

Polymerization behaviour of butyl bis(hydroxymethyl)phosphine oxide: Phosphorus containing polyethers for Li-ion conductivity

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Abstract. Synthesis of phosphorus containing polyethers and their lithium-ion conductivities for the potential use as solid polymer electrolyte (SPE) in high-energy density lithium-ion batteries have been described. Co-polymerization of butyl bis(hydroxymethyl)phosphine oxide with three different dibromo monomers were carried out to produce three novel phosphorous containing polyethers (**P1–P3**). These polymers were obtained via nucleophilic substitution reactions and were characterized by ^1H , ^{31}P NMR spectral data and gel permeation chromatography. SPEs were prepared using polyethers (**P1** and **P2**) with various amounts of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI). The lithium-ion conductivity of **SPE2** containing 40 wt% of LiTFSI was $2.1 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature and $3.7 \times 10^{-4} \text{ S cm}^{-1}$ at 80°C .

Keywords. Phosphorus; polyether; solid polymer electrolyte; lithium-ion conductivity.

1. Introduction

Demand for efficient energy storage devices has increased due to the requirements of higher energy storage capacity and portability.¹ Rechargeable lithium-ion batteries are the major power sources for portable electronics. At present, the performance of lithium-ion battery for miniature portable electronic devices is satisfactory. However, the current technology cannot be promoted to automobile batteries due to the potential fire hazard of organic liquid electrolyte present in batteries.² Moreover, organic liquid electrolytes suffer from volatility, pressure build-up or even explosion hazard, limited operating temperature range and harmful leakage. The fundamental solution to this problem is substitution of the flammable organic liquid electrolyte with non-flammable solid polymer electrolyte (SPE). Besides the safety considerations, other interesting properties such as flexibility, easy manipulation, wide operating temperature range, high electrochemical stability and light weight fabrication allows possibilities for advanced lithium-ion polymer secondary batteries. In addition, both ion conduction and mechanical separation can be attained in a single solid electrolyte membrane. Furthermore, a battery can be fabricated in any desired shape and size due to the flexibility of polymer membranes.³ Therefore, a better SPE with flame

retardant property for high-energy density lithium-ion batteries is always in demand to replace the organic liquid electrolyte.

Wright and co-workers revealed the ability of poly(ethylene oxide) (PEO) to dissolve inorganic salts and exhibiting ion conduction at room temperature.⁴ But, the room temperature ionic conductivity of PEO based polymer electrolyte is too low ($10^{-7} \text{ S cm}^{-1}$) for practicable applications. Our interest is to prepare SPEs having good ionic conductivity with flame retardant property. So, it is necessary to understand the conduction mechanism in order to improve the ionic conductivity of SPEs. The ionic conductivity in amorphous polymers depends on local segmental motions of polymer chains and such a favourable situation was obtained only at temperatures above T_g .⁵ Hence, an amorphous, solid polymer with low glass transition temperature is preferred for ionic conductivity.

Our aim is to induce conformational flexibilities by incorporating phosphorus in the form of C-P-C bonds in the chain. Integration of heteroatoms into the carbon-carbon polymer chain can be an intriguing strategy to tailor the properties to expand the applications of materials. However, incorporation of heavier main-group element in the polymer backbone is synthetically challenging. We have used bis(hydroxymethyl)phosphine oxides as monomer in a co-polymerization reaction to lead to polyethers. Herein, we report the polymerization behaviour of butyl bis(hydroxymethyl)phosphine oxide

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and the influence of phosphorus containing polyethers on ionic conductivity.

