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Polyethers with phosphate pendant groups by monomer activated anionic ring opening polymerization: Syntheses, characterization and their lithium-ion conductivities

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ABSTRACT

This paper describes the preparations and lithium-ion conductivities of various solid polymer electrolytes for potential use in high-energy density lithium-ion batteries. The ring opening polymerization of epoxides (**M1–M6**), catalyzed by Zn(II), Cu(II) and Cd(II) complexes in the presence of tetrabuty-lammonium bromide (TBAB), yielded polyethers (**P1–P6**) in which phosphates were attached as pendant groups. A reaction condition where Zn(II) catalyst used slightly excess to TBAB increased the polymerization rate remarkably and yielded the polyethers with higher molar masses in a short time. These polymerizations proceeded following a "monomer activated anionic ring opening polymerization" mechanism. These living like polymerizations also progressed according to "formation of polymer chain per initiator" model. The solid-state lithium-ion conductivities of these polymers were examined using lithium bis(trifluoromethanesulfonyl)imide (LiTFSI). The conductivity of one of the solid polymer electrolytes with 40 wt% of LiTFSI was 5.2×10^{-5} S cm⁻¹ at room temperature and 2.9×10^{-4} S cm⁻¹ at 80 °C.

1. Introduction

Several variations have been tried to increase the ionic conductivity of poly(ethylene oxide) (PEO) since its room temperature ionic conductivity is low $(10^{-7} \text{ S cm}^{-1})$ for practicable applications [1]. Some effective variations are; the PEO based composites produced by mixing with polymer blends [2], inorganic fillers [3], plasticizers [4] and ionic liquids [5]; PEO based network polymers [6], cross-linked by siloxane polymers [7]; and block copolymers [8]. One of the major reasons causing the low ionic conductivity at ambient temperatures is the large crystalline area of PEO and less conformational flexibility. Therefore, there are interests towards decreasing crystallinity and increasing conformational flexibility. Since the amorphous region is responsible for the ion-conductivity, extending the amorphous phase can also improve the conductivity of polymers [9]. The ionic conductivity in amorphous polymers is caused by mobility of ions promoted by local segmental motion of the polymer chains above T_{g} . Beyond T_{g} , the polymer's superstructures have disordered and flexible environment. Therefore, when the chains are in constant motion, vacant spaces would continually create and disappear through which ions can be

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transported. Because of the conformational flexibility induced by the presence of atoms of varying sizes in the polymer chains, the polyphosphazenes [10] and polysiloxanes [11] showed lithium ion conductivities of 5.0×10^{-5} S cm⁻¹ and 4.5×10^{-4} S cm⁻¹ respectively. Our interest is impelling conformational flexibilities and expanding the amorphous region; and examine the properties like crystallinity, $T_{\rm g}$ and ionic conductivity of the polymer.

Lithium-ion batteries are the major power sources for portable electronics. In the lithium-ion batteries, the electrodes are separated by an inert, porous polymer separator which is usually poly(propylene) soaked with low molecular weight organic liquids containing a dissolved salt. At room temperature, the ionic conductivity of liquid organic electrolytes is in the range of 10^{-3} S cm⁻¹. However, these organic liquids have potential fire hazard especially with large batteries that are useful for electric vehicles [12]. Thus, the research on finding solid polymer electrolyte (SPE) with flameretardant properties to replace organic solvents in high-energy density lithium-ion batteries is always been in demand. The flame-retardant property for polymer electrolytes so far achieved by blending phosphorus containing molecules or covalently attaching them directly to the polymer chains [13]. Varieties of polymers in which phosphorus is a part of polymer chains are wellknown [14–16]. However, the present interest is producing polyethers with bulky rigid pendant groups such as substituted phosphates. These rigid groups would be influencing the assembly of





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chains in the polymer matrices and create perpetual free volume for the mobility of lithium-ion.

Poly(propylene oxide)s and PEO are important classes of polymers [17], they gained importance in biological and industrial applications especially in lithium-ion batteries. These polymers are produced from propylene oxides or EO respectively by cationic, anionic or metal catalyzed ring opening polymerization (ROP). The backbiting side reactions hinder the cationic polymerization leading to form low molecular weight oligomers. Alkali metal derivatives are efficient initiators for the anionic polymerization of cyclic ethers. However, the high basicity of propagating species resulted in proton abstraction leading to form hydroxy ended oligomer chains and allyl alkoxide initiator [18]. More recently, the polyethers with high molecular weights were produced by monomer activated anionic polymerization with restricted transfer to monomer side reactions. This was realised in the presence of combinations of alkali metal salts or ammonium salts and a trialkylaluminium [19]. Similarly, a bimetallic cobalt catalyst/PPNX was reported to be active in catalyzing enantioselective ROP of propylene oxide [20].

Recently, we have reported the syntheses of Zn(II), Cd(II) and Cu(II) complexes of 2,5-bis{N-(2,6-diisopropylphenyl)iminomethyl}pyrrole and their effective catalytic activities for cyclic carbonate synthesis from epoxide and CO₂ at 1 atm [21]. Our interests in the present research are threefold as follows. (i) Designing and synthesis of polymers having conformational flexibility, (ii) production of poly(ethylene oxide)s with phosphates as a pendant group and by it creating suitable superstructure for lithium-ion mobility, (iii) exploring the catalytic activities of above complexes for ring opening polymerization of cyclic ethers.

2. Experimental section

2.1. Materials and instrumentation

All manipulations involving air and moisture sensitive compounds were carried out using standard Schlenk techniques under the atmosphere of dry nitrogen. All solvents to be used under inert atmosphere were thoroughly deoxygenated using freeze-pumpthaw method before use. They were dried and purified by refluxing over a suitable drying agent followed by distillation under nitrogen atmosphere. The compound, 3,3',5,5'-tetra-tert-butyl-1,1'biphenyl-2,2'-diol was synthesized according to the literature procedure [22]. The compounds, chlorodiphenylphosphine oxide (S1), diphenyl phosphoryl chloride (S2), 4-methoxyphenol, 4phenylphenol, biphenyl-2,2'-diol, glycidol and lithium bis(trifluoromethanesulfonyl)imide LiN(SO2CF3)2 (LiTFSI) were purchased from Aldrich and were used as received without purification. The starting materials **S3–S6** were prepared by reacting POCl₃ with suitable equivalents of respective compounds 4-methoxyphenol, 4-phenylphenol, biphenyl-2,2'-diol and 3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diol. Tetrabutylammonium bromide (Merck) was dried at 50 °C for 4 h under vacuum prior to use.

The structures of all the products were confirmed by ¹H, ³¹P, ¹³C NMR spectra and HRMS data. All the NMR spectra were recorded on a Bruker Avance 400 MHz FT NMR spectrometer at room temperature using either CDCl₃ or DMSO-d₆ as a solvent. The chemical shifts are reported in parts per million (δ) relative to tetramethylsilane as a reference for ¹H and ¹³C{¹H} NMR (100 MHz). The ³¹P {¹H} NMR (162 MHz) spectra referenced to 85% H₃PO₄. HRMS spectra were recorded on a Bruker maXis instrument using ESI technique. Single crystal X-ray data collection was carried out at 298(2) K on a Bruker Smart Apex CCD area detector system (λ (Mo K α) = 0.71073 Å) with a graphite monochromator. The data were

reduced using SAINTPLUS and the structures were solved using SHELXS-97 and refined using SHELXL-97 [23]. All hydrogen atoms were refined anisotropically. The Netzsch STA 409 PC model was used for thermogravimetric and differential thermal analysis (TG-DTA) to examine the thermal stability. The decomposition behaviour of polymers was studied from 30 to 900 °C under the nitrogen flow with a heating rate of 10 °C/min. The temperature of 5% weight loss was chosen as an onset point of decomposition (T_d) . The glass transition temperatures (T_g) of polyethers were measured in a Differential Scanning Calorimeter (DSC) from PerkinElmer (Pyris Diamond DSC 8000). The measurements were performed at a heating rate of 10 °C/min under the nitrogen. T_g was assigned as the inflection point in the thermogram. The molecular weights of the polymers were determined by the Gel Permeation Chromatography (GPC) of Shimadzu 10AVP model equipped with refractive index (RI) detector. The separation was achieved using a Phenogel mixed bed column (300 \times 7.80 mm) operated at 30 $^\circ C$ with a flow rate of 0.5 mL/min using tetrahydrofuran (THF) as the eluent. The molecular weight and molecular weight distributions were calculated using polystyrene as a standard.

