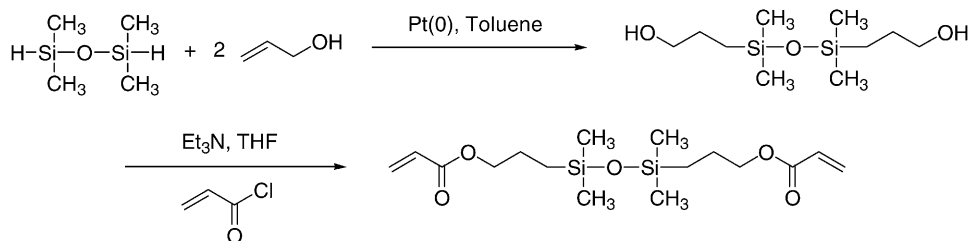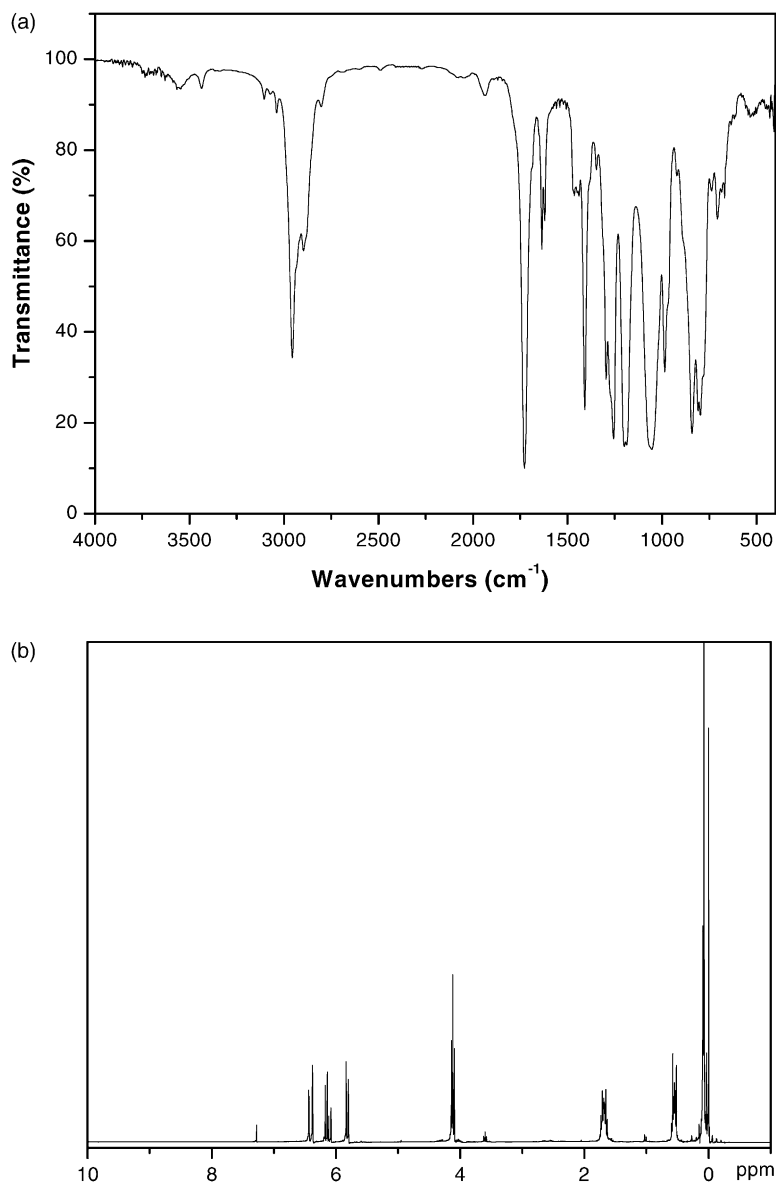

Fig. 5. Synthesis of D_2-1,3-di(propaneacrylate).