2. Experimental

2.1 Materials and instruments

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-pump-thaw method before use. They were dried and purified by refluxing over a suitable drying agent followed by distillation under nitrogen atmosphere. The compounds, tris(hydroxymethyl)phosphine (**S1**),⁶ 1,4-bis(bromomethyl)-2,3,5,6-tetramethylbenzene⁷ (**M3**), 1,4-bis(bromomethyl)-2,3,5,6-tetramethoxybenzene⁸ (**M4**) were synthesized according to the literature procedures. The compounds, tetrakis(hydroxymethyl)phosphonium chloride (Acros); 1,5-dibromo-pentane (**M5**), 1-iodobutane and lithium bis(trifluoromethanesulfonyl)imide $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ (LiTFSI) were purchased from Aldrich and were used as received without purification. K_2CO_3 (Merck) was dried at 100°C for 6 h under vacuum prior to use.

Structures of all the products were confirmed by ^1H , ^{31}P and ^{13}C NMR spectra. All the NMR spectra were recorded on a Bruker Avance 400 MHz FT NMR spectrometer at room temperature using either CDCl_3 or CD_3OD as solvent. The chemical shifts are reported in parts per million (δ) relative to tetramethylsilane as reference for ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz). The $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz) spectra referenced to 85% H_3PO_4 . 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 $10^\circ\text{C}/\text{min}$. The temperature of 5% weight loss was chosen as onset point of decomposition (T_d). The glass transition temperatures (T_g) of polyethers were measured on a Differential Scanning Calorimeter (DSC) from PerkinElmer (Pyris Diamond DSC 8000). The measurements were performed at a heating rate of $10^\circ\text{C}/\text{min}$ under the nitrogen. T_g was assigned as the inflection point in the thermogram. The molecular weights of the polymers were determined by Gel Permeation Chromatography (GPC) of Shimadzu 10AVP model equipped with refractive index (RI) detector. The separation was achieved using a Phenogel mixed bed column (300×7.80 mm) operated at 30°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 to 4 MHz. 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 using the equation $\sigma = d/(\text{AR}_b)$, where d is the thickness of the polymer electrolyte disc, A is the surface area of the pellet and R_b is the bulk resistance value which can be obtained from the Nyquist plot.⁹

2.2 Experimental procedure

2.2a Synthesis of butyl bis(hydroxymethyl)phosphine oxide (M1): The synthesis of **M1** was achieved in three steps as follows: A solution of tris(hydroxymethyl)phosphine (**S1**) (12.60 g, 0.1 mol) in methanol (20 mL) was taken into a 500 mL two-necked flask under nitrogen. To this, deoxygenated mixture of 1-iodobutane (37.43 g, 0.2 mol) and methanol (140 mL) was added dropwise at 0°C for 30 min. The reaction mixture was refluxed for 4 h and the solvent was evaporated under high vacuum to get a viscous oily product. Purification of this product was unsuccessful because it was non-volatile oily liquid.

To the above mixture (25.38 g), dry triethylamine (190 mL) was added in one portion under nitrogen with stirring. The resulting mixture was then heated to 60°C for 1 h and then allowed to cool to room temperature. The solid $[\text{NHEt}_3]\text{Cl}$ byproduct was filtered off and triethylamine solvent was distilled out at atmospheric pressure to give a crude product which was then heated to 90°C for 5 h under reduced pressure. A viscous oily product was obtained.

To the above oily product (10.88 g) in methanol (25 mL), 30% hydrogen peroxide solution (8.3 mL, 72 mmol) was added dropwise at 15°C and stirred for 2 h. The solution was concentrated under vacuum which was purified by column chromatography on silica gel eluting with $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (6:1) to give a clear colourless liquid butyl bis(hydroxy methyl)phosphine oxide (**M1**). (TLC was analyzed by immersing the plate in 5% sulfuric acid in methanol followed by heating using hot-air drier for 2 min. and spots were visualized by naked eye) Yield: 5.40 g, 45%. ^1H NMR (CD_3OD): δ 4.86 (s, 2H, $-\text{OH}$), 3.97 (dd, $J = 26.5, 14.1$ Hz, 4H,