The impedance measurements of polymer electrolytes were performed in Zahner zennium electrochemical work station with built in Thales software for data acquisition. The measurements were done in the frequency range of 1 Hz-4 MHz. Initially films were made by dissolving polymer and LiN(SO₂CF₃)₂ in THF at room temperature, but the films of SPEs were brittle. Therefore, instead of making films, pellets were made for measurements. The consistency of result was checked by repeating the measurements three times. The specimens in the form of pellets were sandwiched between two gold plated electrodes housed in a homemade cell. For variable temperature measurements, cell was equilibrated at each temperature for 30 min before measuring. The conductivity was calculated according to the equation $\sigma = d/(AR_b)$, where *d* is the thickness of the polymer electrolyte disc, A is the surface area of the pellet and $R_{\rm b}$ is the bulk resistance value which can be obtained from the Nyquist plot [24].

2.2. Experimental procedure

2.2.1. Synthesis of chlorodi(4-methoxyphenoxy)phosphine oxide (**S3**)

A solution of 4-methoxyphenol (6.21 g, 50 mmol) in THF (10 mL) was added to a solution of POCl₃ (2.3 mL, 25 mmol) in THF (15 mL) at 0 °C. To this, NEt₃ (7.0 mL, 50 mmol) was slowly added for 10 min at 0 °C. While adding NEt₃, immediate formation of a white precipitate (NEt₃HCl) was observed. This reaction mixture was stirred for 2 h at 0 °C. After this, the reaction mixture was filtered to remove NEt₃HCl and the filtrate was evaporated under vacuum. A crude product was obtained as a colorless viscous oil. As monitored by ³¹P{¹H} NMR spectra, this crude product was not stable at room temperature. This made isolation of pure **S3** unsuccessful. Therefore, it was used without purification for the synthesis of **M3**. ³¹P NMR (162 MHz, CDCl₃) of crude product (**S3**): δ –3.83.

2.2.2. Synthesis of chlorodi(4-phenylphenoxy)phosphine oxide (S4)

A solution of 4-phenylphenol (8.51 g, 50 mmol) in THF (10 mL) was added to a solution of POCl₃ (2.3 mL, 25 mmol) in THF (15 mL) at 0 °C. To this, NEt₃ (7.0 mL, 50 mmol) was slowly added for 10 min at 0 °C. While adding NEt₃, immediate formation of a white precipitate (NEt₃HCl) was observed. This reaction mixture was stirred for 2 h at 0 °C. After this, the reaction mixture was filtered to remove NEt₃HCl and the filtrate was evaporated under vacuum. A crude product was obtained as a white powder which was not stable in room temperature as seen in ³¹P{¹H} NMR spectra. This made isolation of pure **S4** unsuccessful. Therefore, it was used

without purification for the synthesis of **M4**. ³¹P NMR (162 MHz, CDCl₃) of crude product (**S4**): δ –5.21.

2.2.3. Synthesis of (1,1'-biphenyl-2,2'-dioxy)chlorophosphine oxide (**S5**)

A solution of biphenyl-2,2'-diol (4.66 g, 25 mmol) in THF (10 mL) was added to a solution of POCl₃ (2.3 mL, 25 mmol) in THF (15 mL) at 0 °C. To this, NEt₃ (7.0 mL, 50 mmol) was slowly added for 10 min at 0 °C. While adding NEt₃, immediate formation of a white precipitate (NEt₃HCl) was observed. This reaction mixture was stirred for 2 h at 0 °C. After this, the reaction mixture was filtered to remove NEt₃HCl and the filtrate was evaporated under vacuum to obtain pure product (S5). The product was obtained as a white powder (yield 95%). ¹H NMR (400 MHz, CDCl₃): δ 7.60–7.56 (m, 2H, $-C_6H_4$, 7.53–7.47 (m, 2H, $-C_6H_4$), 7.46–7.40 (m, 2H, $-C_6H_4$), 7.38– 7.33 (m, 2H, $-C_6H_4$). ¹³C NMR (100 MHz, CDCl₃): δ 147.5 (d, *J* = 11.4 Hz), 130.5, 130.2, 128.1, 127.4, 121.5 (d, *J* = 4.5 Hz). ³¹P NMR (162 MHz, CDCl₃): δ 9.92. HRMS (ESI) m/z: calcd. for C₁₂H₈ClO₃P [M + Na]⁺ 288.9797, found 288.9797. The molecular structure of **S5** (Fig. 1) determined using X-ray crystallography clearly showed the presence of a seven-membered ring in it.

2.2.4. Synthesis of (3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'dioxy)chlorophosphine oxide (**S6**)

A solution of 3,3',5,5'-tetra-*tert*-butyl-1,1'-biphenyl-2,2'-diol (10.27 g, 25 mmol) in THF (10 mL) was added to a solution of POCl₃ (2.3 mL, 25 mmol) in THF (15 mL) at 0 °C. To this, NEt₃ (7.0 mL, 50 mmol) was slowly added for 10 min at 0 °C. While adding NEt₃, immediate formation of a white precipitate (NEt₃HCl) was observed. This reaction mixture was stirred for 2 h at 0 °C. After this, the reaction mixture was filtered to remove NEt₃HCl and the filtrate was evaporated under vacuum to obtain pure product (**S6**). The product was obtained as a white powder (yield 98%). ¹H NMR (400 MHz, CDCl₃): δ 7.56–7.52 (m, 2H, –C₆H₂), 7.22 (d, *J* = 2.4 Hz, 2H, –C₆H₂), 1.52 (s, 18H, –CH₃), 1.36 (s, 18H, –CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 148.7, 144.3 (d, *J* = 11.7 Hz), 140.2 (d, *J* = 4.9 Hz), 129.8, 126.9, 125.8, 35.6, 34.8, 31.4. ³¹P NMR (162 MHz, CDCl₃): δ 4.32. HRMS (ESI) *m/z*: calcd. for C₂₈H₄₀ClO₃P [M + H]⁺ 491.2482, found 491.2486.

2.2.5. General procedure for the syntheses of monomers M1-M6

A solution of glycidol (1.6 mL, 24 mmol) in THF (10 mL) was added to a solution of appropriate chloro compound (**S1–S6**) (20 mmol) in THF (15 mL) at 0 °C. NEt₃ (5.6 mL, 40 mmol) was slowly added to the reaction mixture at 0 °C for 10 min. The



Fig. 1. ORTEP of the molecular structure S5. Thermal ellipsoids are shown at 30% probability levels. Hydrogen atoms are omitted for clarity.

immediate formation of a white precipitate (NEt₃HCl) was observed. The reaction mixture was stirred for required time and temperature. Then, the reaction mixture was filtered to remove NEt₃HCl and the filtrate was evaporated under vacuum to obtain the products.

2.2.5.1. Synthesis of oxiran-2-ylmethyl diphenylphosphinate (**M1**). Prepared according to the general procedure by using chlorodiphenylphosphine oxide (**S1**) (4.73 g, 20 mmol). After the addition of NEt₃, the reaction mixture was stirred for 12 h at 25 °C. The product was obtained as colorless viscous oil (yield 96%). ¹H NMR (400 MHz, CDCl₃): δ 7.88–7.79 (m, 4H, –C₆H₅), 7.57–7.50 (m, 2H, – C₆H₅), 7.50–7.42 (m, 4H, –C₆H₅), 4.35–4.27 (m, 1H, –POCH₂CH), 3.98–3.89 (m, 1H, –POCH₂CH), 3.31–3.25 (m, 1H, –CH₂CHCH₂), 2.85–2.80 (m, 1H, –OCH₂CH), 2.68–2.63 (m, 1H, –OCH₂CH). ¹³C NMR (100 MHz, CDCl₃): δ 132.4, 131.8–131.5 (m), 130.3 (d, *J* = 16.3 Hz), 128.6 (d, *J* = 12.8 Hz), 65.3 (d, *J* = 5.3 Hz), 50.4 (d, *J* = 7.7 Hz), 44.7. ³¹P NMR (162 MHz, CDCl₃): δ 32.95. HRMS (ESI) *m*/*z*: calcd. for C₁₅H₁₅O₃P [M + Na]⁺ 297.0657, found 297.0655.