(a)

(b)

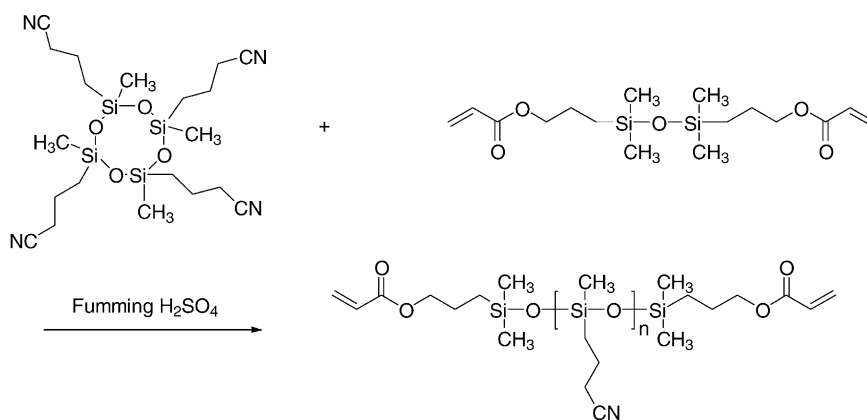Fig. 6. FT-IR (a) and ^{1}H NMR (b) spectrum of D_2-1,3-di(propane-acrylate).

Fig. 7. Synthesis of cross-linkable siloxane polymer.

Table 1
Characterisation of synthesised polymers

Reagents			Degree of polymerisation		Molecular weight (measured)[a]	Sample number
Terminating reagent	D$_4$monomer	Molar ratio	Expected	Measured[a]		
		1.60:4	10	10.8	1,732	D$_4$D$_2$-10
D$_2$-1,3-di(propaneacrylate)	(3-cyanopropyl)methylsiloxane cyclics	1.07:4	15	13.5	2,076	D$_4$D$_2$-15
		0.80:4	20	22.7	3,246	D$_4$D$_2$-20
		0.40:4	40	40.5	5,511	D$_4$D$_2$-40
		0.32:4	50	49.4	6,643	D$_4$D$_2$-50
		0.29:4	55	52.2	6,999	D$_4$D$_2$-55

[a] Calculated by ^{1}H NMR end group analysis.

The characteristics of the polymer synthesised by equilibrium polymerisation of (3-cyanopropyl)methylsiloxane cyclics and D$_2$-1,3-di(propaneacrylate) are shown in Table 1. During polymerisation, the tetramer becomes the main chain and the ends of chain are terminated by an acrylic moiety, guaranteeing $\bar{F}_n = 2$ of acrylate groups. The molecular weight is controlled by the [monomer]/[terminating agent] ratio.

The $\bar{M}_n$ was calculated by 300 MHz proton NMR spectroscopy from the integrated ratio of the methylene protons adjacent to a cyanide group (–CH$_2$CH$_2$C$\underline{H}_2$CN) resonance ($\delta = 2.40$) relative to the proton of a vinyl group (C$\underline{H}_2$=C–) ($\delta = 6.40$), see Fig. 8. Overall, the molecular weights obtained by NMR spectroscopy correlate well with theoretical values.

3.2. Ionic conductivity

The film preparation method of the polymer electrolyte is shown in Fig. 1. The photocross-linked polymer electrolyte was transparent and amorphous at room temperature. The

Table 2
Ionic conductivity of synthesised polymer electrolytes at room temperature

Sample number	[CN]:[Li$^+$] ratio	Film thickness (cm)	Conductivity (S cm^{-1})
D$_4$D$_2$-10	16	0.0106	3.75×10^{-6}
D$_4$D$_2$-15	16	0.0098	6.23×10^{-6}
D$_4$D$_2$-20	16	0.0151	6.37×10^{-6}
D$_4$D$_2$-40	16	0.0090	1.89×10^{-5}
D$_4$D$_2$-50	16	0.0080	1.55×10^{-5}
D$_4$D$_2$-55	16	0.0075	3.38×10^{-5}

dependence of the conductivity of a polymer as a function of a degree of polymerisation is shown in Table 2. The concentration of lithium perchlorate is 16 in the molar ratio of a unit of a cyanide group to a lithium ion ([CN]:[Li$^+$]). The ionic conductivity of all synthesised electrolytes was determined by means of complex plane impedance spectroscopy using ITO glass as blocking electrodes [22–24]. For example, Fig. 9 illustrates the complex plane impedance spectrum obtained at seven different temperatures for the synthesised polymer electrolytes complex. A straight line appears at low
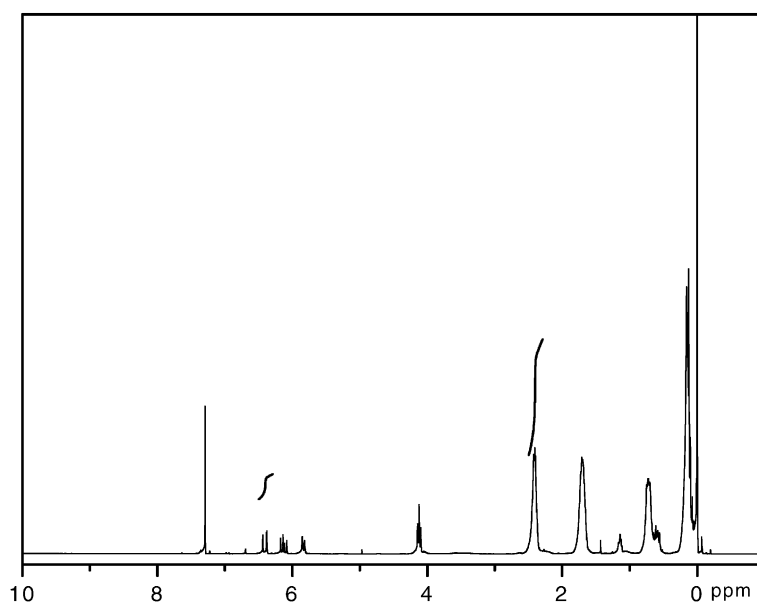