–OCH₂P), 1.91–1.79 (m, 2H, –PCH₂CH₂), 1.71–1.56 (m, 2H, –CH₂CH₂CH₃), 1.53–1.41 (m, 2H, –CH₂CH₃), 0.96 (t, $J = 7.3$ Hz, 3H, –CH₃). ¹³C NMR (CD₃OD): δ 58.45 (d, $J = 79$ Hz, –PCH₂O), 26.39 (d, $J = 13$ Hz, –CH₂), 24.98 (d, $J = 4$ Hz, –CH₂), 24.13 (d, $J = 62$ Hz, –CH₂), 15.07 (s, –CH₃). ³¹P NMR (CD₃OD): δ 51.54. EI-MS: m/z 333 (2M⁺+1, base peak). Anal. calcd for C₆H₁₅O₃P: C, 43.37; H, 9.10. Found: C, 43.28; H, 9.25. Further continuation of elution yielded tris(hydroxymethyl)phosphine oxide (**M2**). Yield: 1.50 g, 12%. ¹H NMR (CD₃OD): δ 4.11 (s, 6H, –CH₂), 2.55 (s, –OH). ¹³C NMR (CD₃OD): δ 57.14 (d, $J = 76$ Hz, –CH₂). ³¹P NMR (CD₃OD): δ 46.00.

2.2b General procedure for the copolymerization of M1 with M3–M5: A typical polymerization procedure is as follows. The mixture of BuP(O)(CH₂OH)₂ (**M1**) (3 mmol), corresponding co-monomer (**M3**, **M4** or **M5**) (3.3 mmol) and K₂CO₃ (7.2 mmol) in N, N-dimethylacetamide (2.5 mL) was taken in a 100 mL round-bottom flask equipped with a Dean-Stark trap. To this, toluene (20 mL) was added as an azeotrope. The reaction mixture was heated to 130°C for 5 h in order to remove water that formed during the reaction. Then, the reaction mixture was heated to 160°C and maintained for 30 h. The viscous reaction mixture was poured into ethanol and filtered off. The product was purified by dissolving in THF and reprecipitating in hexane. This process was repeated for three more times to obtain pure polymers.

Polymer 1 (P1) (Copolymer of M1 and M3): After purification, **P1** was obtained as a white colour powder. Yield: 83%. ¹H NMR (CDCl₃): δ 4.81–4.62 (m, 4H, OCH₂Ph), 3.98–3.82 (m, 4H, PCH₂O), 2.45–2.18 (m, 12H, –CH₃), 1.79–1.65 (m, 2H, –PCH₂), 1.63–1.50 (m, 2H, –CH₂), 1.48–1.31 (m, 2H, –CH₂CH₃), 0.88 (t, 3H, –CH₃). ³¹P NMR (CDCl₃): δ 44.15.

Polymer 2 (P2) (Copolymer of M1 and M4): After purification, **P2** was obtained as a white color powder. Yield: 80%. ¹H NMR (CDCl₃): δ 4.77–4.56 (m, 4H, OCH₂Ph), 4.32–3.91 (m, 4H, PCH₂O), 3.90–3.68 (m, 12H, –OCH₃), 1.93–1.78 (m, 2H, –PCH₂), 1.66–1.51 (m, 2H, –CH₂), 1.48–1.35 (m, 2H, –CH₂CH₃), 0.88 (t, 3H, –CH₃). ³¹P NMR (CDCl₃): δ 45.75.

Polymer 3 (P3) (Copolymer of M1 and M5): After purification, **P3** was obtained as a colorless liquid. Yield: 82%. ¹H NMR (CDCl₃): δ 3.95–3.68 (m, 4H, OCH₂P), 3.57–3.38 (m, 4H, –CH₂O), 1.86–1.69 (m,

2H, –PCH₂), 1.67–1.50 (m, 6H, –CH₂), 1.48–1.24 (m, 4H, –CH₂), 0.87 (t, 3H, –CH₃). ³¹P NMR (CDCl₃): δ 44.92.

2.2c General preparation of solid polymer electrolytes SPE1 and SPE2: The polymers **P1** and **P2** were dried at 60°C and 40°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 in to 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 home-made cell for conductivity studies. The consistency of results was checked by repeating the experiment three times.