2.2.5.2. Synthesis of oxiran-2-ylmethyl diphenylphosphate (**M2**). Prepared according to the general procedure by using diphenyl phosphoryl chloride (**S2**) (5.37 g, 20 mmol). After the addition of NEt₃, the reaction mixture was stirred for 12 h at 25 °C. The product was obtained as colorless viscous oil (yield 98%). ¹H NMR (400 MHz, CDCl₃): δ 7.38–7.31 (m, 4H, $-C_6H_5$), 7.26–7.17 (m, 6H, $-C_6H_5$), 4.35–4.28 (m, 1H, $-POCH_2CH$), 4.19–4.10 (m, 1H, $-POCH_2CH$), 3.27–3.21 (m, 1H, $-C_1_2CHCH_2$), 2.85–2.80 (m, 1H, $-OCH_2CH$), 2.65 (dd, J = 4.8 Hz and J = 2.6 Hz, 1H, $-OCH_2CH$). ¹³C NMR (100 MHz, CDCl₃): δ 150.4 (d, J = 6.0 Hz), 129.9, 125.5, 120.1, 69.4 (d, J = 5.7 Hz), 49.8 (d, J = 7.7 Hz), 44.5. ³¹P NMR (162 MHz, CDCl₃): δ –11.81. HRMS (ESI) m/z: calcd. for C₁₅H₁₅O₅P [M + Na]⁺ 329.0555, found 329.0555.

2.2.5.3. Synthesis of bis(4-methoxyphenyl)oxiran-2-ylmethyl phosphate (**M3**). Prepared according to the general procedure by using chlorodi(4-methoxyphenoxy)phosphine oxide (**S3**) (6.57 g, 20 mmol). After the addition of NEt₃, the reaction mixture was stirred for 2 h at 0 °C. The crude product was purified by column chromatography on silica gel eluting with hexane/ethylacetate (1:1) to give pure light brown color viscous oil (yield 88%). ¹H NMR (400 MHz, CDCl₃): δ 7.16–7.11 (m, 4H, –C₆H₅), 6.86–6.81 (m, 4H, – C₆H₅), 4.47–4.40 (m, 1H, –POCH₂CH), 4.15–4.06 (m, 1H, – POCH₂CH), 3.77 (s, 6H, –OCH₃), 3.26–3.20 (m, 1H, –CH₂CHCH₂), 2.84–2.80 (m, 1H, –OCH₂CH), 2.64 (dd, *J* = 4.8 Hz and *J* = 2.6 Hz, 1H, –OCH₂CH). ¹³C NMR (100 MHz, CDCl₃): δ 157.0, 144.0 (d, *J* = 6.6 Hz), 121.0, 114.7, 69.3 (d, *J* = 5.8 Hz), 55.6, 49.8 (d, *J* = 7.8 Hz), 44.5. ³¹P NMR (162 MHz, CDCl₃): δ –10.72. HRMS (ESI) *m/z*: calcd. for C₁₇H₁₉O₇P [M + H]⁺ 367.0947, found 367.0948.

2.2.5.4. Synthesis of dibiphenyl-4yl-oxiran-2-ylmethyl phosphate (M4). Prepared according to the general procedure by using chlorodi(4-phenylphenoxy)phosphine oxide (S4) (8.42 g, 20 mmol). After the addition of NEt₃, the reaction mixture was stirred for 2 h at 0 °C. The crude product was purified by column chromatography on silica gel eluting with hexane/ethylacetate (3:1) to give pure white color powder (yield 81%). ¹H NMR $(400 \text{ MHz}, \text{CDCl}_3)$: δ 7.60 (t, $J = 8.6 \text{ Hz}, 8\text{H}, -C_6H_5$), 7.47 (t, J = 7.2 Hz,4H, -C₆H₅), 7.42-7.34 (m, 6H, -C₆H₅), 4.62-4.52 (m, 1H, -POCH2CH), 4.29-4.18 (m, 1H, -POCH2CH), 3.37-3.30 (m, 1H, -CH₂CHCH₂), 2.93-2.85 (m, 1H, -OCH₂CH), 2.77-2.70 (m, 1H, -OCH₂CH). ¹³C NMR (100 MHz, CDCl₃): δ 149.9 (d, J = 7.2 Hz), 140.1, 138.8, 128.9, 128.6, 127.5, 127.1, 120.5–120.3 (m), 69.6 (d, *J* = 5.8 Hz), 49.8 (d, J = 7.6 Hz), 44.6. ³¹P NMR (162 MHz, CDCl₃): $\delta - 11.53$. HRMS (ESI) m/z: calcd. for C₂₇H₂₃O₅P [M + H]⁺ 459.1361, found 459.1360. The molecular structure of **M4** (Fig. 2) determined using X-ray crystallography.

2.2.5.5. Synthesis of 2-(((1,1'-biphenyl-2,2'-dioxy)phosphine oxide) methyl)oxirane (**M5**). Prepared according to the general procedure by using (1,1'-biphenyl-2,2'-dioxy)chlorophosphine oxide (**S5**) (5.33 g, 20 mmol). After the addition of NEt₃, the reaction mixture was stirred for 2 h at 0 °C. The product was obtained as a pale yellow color powder (yield 90%). ¹H NMR (400 MHz, CDCl₃): δ 7.55 (d, *J* = 7.6 Hz, 2H, -C₆H₄), 7.49–7.43 (m, 2H, -C₆H₄), 7.39 (d, *J* = 7.5 Hz, 2H, -C₆H₄), 7.37–7.31 (m, 2H, -C₆H₄), 4.62–4.54 (m, 1H, -POCH₂CH), 4.26–4.17 (m, 1H, -POCH₂CH), 3.36–3.30 (m, 1H, -CH₂CHCH₂), 2.92–2.87 (m, 1H, -OCH₂CH), 2.74–2.69 (m, 1H, -OCH₂CH). ¹³C NMR (100 MHz, CDCl₃): δ 147.7 (d, *J* = 14.9 Hz), 130.2, 129.9, 128.2, 126.6, 121.4, 69.8 (d, *J* = 4.3 Hz), 49.8 (d, *J* = 7.4 Hz), 44.6. ³¹P NMR (162 MHz, CDCl₃): δ 1.76. HRMS (ESI) *m/z*: calcd. for C₁₅H₁₃O₅P [M + H]⁺ 305.0579, found 305.0579.

2.2.5.6. Synthesis of 2-(((3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'*dioxy*)*phosphine oxide*)*methyl*)*oxirane* (*M6*). Prepared according to the general procedure by using (3,3',5,5'-tetra-tert-butyl-1,1'biphenyl-2,2'-dioxy)chlorophosphine oxide (**S6**) (9.82 g, 20 mmol) and NaH (40 mmol) as a base instead of NEt₃. After the addition of NEt₃, the reaction mixture was stirred for 2 h at 0 °C. The crude product was purified by column chromatography on silica gel eluting with hexane/ethylacetate (3:1) to give pure a white color powder (yield 84%). ¹H NMR (400 MHz, CDCl₃): δ 7.50 (s, 2H, - C_6H_2), 7.22–7.19 (m, 2H, $-C_6H_2$), 4.48–4.40 (m, 1H, $-POCH_2CH$), 4.19-4.10 (m, 1H, -POCH₂CH), 3.28-3.22 (m, 1H, -CH₂CHCH₂), 2.85-2.80 (m, 1H, $-OCH_2CH$), 2.65 (dd, J = 4.8 Hz and J = 2.5 Hz, 1H, $-OCH_2CH$), 1.52 (d, J = 3.4 Hz 18H, $-CH_3$), 1.36 (s, 18H, $-CH_3$). ¹³C NMR (100 MHz, CDCl₃): δ 148.0, 144.4 (d, J = 9.5 Hz), 140.1 (d, J = 4.5 Hz), 130.0, 126.7, 125.3, 69.8 (d, J = 6.0 Hz), 49.8 (d, J = 7.0 Hz), 44.7, 35.5, 34.7, 31.4, 31.1. ³¹P NMR (162 MHz, CDCl₃): δ -3.01. HRMS (ESI) *m*/*z*: calcd. for C₃₁H₄₅O₅P [M + Na]⁺ 551.2902, found 551.2903.