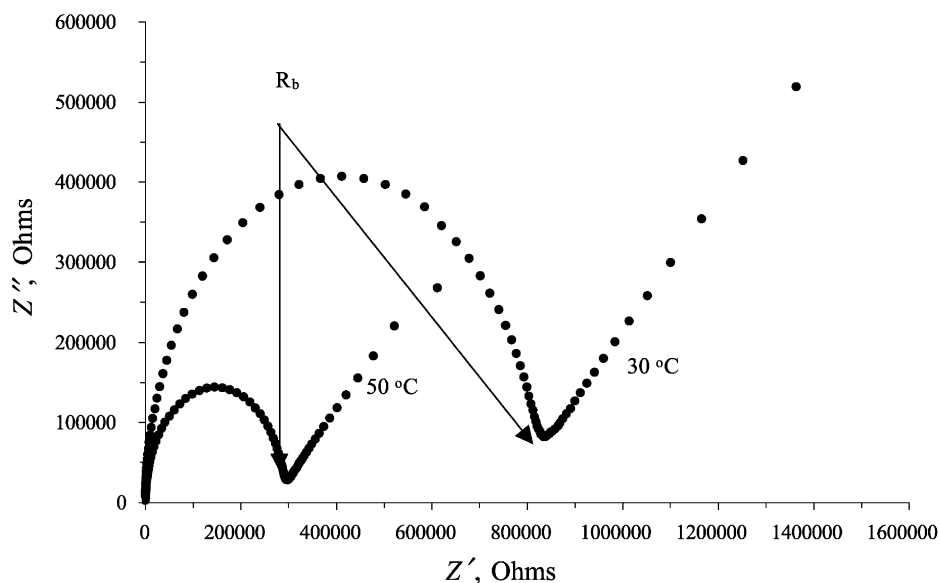Fig. 8. ^{1}H NMR spectrum of D$_4$D$_2$-15 ($n = 15$).

Fig. 9. Impedance spectroscopy analysis at 30 °C and 50 °C of D$_4$D$_2$-40 complex with [CN]:[Li$^+$] ratio of 16:1.