3. Results and Discussion

The following methods are generally used to achieve flame retardant property for polymers: (a) blending polymers with phosphorus containing molecules; (b) covalently attaching phosphorus containing molecules as pendant group to the polymer chains; (c) phosphorus containing polymers in which phosphorus present in main chain of polymer.¹⁰ We are interested to synthesize polyethers having phosphorus in main chain of polymer. It is known that the hydroxymethyl groups of alkyl bis(hydroxymethyl)phosphine RP(CH₂OH)₂ behaved like masked –PH₂ group. But it behaves as a normal diol when the phosphine was converted to phosphine oxide RP(O)(CH₂OH)₂.¹¹ A variety of natural and synthetic polymers where phosphorus is in main chain with O-P-O linkages are known. However, polymers with C-P-C linkages are challenging for synthesis. Therefore, use of alkyl substituted bis(hydroxymethyl) phosphine oxide as monomer to produce polyether is attractive methodology to obtain polymers with C-P-C links.

3.1 Synthesis of monomer (M1)

While tris(hydroxymethyl)phosphine (**S1**) was treated with 1-iodobutane in methanol, followed by the addition of triethylamine and hydrogen peroxide yielded **M1** as a major product and **M2** as a minor product

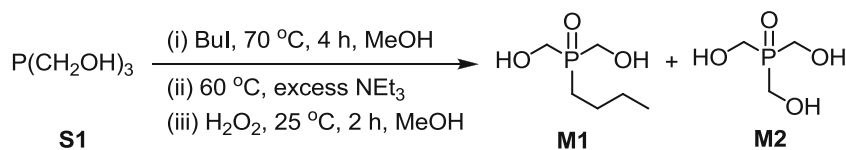
(scheme 1). These compounds were separated by column chromatography. The compound $P(CH_2OH)_3$ **S1** was known to release formaldehyde (HCHO) when heated. The HCHO thus formed in turn reacted with unreacted $P(CH_2OH)_3$ similar to well-known Wittig reaction forming **M2**. This is also a reason for low yield of **M1**. The structures of **M1** and **M2** were confirmed by 1H , ^{13}C and ^{31}P NMR spectral data.

3.2 Synthesis of polyethers (**P1–P3**)

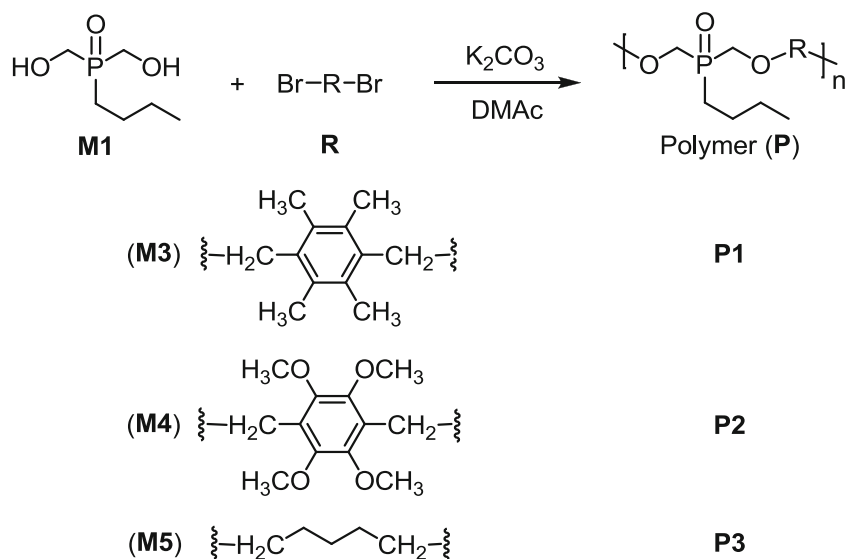
1,4-bis(bromomethyl)-2,3,5,6-tetramethylbenzene (**M3**) and 1,4-bis(bromomethyl)-2,3,5,6-tetramethoxybenzene (**M4**) were synthesized from durene and 2,5-dihydroxy-1,4-benzoquinone respectively according to the literature procedures.^{7,8} The butyl bis(hydroxy methyl)phosphine oxide **M1** was copolymerized with different dibromo monomers such as **M3**, **M4** and 1,5-dibromopentane **M5** to obtain polyethers **P1–P3** respectively via