2.2.6. General procedure for the ROP of epoxides

All the polymerization reactions were performed in the pressure tube. To the solution of monomer (**M1–M6**) (10 mmol) in THF (2.5 mL), catalyst (0.1 mmol) and TBAB (0.067 mmol) was added under stirring. The pressure tube was heated to 70 °C and stirred for the required time. After the reaction time, methanol was added to the reaction mixture to quench the polymerization and the solvent was evaporated under vacuum. The product was purified by dissolving in THF and reprecipitated in hexane and this process was repeated for three more times.



2.2.6.2. Synthesis of polymer **P2**. The ROP was carried out according to the general procedure by using oxiran-2-ylmethyl diphenylphosphate (**M2**). Yield 98%. ¹H NMR (400 MHz, CDCl₃): δ 7.43–7.09 (m, $-C_6H_5$), 7.03–6.75 (m, $-C_6H_5$), 4.33–3.99 (m, $-POCH_2CH$), 3.93-3.72 (m, $-OCH_2CH$ and $-CH_2CHCH_2$). ¹³C NMR (100 MHz, CDCl₃): δ 158.9, 129.8, 120.2, 115.1, 80.8, 70.1, 67.3. ³¹P NMR (162 MHz, CDCl₃): δ –0.75.

2.2.6.3. Synthesis of polymer **P3**. The ROP was carried out according to the general procedure by using bis(4-methoxyphenyl)oxiran-2-ylmethyl phosphate (**M3**). Yield 95%. ¹H NMR (400 MHz, CDCl₃): δ 6.99–6.78 (m, -C₆H₅), 6.75–6.62 (m, -C₆H₅), 4.43–4.15 (m, – POCH₂CH), 4.09–3.80 (m, –OCH₂CH and –CH₂CHCH₂), 3.70–3.60 (m, –OCH₃). ³¹P NMR (162 MHz, CDCl₃): δ –5.82.

2.2.6.4. Synthesis of polymer **P4**. The ROP was carried out according to the general procedure by using dibiphenyl-4yl-oxiran-2-ylmethyl phosphate (**M4**). Yield 90%. ¹H NMR (400 MHz, CDCl₃): δ 7.66–7.50 (m, –C₆H₅), 7.44–7.35 (m, –C₆H₅), 7.32–7.19 (m, –C₆H₅), 4.32–4.16 (m, –POCH₂CH), 3.95–3.73 (m, –OCH₂CH and –CH₂CHCH₂). ³¹P NMR (162 MHz, CDCl₃): δ –4.69.

2.2.6.5. Synthesis of polymer **P5**. The ROP was carried out according to the general procedure by using 2-(((1,1'-biphenyl-2,2'-dioxy) phosphine oxide)methyl)oxirane (**M5**). Yield 78%. ¹H NMR (400 MHz, CDCl₃): δ 7.83–7.30 (m, $-C_6H_5$), 4.27–3.83 (m), 3.81–3.65 (m), 3.59–3.44 (m), 3.41–3.19 (m). ¹³C NMR (100 MHz, CDCl₃): δ 158.6, 157.6, 129.3, 128.2, 127.7, 127.5, 127.2, 126.7, 126.4, 120.8, 116.2, 115.4, 78.2, 73.2, 68.7, 63.6, 60.8. ³¹P NMR (162 MHz, CDCl₃): δ 1.77, –0.72.

2.2.6.6. Synthesis of polymer **P6**. The ROP was carried out according to the general procedure by using 2-(((3,3',5,5'-tetra-*tert*-butyl-1,1'-biphenyl-2,2'-dioxy)phosphine oxide)methyl)oxirane (**M6**). Yield 81%. ¹H NMR (400 MHz, CDCl₃): δ 7.53–7.49 (m, –C₆H₂), 7.33–7.30 (m, –C₆H₂), 7.26–7.22 (m, –C₆H₂), 7.05–7.01 (m, –C₆H₂), 4.38–4.21 (m), 4.20–4.07 (m), 4.04–3.84 (m), 1.48–1.42 (m, –CH₃), 1.33–1.27 (m, –CH₃). ³¹P NMR (162 MHz, CDCl₃): δ –2.80, –5.61.

2.2.7. General preparation of solid polymer electrolytes SPEs

The polymers (**P1**, **P2** and **P4–P6**) were dried at 60 °C under vacuum for 8 h. LiN(SO₂CF₃)₂ was dried at 150 °C under vacuum for 10 h before use. All manipulations were carried out in an MBraun glove box filled with ultrapure nitrogen gas. Electrolytes with different ratio were prepared as follows: the polymer was dissolved in THF with lithium salt and stir for 12 h at 25 °C. After this, THF was evaporated under vacuum and dried the residue at 60 °C for 12 h. The residue was loaded into a die and then pressed to make a pellet. Specimens of 0.07–0.08 cm thickness and 0.9 cm diameter were obtained for conductivity studies. These pellets were sandwiched between two gold plated electrodes housed in a homemade cell for conductivity studies. The consistency of results was checked by repeating three times.

3. Results and discussion

Integrating phosphorus into polymer chains would increase the conformational flexibility, thus leading to interesting chemical and



Fig. 2. ORTEP of the molecular structure M4. Thermal ellipsoids are shown at 30% probability levels. Hydrogen atoms are omitted for clarity.



Scheme 1. Syntheses of phosphorus containing linear polyethers by ROP of epoxide.

physical properties including amorphous nature, high temperature stability and flame-retardancy [25]. Although phosphorus containing polymers are attractive mainly because of their flameretardant property [26], in recent years, their biodegradability is also much sought. The biodegradable polymers — polyphosphoesters (PPE) [27] are promising for clinical and pharmaceutical applications, whereas the solid polymer electrolyte based on PPE is unexplored [9c,28]. Our interest is producing polyethers with phosphate pendant groups as solid polymer electrolyte for lithium-ion transport.

3.1. Synthesis of monomers (M1–M6)

Chosen monomers M1-M6 having bulky groups were to get preferably linear polymers in which the bulky groups would be side groups. Because of the uneven shapes and sizes of these bulky groups, they would influence the orientation of polymer chains and thus expected to enlarge the amorphous region. Schemes 1 and 2 show the syntheses of monomers (M1-M6). The reactions of starting materials S1-S5 with glycidol in THF in the presence of NEt₃ yielded the monomers M1-M5 respectively. Similarly, a reaction of S6 with glycidol in THF but in the presence of NaH yielded the monomer M6 in good yield. The monomers M1, M2 and M5 were isolated in pure by filtering the reaction mixtures followed by evaporating the filtrates. The other monomers M3, M4 and M6 were purified by column chromatography. The monomers (M1-M6) were characterized using ¹H, ¹³C{¹H} and ³¹P{¹H} NMR spectral data which showed the data were consistent with expected molecular structures. The crystal structure of M4 (Fig. 2) determined using X-ray crystallography clearly showed the spatial orientations of the bulky groups around tetrahedral phosphorus. The monomers **M1–M3** were liquids whereas **M4–M6** were solids.

3.2. Ring opening polymerization

Recently, we reported in detail about the Zn(II) **1**, Cd(II) **2–3** and Cu(II) **4** (Fig. 3) complexes of 2,5-bis{N-(2,6-diisopropylphenyl) iminomethyl}pyrrole **LH** [21]. We also proved their efficiencies of catalyzing cyclic carbonates formation from epoxides and CO₂ (1 atm) in the presence of TBAB under mild temperature. They were effective for converting monosubstituted terminal epoxides, disubstituted terminal and internal epoxides. In our continuous interest on these complexes (**1–4**), we have further explored their catalytic activities for the ring opening polymerization of epoxides. At first, the catalytic activity of Zn(II) complex **1** for the ROP of oxiran-2-ylmethyl diphenylphosphate (**M2**) in the presence of TBAB as initiator at 70 °C in THF was tested. It was found to be a good catalyst by yielding the polyether (**P2**) with narrow polydispersity.