frequency, due to diffusion impedance at the electrode vertical line electrolyte interface, followed by a semicircle with a Z' intercept in the higher frequency range. From the Z'' versus Z' plot, ionic conductivity values were calculated at each temperature from the intercept of the curve with the real axis. The same behaviour is observed for the entire network of polymer electrolytes. The ionic conductivity shows a similar trend. The ionic conductivity is about 3.38×10^{-5} S cm^{-1} at 30 °C and 1.38×10^{-4} S cm^{-1} at 60 °C in an ITO electrode. These values are higher than those for the polyethylene oxide electrolytes complexed with lithium salts by l–2 orders of magnitude. The improvement of the conductivity for the synthesised polymer electrolyte may be attributed to the increase in ion solvation.
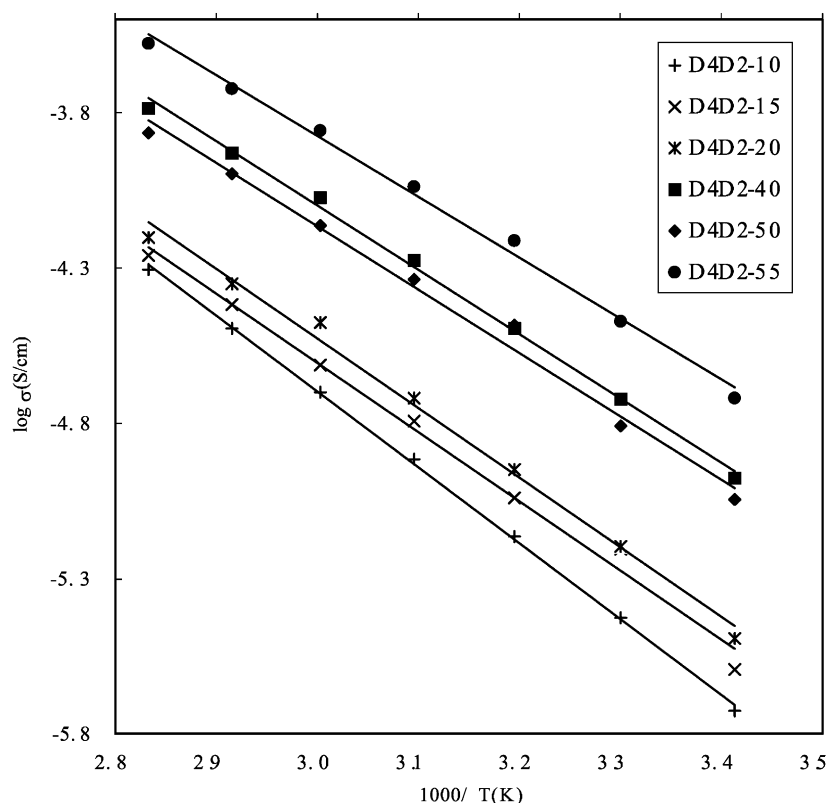

Fig. 10. Temperature dependence of conductivity for synthesised polymer electrolyte complexes with [CN]:[Li$^+$] ratio of 16:1.
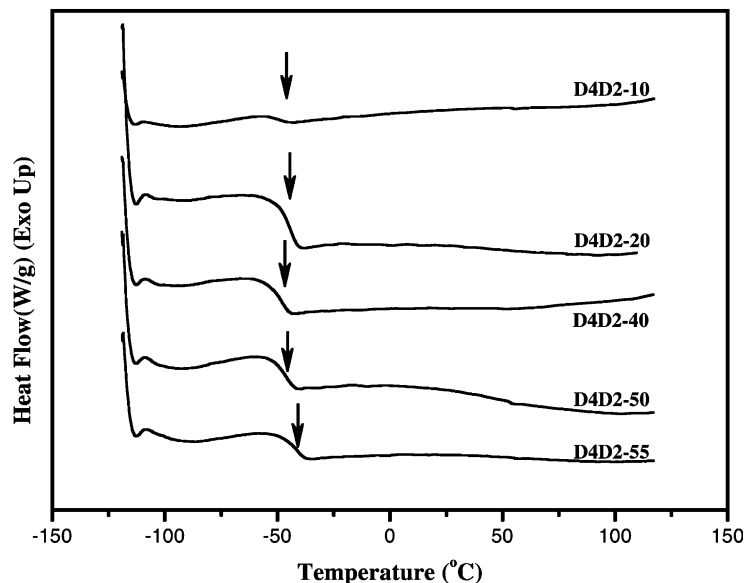
Fig. 11. DSC thermograms of polymer electrolyte complexes based on D_4D_2-n with a [CN]/[Li$^+$] ratio of 16:1.

Also, it is considered that the dielectric constant of the cyanide group (ex. acetonitrile), viz., $\varepsilon = 38.8$, is higher than that of polyether viz., $\varepsilon = 5$–8.

The temperature dependence of ionic conductivity is shown in Fig. 10 for all samples. It is generally observed that log σ versus $1/T$ plots conform to one of the following types of the behaviour [28]: (a) Vogel–Tammann–Fulcher (VTF) behaviour throughout the available thermal range; (b) Arrhenius behaviour for low temperatures and VTF behaviour at higher temperatures; (c) Arrhenius behaviour throughout, but with two different activation energies, high E_A closer to T_g, and a smaller E_A at higher temperatures; (d) VTF behaviour for temperatures slightly greater than T_g, but Arrhenius behaviour at higher temperatures: (e) behaviour which is very unlike either Arrhenius or VTF at all temperatures. Given the results, it can be concluded that the ionic conductivity mechanism of the present synthesised network polymer electrolytes should follow the empirical VTF equation, i.e.

$$\sigma = AT^{-1/2} \exp\left[-\frac{B}{R(T - T_0)}\right] \tag{1}$$

where A and B are constants related to the number of charge carriers and the conduction activation energy, respectively; T is absolute temperature; T_0 a temperature related to T_g. According to a Gibbs configurational entropy model, T_0 50 K below the measured T_g.