nucleophilic substitution reactions (scheme 2). The condensation polymers were synthesized in the presence of K_2CO_3 as base in N, N-dimethylacetamide (DMAc). The polymerization procedure was carried out in two stages. First, toluene was added to the reaction mixture and azeotropic distillation was continued until water that formed during the reaction was removed from the reaction mixture.¹² In the later stage, temperature was increased to 160°C and polymerization was progressed for required time. All the crude polymers were purified by reprecipitation from THF in hexane.

The polyethers **P1** and **P2** are solids while **P3** is liquid and they are readily soluble in chloroform, THF and dimethyl sulfoxide. The polyethers **P1–P3** were characterized by 1H and ^{31}P NMR spectral data which showed that the data were consistent with the expected molecular structure. The $^{31}P\{^1H\}$ NMR spectra of polymers **P1–P3** showed a single peak and appeared at δ 44.15, 45.75 and 44.92 ppm respectively. The decomposition



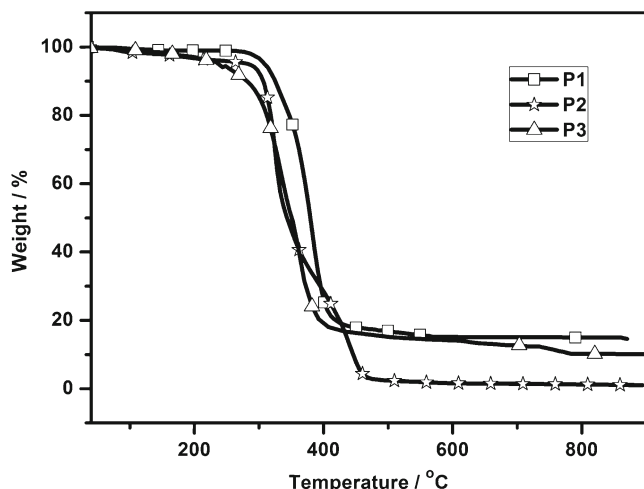
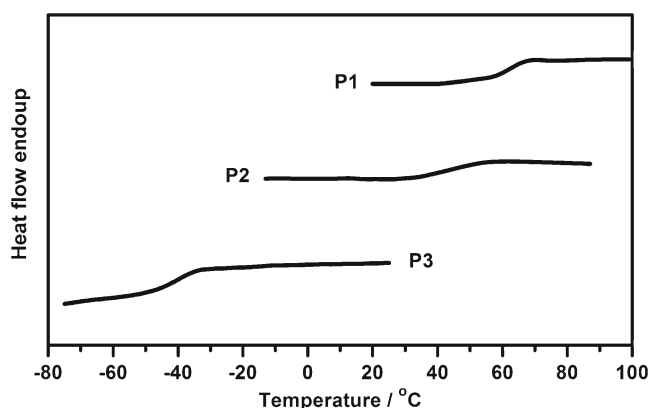
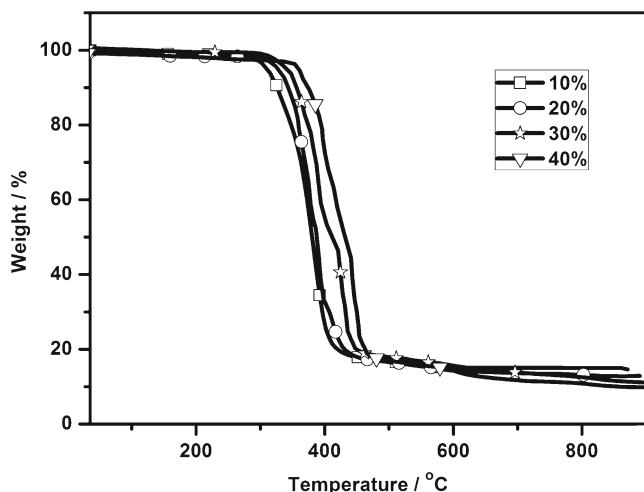
Scheme 1. Synthesis of butyl bis(hydroxymethyl)phosphine oxide (**M1**).