A set of controlled experiments was performed in THF at 70 °C to understand the role of both catalyst and initiator (C and I). Either catalyst or initiator alone did not catalyze the reactions. However, when both of them are present in different molar ratios, we observed the following; (i) when the C/I molar ratio was less than 1, only subtle polymerization occurred. (ii) When the C/I molar ratio equalled 1, the reaction yielded little more polyether (Table 1, entries 3 and 4) but did not complete within 24 h as checked by ¹H NMR. (iii) When the C/I molar ratio exceeded slightly 1, say 1.1 (Table 1, entry 5), the ROP proceeded much faster and reached completion within 7 h. So the reaction-condition was optimized by varying the C/I (1/TBAB) molar ratio, temperature and time to achieve good conversion and higher molecular weight with narrow PDI (Table 1, entries 3–10). Among the different catalyst/initiator loadings tried, the C/I molar ratio of 1.5 yielded the polymer within 4 h at 70 °C with moderate properties (Table 1, entry 8). From here, this molar ratio (C/I) was fixed for further investigations. Under this reaction-condition. the catalysts 2-4 were examined for the ROP of M2 in the presence of TBAB in THF at 70 °C (Table 1, entries 11–13). The ROP proceeded faster using 1 as a catalyst in comparison with complexes 2-4. The presence of bulky groups was helpful to protect metal center as well as in controlling PDI by retarding the side reactions. The molecular weight $[M_n(exp)]$ measured by GPC matched well with theoretical molecular weight $[M_n(\text{theo})]$ calculated (based on a formation of one polymer chain per initiator) from the initial monomer/initiator ratio, and their PDIs were also in a narrow range.

The ROP of **M2** was examined with a different initiator, bis(-triphenylphosphine)iminium chloride (PPNCl) in the presence of **1** at 70 °C in THF (Table 1, entry 16). Even after 24 h, the ROP did not complete probably because of the poor solubility of PPNCl in THF.



Scheme 2. Syntheses of phosphorus containing branched polyethers by ROP of epoxide.



Fig. 3. Structure of the ligand LH and its complexes 1-4.

So, the reaction was carried out in dichloromethane (DCM) at 40 °C (Table 1, entry 17). But since the high molecular mass polyether (**P2**) was insoluble in DCM, once the reaction progressed, the polymer precipitated out from the reaction mixture. Instead of 1/ TBAB, a well-known anionic initiator potassium *tert*-butoxide (*t*-BuOK) was examined for the ROP of **M2** (Table 1, entries 18 and 19). In this case, the significant contribution of side reactions probably resulted in low molecular weight polymer with broader PDI and this also was consuming extensive time for polymerization. These facts confirmed the usefulness of our catalyst in these ROP reactions.

 Table 1

 Results of optimization studies for ROP^a of M2 to form P2.

Entry	Catalyst	$[C]_0/[I]_0$	[M2] ₀	Reaction	Properties of the P2			
	(C)			time (h)	$M_{ m n}$ (kg mol ⁻¹) (exp) ^b	M_n (kg mol ⁻¹) (theo) ^c	PDI ^d	
1 ^e	_	_	100	120			_	
2 ^f	1	_	100	120	_	_	_	
3	1	0.5	100	24	-	30.6	-	
4	1	1.0	100	24	-	30.6	-	
5	1	1.1	100	7	31.4	33.6	1.21	
6	1	1.3	100	6 40 24 43 4 40	40.2	39.8	1.18	
7 ^g	1	1.5	100		43.1	45.9	1.08	
8	1	1.5	100		46.9	45.9	1.15	
9	1	1.8	100	3	57.8	55.1	1.23	
10	1	2.0	100	3	64.2	61.2	1.28	
11	2	1.5	100	14	42.3	45.9	1.27	
12	3	1.5	100	16	43.2	45.9	1.34	
13	4	1.5	100	10	46.0	45.9	1.19	
14	1	1.5	200	15	90.6	91.8	1.18	
15	1	1.5	300	48	136.7	137.8	1.20	
16	1	1.5 ^h	100	24	-	45.9	-	
17 ⁱ	1	1.5 ^h	100	10	16.3	45.9	1.25	
18 ^j	-	t-BuOK	100	168	16.5	-	1.64	
19 ^j	-	t-BuOK	100	72	20.8	-	1.85	

 $^{\rm a}$ Reactions were conducted in THF at 70 $^{\circ}C$ in presence of catalyst (C) and TBAB (I) as an initiator. The reactions were carried out up to 100% conversion based on ^{1}H NMR.

 $^{\rm b}$ Molecular weight measured by GPC and calibrated against polystyrene standard.

 c Molecular weight calculated from ([M]_0/[I]_0) \times molecular weight of monomer \times conversion.

^d Obtained from GPC analysis.

- ^e In the presence of TBAB alone.
- ^f In the presence of catalyst alone.
- ^g Reaction at 25 °C.
- ^h In presence of PPNCl as an initiator instead of TBAB.
- ⁱ Conducted in DCM at 40 °C.
- ^j Without catalyst.

The scope of the catalyst was further explored for the ROP of various substituted epoxides having phosphorus as monomers (**M1**, **M3** and **M4**). These reactions yielded the polymers **P1**, **P3** and **P4** respectively. Table 2 displays the properties of polymers obtained from these reactions. The ROP of **M1**, **M3** and **M4** was also progressing according to the mechanism of polymer chain per initiator. This was reflected by good agreement of measured molecular weight [$M_n(exp)$] with calculated molecular weight [$M_n(theo)$]. Even though the active nucleophilic site (epoxide oxygen) was away from substituents, electron releasing groups attached to phosphorus indicated a trend in the rate of ROP. According to the results displayed in Table 2 (entries 1–4), in the presence of catalyst **1**, the rate of conversion of monomers to polymers was in the order **M3** > **M4** > **M2** > **M1**.

3.3. Branched polymers

The epoxide ring opening polymerization (in THF at 70 °C) of monomers M5 and M6 was interesting since they differed from the other four monomers. These monomers yielded respective polyethers (P5 and P6; Table 2, entries 5 and 6) whose measured molecular weights $[M_n(exp)]$ were much lower than theoretical molecular weights $[M_n(\text{theo})]$. This suggested the ROP did not follow the polymer chain per initiator mechanism while other monomers following. The monomer M6 underwent faster polymerization than M5 showing the bulky groups in it did not disturb the growth of PEO chain since the electronic effects dominated; also the bulky group is much away from the growing chain. To deduce the structure of polymers P5 and P6, we analysed the following observations. (i) Both these polymers were soluble in polar solvents. (ii) At start of the reaction, number of initiator molecules were much less than monomer molecules. (iii) No monomers remained unreacted in these reactions. (iv) The ³¹P{¹H} NMR spectra of P5 displayed two kinds of peaks at 1.77 and -0.72 ppm. Comparing with the chemical shift of the monomer, the minor peak at 1.77 ppm might represent the phosphorus at a terminal repeating unit of a chain, while the broad peak at -0.72 ppm representing the phosphorus atoms in the chain [29]. In the ¹H NMR of **P5**, the peaks of all aromatic protons merged (Fig. 5) while the aliphatic protons merged among themselves. The polymer **P6** also presented a similar ${}^{31}P{}^{1}H$ and ${}^{1}H$ NMR. The peaks of aliphatic carbon were assigned in ${}^{13}C$ NMR spectrum of **P5** (Fig. 5). Due to the rigid structure of polymer the peaks were not resolved clearly and so it was difficult to assign the peaks exactly to other carbons.

Table 2
Results of syntheses of various phosphorus containing polyethers (P1-P6) ^a and its
properties.

Entry	Epoxides (M)	Time (h)	Polymers (P)	Properties of polymers						
				$\frac{M_{\rm n}}{(\rm kg\ mol^{-1})} \\ (\rm exp)^{\rm b}$	M_n (kg mol ⁻¹) (theo) ^c	PDI ^d	<i>T</i> _d (°C)	<i>T</i> g (°C)		
1	M1	10	P1	40.6	41.1	1.21	350.1	227.7		
2	M2	4	P2	46.9	45.9	1.15	159.5	80.8		
3	M3	3	P3	56.0	55.0	1.19	144.7	-10.6		
4	M4	4	P4	67.9	68.8	1.16	159.3	82.5		
5	M5	8	P5	32.2	45.6	1.20	167.9	98.4		
6	M6	6	P6	50.3	79.3	1.18	203.4	74.7		

^a Reaction condition: $[\mathbf{M}]_0:[C]_0:[I]_0 = 100:1:0.67$ in THF at 70 °C, $[\mathbf{M}]_0 = 0.94$ M. ^b Molecular weight measured by GPC and calibrated against polystyrene standard.

 c Molecular weight calculated from ([M]_0/[I]_0) \times molecular weight of monomer \times conversion.

^d Obtained from GPC analysis.



Fig. 4. Possible branching structures of P5 and P6.