3.3. Thermal property

The thermal properties of D_4D_2-n and its salt complex, which were investigated by differential scanning calorimetry, are shown in Fig. 11. Glass transition temperatures are observed at -50 to -40 °C in DSC scans for a network polymer electrolytes complex.

4. Conclusions

A photocross-linked polymer electrolyte based on a siloxane backbone containing a cyanide pendant has been synthesised by photo-occurring of an acrylate group. FT-IR and ^{1}H NMR data indicate the structure of (3-cyanopropyl)methylsiloxane cyclics, D_2-1,3-di(propaneacrylate) and polymers. The maximum conductivity, 3.38×10^{-5} S cm^{-1} at room temperature, is observed for $n = 55$ of the polymer at a concentration of 16 cyanide groups per lithium perchlorate. The improvement in conductivity for the synthesised polymer electrolyte is attributed to an increase in ion solvation It is thought that the dielectric constant of the cyanide group is stronger than that of polyether.

Acknowledgements

References

[1] M.B. Armand, Amu. Rev. Mater. Sci. 16 (1986) 245.
[2] C.A. Vicent, Chem. Br. (1989) 391.
[3] M.A. Ratner, D.F. Shriver, Chem. Rev. 88 (1988) 109.
[4] M. Watanabe, N. Ogata, Br. Polym. J. 20 (1988) 181.
[5] B.L. Papke, D.F. Shriver, J. Electrochem. Sci. 129 (1982) 1694.
[6] P.V. Wright, Br. Polym. J. 7 (1975) 319.
[7] M. Mclin, C.A. Angell, Solid State Ionics 56 (1992) 1027.
[8] P.G. Hall, R.G. Devries, J.E. McIntyre, I.M. Ward, D.J. Bannister, K.M.F. Le Brocq, Polym. Commun. 27 (1986) 98.
[9] M. Watanabe, S. Nagano, K. Saniu, N. Ogata, J. Power Sources 20 (1987) 327.
[10] I.M. Khan, Y. Yuan, D. Fish, E. Wu, J. Smid, Macromolecules 21 (1988) 2648.

[11] R. Spindler, D.F. Shriver, Macromolecules 21 (1988) 648.

[12] G. Zhou, Z.M. Khan, J. Smid, Macromolecules 26 (1993) 2202.

[13] N. Kunde, R.D.A. Paulmer, S. Shyamada, N.K. Khosla, A.R. Kulkarni, J. Mater. Sci. Lett. 14 (1955) 271.

[14] K. Nagaoka, H. Naruse, I. Shinohara, M. Watanabe, J. Polym. Sci., Polym. Lett. Ed. 22 (1984) 659.

[15] D. Fish, I.M. Khan, J. Smid, Macromol. Chem. Rapid. Commun. 7 (1986) 115.

[16] R. Spindler, D.F. Shriver, J. Am. Chem. Soc. 10 (1988) 3036.

[17] D. Fish, I.M. Khan, J. Smid, Br. Polym. J. 20 (1988) 281.

[18] Z.C. Zhang, S. Fang, Electrochem. Acta 45 (2000) 2131.

[19] S.S. Hou, Y.P. Chung, C.K. Chan, P.L. Kuo, Polymer 41 (2000) 3263.

[20] M.A. Sherman, J.P. Kennedy, J. Polym. Sci. A: Polym. Chem. 36 (1998) 1891.

[21] S. Feng, M. Cui, React. Funct. Polym. 45 (2000) 79.

[22] Y. Kang, H.J. Kim, E. Kim, B. Oh, J.H. Cho, J. Power Sources 92 (2001) 255.

[23] K.M. Abraham, M. Alamgir, R.K. Reynolds, J. Electrochem. Soc. 136 (1989) 3576.

[24] E. Morales, J.L. Acosta, Electrochim. Acta 45 (1999) 1049.

[25] P.G. Bruce, in: J.R. MacCllum, C.A. Vincent (Eds.), Polymer Electrolyte Reviews, Elsevier, New York, 1987 (Chapter 8).

[26] L. Lestel, S. Boileau, H. Cheradame, Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) 30 (1989) 133.

[27] H.R. Kricheldorf Silicon in Polymer Synthesis, Springer, Germany, 1996.

[28] M.A. Ratner, in: J.R. MacCllum, C.A. Vincent (Eds.), Polymer Electrolyte Reviews, Elsevier, New York, 1987 (Chapter 7).