Scheme 2. Synthesis of phosphorus containing polyethers **P1–P3**.

Table 1. Properties of polyethers **P1–P3**.

Entry	Co-monomer	Polymer (P)	T_d (°C)	T_g (°C)	M_n (g mol ⁻¹)	M_w (g mol ⁻¹)	PDI
1	M3	P1	308.2	65.1	9414	15156	1.61
2	M4	P2	279.9	43.4	8420	14230	1.69
3	M5	P3	240.7	-40.5	10077	16425	1.63

Figure 1. TGA plots of polyethers **P1–P3**.Figure 2. DSC plots of polyethers **P1–P3**.Figure 3. TGA plots of **SPE1 (10–40%)**.

temperature (T_d), glass-transition temperature (T_g), molecular weight (M_n and M_w) and PDI of polyethers **P1–P3** are listed in table 1. The copolymers **P1–P3** have molecular weight (M_w) in the range of 14.2–16.4 kg mol⁻¹. Thermogravimetric analyses (figure 1) revealed the thermal stability of polymers **P1–P3** lies in the range of 240–308°C. The polymers **P1–P3** are completely amorphous and they did not show any peak corresponds to melting temperature (T_m) on DSC analyses (figure 2).

3.3 Solid polymer electrolyte (SPE)

P1 and **P2** were utilized to prepare **SPE1** and **SPE2** using various amounts of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) (10, 20, 30 and 40 wt%). The liquid polymer **P3** was not used to make an electrolyte. The polymers and lithium salt was dissolved in THF at 25°C and maintained for 12 h. THF was evaporated and dried under vacuum to obtain SPEs. Compared to **P1** and **P2**, thermal stability of **SPE1** and **SPE2** was increased with increasing lithium salt content from 10 wt% of LiTFSI (**10%**) to 40 wt% of LiTFSI (**40%**) (figure 3 and S1; table 1 and 2). Likewise, T_g of **SPE1** and **SPE2** increased continuously with the addition of lithium salt from 10% to 40% (figure 4 and S2; table 1 and 2). The rise in T_d and T_g compared to their corresponding polymer might be due to the effective coordination of polymer chains with lithium-ion. Based on the following observations from DSC analyses: (a) absence of peaks matching the melting temperature (T_m) of lithium salt; (b) a single T_g ; (c) increase in T_g with the addition of lithium salt; it was concluded, LiTFSI is completely miscible in **P1** and **P2** that affords a homogeneous amorphous phase and did not exist as aggregates. The absence of melting point of salts is attributable to the solvation of lithium-ions by coordination of polymer.

The conductivities of **SPE1** with 10–40 wt% of LiTFSI [**SPE1(10–40%)**] and **SPE2** with 10–40 wt% LiTFSI [**SPE2(10–40%)**] were calculated from the bulk resistance determined from complex impedance spectra.¹³ The ionic conductivities at 30°C and 80°C of **SPE1(10–40%)** and **SPE2(10–40%)** are listed in table 2. Figure 5 shows the temperature dependent

Table 2. Properties of **SPE1 (10–40%)** and **SPE2 (10–40%)**.