From these observations we inferred as follows. At first, it appeared the pendant rings opened by reaction with initiators were taking part in side reactions with proximal pendant groups along the same chain. This parallel chain could be formed because of breaking of the P–O bonds in the seven membered rings in the monomers. This side reaction would consume few initiator molecules. Also, no monomers remained unconsumed. Breaking C–O bond in the same ring was ruled out because such a case should yield a positive-charge on the biphenyl group of tricyclic ring. In these circumstances, according to the polymer chain per initiator

mechanism, the measured molecular weights should be higher than the theoretical molecular weights. Thus the parallel chain model would not explain the much lower measured molecular weight than the theoretical value. Solubility of the polymers in polar solvents ruled out the possibility of inter-chain side reaction leading to traditional cross-linked polymers. Finally, we inferred the polymers **P5** and **P6** as comb-like branched polymers (Fig. 4) [30]. This was possible because of the breaking of P–O bonds in the seven membered rings in the pendant ring and reacting with a new monomer instead the proximal monomer leading the growth of



Fig. 5. ¹H, ³¹P and ¹³C NMR spectra of P2 (left) and P5 (right).



Fig. 6. TGA plots of polyethers P1-P6.



Fig. 7. DSC plots of polyethers P1-P6.





Fig. 8. Plot of molecular weight (M_n) and polydispersity (PDI) *versus* $[M2]_0/[I]_0$ for the ROP of M2 catalyzed by 1 in the presence of TBAB. Reaction condition: $[M2]_0:[C]_0:[I]_0 = 100:1:0.67$ in THF at 70 °C, $[M2]_0 = 0.94$ M.



Fig. 9. Plot of $\ln([M2]_0/[M2]_t)$ versus time for the ROP of M2 catalyzed by 1 in the presence of TBAB. Reaction condition: $[M2]_0:[C]_0:[I]_0 = 100:1:0.67$ in THF at 70 °C, $[M2]_0 = 0.94$ M.

peaks in the ³¹P NMR because there were two different kinds of repeating units (in chain and terminal) in the pendant chain.

3.4. Properties of the polymers

The polymers **P1**, **P2** and **P4–P6** were solids, while **P3** was a liquid. All these polymers **P1–P6** were soluble in polar solvents like THF, dimethyl sulphoxide, and dimethyl acetamide. Table 2 lists the glass-transition temperature (T_g), decomposition temperature (T_d), molecular weight (M_n) and PDI of all these polymers. The molecular weights (M_n) of polymers **P1–P6** were in the range 40–80 kg mol⁻¹. Thermogravimetric analyses (Fig. 6) disclosed the polymers **P2–P6** were thermally stable until heated up to 160 °C while **P1** was stable up to 350 °C. The T_g of the polymers **P2** and **P4** – **P6** lies in the temperature range 75 °C–100 °C while the polymers **P1** and **P3** have T_g at 227 °C and –10 °C respectively (Fig. 7). All were amorphous polymers since the DSC graphs did not show crystalline melting temperature peak for any polymers. Compared with **P2–P6**, the **P1** had higher thermal stability (T_d) and high T_g . This could be explained by the columnar stacking of phenyl rings



Fig. 10. Plot of molecular weight (M_n) and polydispersity (PDI) *versus* monomer conversion for the ROP of **M2** catalyzed by **1** in the presence of TBAB. Reaction condition: [**M2**]₀:[C]₀:[I]₀ = 100:1:0.67 in THF at 70 °C, [**M2**]₀ = 0.94 M.



Scheme 3. Proposed mechanism for the monomer activated anionic ROP of epoxide.



Fig. 11. a) TGA and b) DTG plots of SPE2 (10%-40%).

because of strong non-covalent interactions that would ensure a space efficient packing. Thus the phosphate group attached to PEOs provided significant changes in their properties especially the crystallinity and T_{g} . Films of these polymers were observed to be brittle probably because of chain rigidity. But their flexibility can be improved by tuning the molecular structure of the polymers by introducing various alkyl chain spacers. Some plasticizers can also be added to improve the flexibility.

3.5. Mechanism of polymerization

The reaction optimization study showed that while increasing the monomer/initiator molar ratio (M/I), the molecular weight of the resultant polymers was increasing but with narrow PDI (Table 1, entries 8, 14 and 15). In these reactions, existed linear-relationship (Fig. 8) of molecular weight with the ratio of initial monomer to initiator concentrations that is $[M2]_0/[I]_0$ also confirmed the dependent of the molecular weight on monomer concentration. To understand the order of ROP, reactions were monitored with time in the presence of 1 and TBAB in THF at 70 °C. Semi logarithmic plot of ln[M2]₀/[M2]_t versus time (Fig. 9) revealed the linearity proving the first order dependence of polymerization on monomer concentration. Further, the molecular weights of resultant polymers were increasing linearly with increasing monomer conversion which inferred that the polymerization proceeded with a living polymerization manner (Fig. 10). All these observations revealed the ROP underwent in a controlled living like polymerization and clearly suggested the negligible contribution of "transfer to monomer process" to the molecular weight as reflected by PDI.

Though we could not isolate any intermediate species, based on our observations and earlier reports [16,18], we postulate a mechanism for ROP as shown in Scheme 3. The first step involved activating epoxide monomer by coordinating with a zinc catalyst. In the presence of TBAB, the activated monomer underwent epoxide ring opening by the nucleophilic attack of bromide ions to form initiating complex (**b**). Further, the excess zinc catalyst activated the monomer (**a**) for the nucleophilic attack of initiating complex to yield the growing species (**c**). Thus the propagation step proceeded and polymerization happened rapidly. When the C/I molar ratio was less than or equal to 1, the zinc catalyst involved in forming of initiating complex only. Therefore, little excess of catalyst required to trigger the polymerization. This was matching well with the living like polymerization mechanism.

3.6. Lithium-ion conductivity

Solid polymer electrolytes (**SPE1**, **SPE2** and **SPE4–SPE6**) were prepared by dissolving respective polymers (**P1**, **P2** and **P4–P6**)



Fig. 12. DSC plots of SPE2 (10%-40%).

Table 3

Properties of SPE2 (10)%–40%) and SPE4 ((10%–40%).
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SPEs (wt% of LiTFSI)	SPE2					SPE4					
	O:Li	Conductivity σ (S cm ⁻¹)		$T_{\rm d}$ (°C)	$T_{g}(^{\circ}C)$	O:Li	Conductivity σ (S cm ⁻¹)		$T_{\rm d}$ (°C)	$T_{g}(^{\circ}C)$	
		30 °C	80 °C				30 °C	80 °C			
SPE (10%)	42.2:1	2.7×10^{-6}	1.1×10^{-5}	167.5	89.7	28.2:1	$3.9 imes10^{-9}$	3.8×10^{-8}	166.7	99.2	
SPE (20%)	18.8:1	$3.3 imes 10^{-6}$	$2.6 imes 10^{-5}$	168.9	108.3	12.5:1	$2.5 imes 10^{-8}$	$2.0 imes 10^{-7}$	168.4	107.0	
SPE (30%)	10.9:1	$5.3 imes 10^{-6}$	$3.2 imes 10^{-5}$	177.4	124.1	7.3:1	$7.7 imes 10^{-7}$	$6.5 imes 10^{-6}$	180.0	110.1	
SPE (40%)	7.0:1	$5.2 imes 10^{-5}$	2.9×10^{-4}	188.8	133.5	4.7:1	$\textbf{4.8}\times \textbf{10}^{-5}$	1.8×10^{-4}	182.1	130.3	

Table 4

Properties of SPE5 (10%-40%) and SPE6 (10%-40%).

SPEs (wt% of LiTFSI)	SPE5					SPE6				
	O:Li	Conductivity σ (S cm ⁻¹)		$T_{\rm d}$ (°C)	$T_{g}(^{\circ}C)$	O:Li	Conductivity σ (S cm ⁻¹)		$T_{\rm d}$ (°C)	<i>T</i> _g (°C)
		30 °C	80 °C				30 °C	80 °C		
SPE (10%) SPE (20%)	42.5:1 18.9:1	$\begin{array}{c} 1.2 \times 10^{-8} \\ 4.0 \times 10^{-8} \end{array}$	$\frac{1.8 \times 10^{-7}}{3.9 \times 10^{-7}}$	183.7 190.0	110.0 119.4	24.5:1 10.9:1	$\frac{2.2 \times 10^{-9}}{3.1 \times 10^{-8}}$	$\begin{array}{c} 1.1 \times 10^{-8} \\ 3.2 \times 10^{-7} \end{array}$	210.4 215.8	102.0 111.2
SPE (30%) SPE (40%)	11.0:1 7.1:1	$\begin{array}{l} 2.7 \times 10^{-7} \\ 9.8 \times 10^{-7} \end{array}$	$\begin{array}{l} 2.7\times 10^{-6} \\ 1.0\times 10^{-5} \end{array}$	193.9 198.7	122.1 130.3	6.3:1 4.1:1	$\begin{array}{l} 4.5 \times 10^{-8} \\ 5.0 \times 10^{-8} \end{array}$	$\begin{array}{l} 3.5 \times 10^{-7} \\ 4.7 \times 10^{-7} \end{array}$	220.6 228.5	123.5 130.7



Fig. 13. Temperature dependence Nyquist plots of SPE2 a) 10%, b) 20%, c) 30%, d) 40%. Arrhenius plot of temperature dependence conductivity of e) SPE1, f) SPE2, g) SPE4, h) SPE5, i) SPE6 (10%-40%).

and varying amounts of lithium salt (LiTFSI) in THF. Since the polymer P3 was liquid we did not make electrolyte from it. After evaporating and drying the solvent, the residues were made into pellets for conductivity measurements. To understand the thermal properties, TGA and DSC analyses on the solid electrolytes SPE1, SPE2 and SPE4–SPE6 were performed. Figs. 11 and 12 depict the TGA and DSC plots of SPE2 with varying amounts of lithium salt as an example. Absence of peaks matching the melting temperature $(T_{\rm m})$ of lithium salt in DSC curves for any **SPE**s revealed the salt did not exist as aggregates. The absence of melting point of salts might because of solvation of lithium ions by polymers. The possibility of polymer chain coordination with lithium ion would facilitate the solvation. The SPEs with 40 wt% of LiTFSI [SPEs (40%)] also did not show the peak for $T_{\rm m}$ which inferred the effective solvation by polymers even for higher wt% of lithium salt.

The TGA and DTG analyses on SPEs revealed an increase in the thermal stabilities of SPE1, SPE2 and SPE4-SPE6 compared with their respective polymers P1, P2 and P4–P6 (Tables 3 and 4 and S2; Fig. 11, S1–S4). The glass transition temperatures (T_g) of **SPE**s having 10-40 wt% of LiTFSI respectively [SPEs (10%-40%)] determined through DSC analyses are shown in Tables 3 and 4. As seen in DSC plots, there were increase in T_g of **SPE**s compared with their respective polymers. The increase was more with increasing salt contents. The increased T_d and T_g can be explained through coordination of polymer chains with lithium ions by as follows. Coordination of polymer with lithium ions would affect the stretching of polymer chains thus restricting their segmental motion. Obviously, more salt molecules would encourage more coordination by polymer chains and increased control on the segmental motion of the chains leading increased T_{g} . Similarly, because of the coordination of polymer chains with lithium ions, it needs more energy to break the coordination bonds at first followed by to break the polymer chains.

The bulk resistances determined from complex impedance spectra revealed the Li-ion conductivities of SPE1, SPE2 and SPE4-**SPE6** [31]. The measured conductivities of **SPE**s at room temperature as well as at 80 °C are presented in Tables 3and 4. Fig. 13 displays the temperature dependent (30-80 °C with increment of 10 °C) Nyquist plots of SPE2 (10%-40%) as well as Arrhenius plots of conductivities for SPE1 (10%-40%), SPE2 (10%-40%) and SPE4-SPE6 (10%-40%). The electrolyte SPE1 showed the lowest conductivity among all in room temperature as well as at elevated temperatures. The conductivities of SPEs at room temperature lie in the range of 2.7×10^{-9} – 5.2×10^{-5} S cm⁻¹. Among all **SPE**s prepared the SPE2 (40%) has demonstrated highest conductivity of 5.2×10^{-5} S cm⁻¹ at room temperature. It is worth mentioning here is that at room temperature, the ionic conductivity of liquid organic electrolytes is in the range of 10⁻³ S cm⁻¹. Further, the conductivities of SPE1 (10%-40%), SPE2 (10%-40%) and SPE4-SPE6 (10%-**40%**) were increasing with the amounts of lithium salt. As expected. they were also increasing with temperature. Thus the SPE2 (40%) attained maximum conductivity of 2.9 \times 10⁻⁴ S cm⁻¹ at 80 °C. Comparing with SPEs made up of linear polymer, the ionic conductivity of SPEs prepared from branched polymers was lesser probably because of its higher T_{g} .

4. Conclusions

In conclusion, we have designed and synthesized polyethers having suitable superstructure for lithium-ion mobility. The catalytic activity of our complexes (1–4) was successfully explored for the ring opening polymerization of epoxides with phosphate sidegroups. Compared with the conventional anionic initiators, our system (Zn(II)/TBAB) catalyzed the polymerization without any side reactions and yielded the polymers with fairly high molecular weights. So far, other than poly(ethylene oxide), only few polymers like polysiloxane, polyphosphazene have shown potential as lithium ion conducting polymer electrolytes; but, both are liquids at room temperature. However, the polyethers (P1–P6) produced by us are stable, solids (except P3) at room temperature and completely amorphous in nature. Therefore, the polymers P2 and P4 demonstrated promising solid-state ionic conductivity. The solid polymer electrolyte SPE2 (40%), prepared from P2, showed the highest conductivity of 2.9×10^{-4} S cm⁻¹ at 80 °C. Apart from these, the presence of phosphorus in these polymers would impart flame-retardant property to SPEs. These polyethers could find use as solid polymer electrolytes in lithium-ion batteries.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http:// dx.doi.org/10.1016/j.polymer.2013.12.005.

References

- [1] (a) Fenton DE, Parker JM, Wright PV. Polymer 1973;14:589; (b) Wright PV. Br Polym J 1975;7:319-27;
- (c) Wright PV. J Polym Sci Polym Phys Ed 1976;14:955-7.
- [2] (a) Chinnam PR, Wunder SL. J Mater Chem A 2013;1:1731–9;
- (b) Wang S, Min K. Polymer 2010;51:2621-8.
- [3] Wang X-L, Fan L-Z, Xu Z-H, Lin Y-H, Nan C-W. Solid State Ionics 2008;179: 1310-3
- [4] Wakihara M, Kadoma Y, Kumagai N, Mita H, Araki R, Ozawa K, et al. J Solid State Electrochem 2012;16:847-55
- [5] Joost M, Kunze M, Jeong S, Schonhoff M, Winter M, Passerini S. Electrochim Acta 2012;86:330-8.
- [6] (a) Lin Y, Zeng-guo F, Yu-mei Z, Feng W, Shi C, Guo-qing W. J Polym Sci Part A Polym Chem 2006;44:3650-65; (b) Yarmolenko OV, Khatmullina KG, Tulibaeva GZ, Bogdanova LM, Shestakov AF. J Solid State Electrochem 2012;16:3371-81; (c) Ramanjaneyulu K, Bar N, Shah MdSAS, Manorama SV, Basak P. J Power Sources 2012;217:29-36.
- [7] (a) Lee IJ, Song GS, Lee WS, Suh DH. J. Power Sources 2003;114:320-9; (c) Kang Y, Lee J, Lee J-I, Lee C. J Power Sources 2007;165:92–6; (c) Kang Y, Lee J, Suh DH, Lee C. J Power Sources 2005;146:391–6.
- [8] (a) Ji J, Keen J, Zhong W-H. J Power Sources 2011;196:10163-8;
- (b) Simone PM, Lodge TP. ACS Appl Mater Inter 2009;1:2812-20; (c) Young W-S, Albert JNL, Schantz AB, Epps TH. Macromolecules 2011;44: 8116-23; (d) Gomez ED, Panday A, Feng EH, Chen V, Stone GM, Minor AM, et al. Nano
- Lett 2009:9:1212-6 [9] (a) Nishimoto A, Agehara K, Furuya N, Watanabe T, Watanabe M. Macro-
- molecules 1999:32:1541-8: (b) Guhathakurta S, Min K. Polymer 2010;51:211-21;
- (c) Li N, Wang L, He X, Wan C, Jiang C. Ionics 2008;14:463-7. [10] (a) Allcock HR, O'Connor SJM, Olmeijer DL, Napierala ME, Cameron CG. Macromolecules 1996;29:7544-52; (b) Allcock HR, Olmeijer DL, O'Connor SJM. Macromolecules 1998;31:753-9; (c) Sanderson S, Zawodzinski T, Hermes R, Davey J, Dai H. Proc Electrochem
- Soc 1997:96-17:136.
- [11] Hooper R, Lyons LJ, Mapes MK, Schumacher D, Moline DA, West R. Macromolecules 2001;34:931-6.
- [12] Thielen J, Meyer WH, Landfester K. Chem Mater 2011;23:2120-9.
- [13] (a) Bourbigot S, Duquesne S. J Mater Chem 2007;17:2283–300;
- (b) Lu SY, Hamerton I. Prog Polym Sci 2002;27:1661-712. [14] (a) Baumgartner T, Reau R. Chem Rev 2006;106:4681-727; (b) Lucht BL, Onge NOSt. Chem Commun 2000:2097-8;
 - (c) Allcock HR. Chemistry and applications of polyphosphazenes. Wiley Interscience; 2003;
 - (d) Chandrasekhar V. Inorganic and organometallic polymers. Springer; 2005; (e) Sato M, Tada Y, Yokoyama M. Eur Polym J 1980;16:671-6.
- [15] (a) Tsang CW, Baharloo B, Reindl D, Yam M, Gates DP. Angew Chem Int Ed 2004;43:5682-5;