SPEs (wt% of LiTFSI)	SPE1		T _d (°C)	T _g (°C)	SPE2		T _d (°C)	T _g (°C)
	Conductivity σ (S cm ⁻¹)				Conductivity σ (S cm ⁻¹)			
	30°C	80°C			30°C	80°C		
SPE (10%)	5.1×10^{-7}	5.6×10^{-6}	324.1	78.9	3.2×10^{-6}	2.3×10^{-5}	290.2	52.4
SPE (20%)	6.5×10^{-7}	8.3×10^{-6}	332.5	86.7	6.5×10^{-6}	8.8×10^{-5}	298.1	65.3
SPE (30%)	9.5×10^{-7}	4.4×10^{-5}	341.6	102.4	1.2×10^{-5}	1.4×10^{-4}	310.5	70.6
SPE (40%)	2.6×10^{-6}	7.3×10^{-5}	355.8	116.2	2.1×10^{-5}	3.7×10^{-4}	321.7	78.1

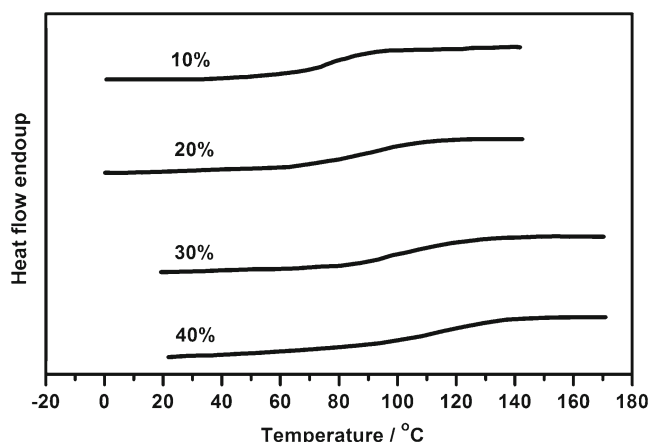


Figure 4. DSC plots of SPE1 (10–40%).

nyquist plots of SPE1 (10–40%) and Arrhenius plots of SPE1 (10–40%) and SPE2 (10–40%). While increasing the lithium salt content progressively from 10% to 40%, the ionic conductivity of SPE1 and SPE2 increased. Further, ionic conductivity of SPE1 (10–40%) and SPE2 (10–40%) were increasing with temperature. The room temperature ionic conductivity of SPE1 (10–40%) and SPE2 (10–40%) lies in the range of $5.1 \times 10^{-7} - 2.1 \times 10^{-5} \text{ S cm}^{-1}$. The maximum conductivity of $3.7 \times 10^{-4} \text{ S cm}^{-1}$ was attained for SPE2 (40%) at 80°C. Among SPE1 and SPE2, SPE2 exhibited better ionic conductivity with various amounts of lithium salt and with temperature. The presence of more

coordinating group (-OMe) in P2 as well as low T_g of P2 compared to P1 makes a better host polymer for lithium-ion conductivity.

4. Conclusions

In conclusion, we have described the synthesis of phosphorus containing polyethers wherein phosphorus exists in the main chain of polymer with C-P-C links. The utilization of alkyl substituted bis(hydroxyl-methyl)phosphine oxide as monomer for polymer synthesis was studied. The completely amorphous, highly stable and flame retardant polymers (P1–P3) were obtained by condensation polymerization. The solid polymer electrolytes SPE1 and SPE2 were prepared and their ionic conductivity behaviour was examined. The SPE2 (40%), prepared from P2, showed the highest conductivity of $3.7 \times 10^{-4} \text{ S cm}^{-1}$ at 80°C. SPE2 may be a promising SPE having good ionic conductivity with possible flame retardant property that would find potential application in larger batteries.

Supplementary Information

TGA, DSC and nyquist plots of SPE2, ^1H , ^{13}C and ^{31}P NMR of M1 and M2, ^1H and ^{31}P NMR of P1–P3 are available at www.ias.ac.in/chemsci.