(b) Vanderark LA, Clark TJ, Rivard E, Manners I, Slootwegc JC, Lammertsma K. Chem Commun 2006:3332-3;

- (c) Senear AE, Valient W, Wirth J. J Org Chem 1960;25:2001-6;
- (d) Fenimore CP, Martin F. J Mod Plast 1966;4:141-2;

(e) Cabasso I, Jagur-Grodzinski J, Vofsi D. J Appl Polym Sci 1974;18:1969-86. 2137-47.

- [16] (a) Millich F, Lambing LL. J Polym Sci Part A Polym Chem 1980;18:2155–62;
 (b) Imai Y, Sato N, Ueda M. Macromol Chem Rapid Commun 1980;1:419–22;
 (c) Dorn H, Rodezno JM, Brunnhofer B, Rivard E, Massey JA, Manners I. Macromolecules 2003;36:291–7;
 - (d) Vlad-Bubulac T, Hamciuc C. Polymer 2009;50:2220-7;
 - (e) Zhao C-S, Chen L, Wang Y-Z. J Polym Sci Part A Polym Chem 2008;46: 5752–9.
- [17] (a) Tonhauser C, Schull C, Dingels C, Frey H. ACS Macro Lett 2012;1:1094–7;
 (b) Cheng G, Fan X, Tian W, Liu Y, Kong J. Polym Int 2010;59:543–51;
 (c) Obermeier B, Wurm F, Mangold C, Frey H. Angew Chem Int Ed 2011;50: 7988–97.
- [18] (a) Billouard C, Carlotti S, Desbois P, Deffieux A. Macromolecules 2004;37: 4038–43:

(b) Brocas A-L, Mantzaridis C, Tunc D, Carlotti S. Prog Polym Sci 2013;38:845-73;

(c) Gervais M, Brocas A-L, Deffieux A, Ibarboure E, Carlotti S. Pure Appl Chem 2012;84:2103–11.

[19] (a) Labbe A, Carlotti S, Billouard C, Desbois P, Deffieux A. Macromolecules 2007;40:7842-7;

(b) Labbe A, Brocas A-L, Ibarboure E, Ishizone T, Hirao A, Deffieux A, et al. Macromolecules 2011;44:6356-64;

(c) Gervais M, Labbe A, Carlotti S, Deffieux A. Macromolecules 2009;42:2395-400;

(d) Carlotti S, Labbe A, Rejsek V, Doutaz S, Gervais M, Deffieux A. Macro-molecules 2008;41:7058–62;

(e) Rejsek V, Sauvanier D, Billouard C, Desbois P, Deffieux A, Carlotti S. Macromolecules 2007;40:6510-4.

[20] (a) Hirahata W, Thomas RM, Lobkovsky EB, Coates GW. J Am Chem Soc 2008;130:17658–9;

(b) Widger PCB, Ahmed SM, Hirahata W, Thomas RM, Lobkovsky EB, Coates GW. Chem Commun 2010;46:2935–7;

- (c) Thomas RM, Widger PCB, Ahmed SM, Jeske RC, Hirahata W, Lobkovsky EB, et al. J Am Chem Soc 2010;132:16520–5.
- [21] Babu HV, Muralidharan K. Dalton Trans 2013;42:1238-48.
- [22] (a) Coetzee J, Eastham GR, Slawina AMZ, Cole-Hamilton DJ. Org Biomol Chem 2012;10:3677–88;
 - (b) Buisman GJH, Kamer PCJ, Leeuwert PWNMV. Tetrahedron Asymmetry 1993;4:1625–34.

- (a) Sheldrick GM. SHELXS-97. Program for crystal structure solution. Gottingen, Germany: University of Gottingen; 1997;
 (b) Sheldrick GM. SHELXL-97. Program for crystal structure solution. Gottingen, Germany: University of Gottingen; 1997.
- [24] (a) Kumar J, Rodrigues SJ, Kumar B. J Power Sources 2010;195:327–34;
 (b) Lee K-H, Park J-K, Kim W-J. Electrochim Acta 2000;45:1301–6;
 (c) Morales E, Acosta IL. Electrochim Acta 1999;45:1049–56.
- [25] (a) Wright VA, Gates DP. Angew Chem Int Ed 2002;41:2389–92;
 (b) Cao L, Manners I, Winnik MA. Macromolecules 2001;34:3353–60;
 (c) Archer RD. Inorganic and organometallic polymers. New York: Wiley-VCH; 2001;
 - (d) Allcock HR, Taylor JP. Polym Eng Sci 2000;40:1177-89;
 - (e) Braun U, Schartel B, Hoffmann T, Pospiech D, Artner J, Ciesielski M, et al. Macromol Chem Phys 2006;207:1501–14.
- [26] (a) Liu W, Wang Z, Chen Z, Zhao L. Polym Degrad Stab 2012;97:810-5;
 (b) Wang C-S, Shieh J-Y. Polymer 1998;39:5819-26;
 (c) Alcon MJ, Espinosa MA, Galia M, Cadiz V. Macromol Rapid Commun 2001;22:1265-71;
 - (d) Liu Y-L, Hsiue G-H, Chiu Y-S. J Polym Sci A Polym Chem 1997;35:565–74; (e) Liu YL. Polymer 2001;42:3445–54.
- [27] (a) Clement B, Grignard B, Koole L, Jerome C, Lecomte P. Macromolecules 2012;45:4476-86;
 (b) Xiong M-H, Bao Y, Yang X-Z, Wang Y-C, Sun B-L, Wang J. J Am Chem Soc

(b) Xiong M-H, Bao Y, Yang X-Z, Wang Y-C, Sun B-L, Wang J. J Ani Chem Soc 2012;134:4355–62;

(c) Zhang S, Li A, Zou J, Lin LY, Wooley KL. ACS Macro Lett 2012;1:328–33; (d) Xiong M-H, Wu J, Wang Y-C, Li L-S, Liu X-B, Zhang G-Z, et al. Macromolecules 2009;42:893–6;

(e) Iwasaki Y, Wachiralarpphaithoon C, Akiyoshi K. Macromolecules 2007;40: 8136–8.

- [28] Shibutani R, Tsutsumi H. J Power Sources 2012;202:369–73.
- [29] (a) Morisaki Y, Ouchi Y, Tsurui K, Chujo Y. J Polym Sci Part A Polym Chem 2007;45:866–72;
 - (b) Morisaki Y, Ouchi Y, Naka K, Chujo Y. Chem Asian J 2007;2:1166-73.
- [30] Puskas JE, Burchard W, Heidenreich AJ, Santos LD. J Polym Sci Part A Polym Chem 2012;50:70–9.
- [31] (a) Abraham KM, Jiang Z, Carroll B. Chem Mater 1997;9:1978–88;
 (b) Yoshida K, Nakamura M, Kazue Y, Tachikawa N, Tsuzuki S, Seki S, et al. J Am Chem Soc 2011;133:13121–9;
 (c) Britz J, Meyer WH, Wegner G. Macromolecules 2007;40:7558–65.