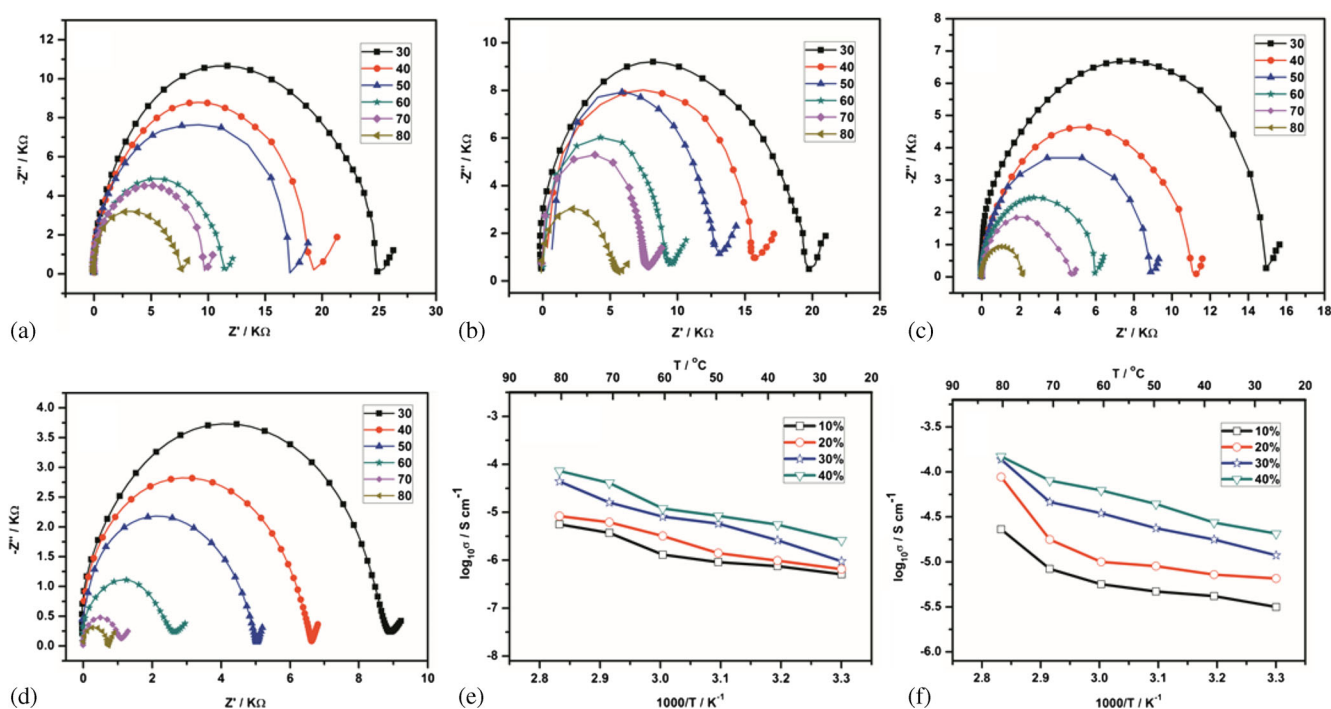


Figure 5. Temperature dependent nyquist plots of SPE1 (a) 10% (b) 20% (c) 30% (d) 40%. Arrhenius plots of temperature dependent conductivities of e) SPE1 (10–40%) f) SPE2 (10–40%).

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References

1. Bruce P G, Freunberger S A, Hardwick L J and Tarascon J-M 2012 *Nature Mater.* **11** 19
2. (a) Thielen J, Meyer W H and Landfester K 2011 *Chem. Mater.* **23** 2120; (b) Bruce P G, Scrosati B and Tarascon J-M 2008 *Angew. Chem. Int. Ed.* **47** 2930; (c) Arico A S, Bruce P G, Scrosati B, Tarascon J-M and Schalkwijk W V 2005 *Nature Mater.* **4** 366
3. Chandrasekhar V, Krishnan V, Athimoolam A and Nagendran S 2000 *Curr. Sci.* **78** 464
4. (a) Fenton D E, Parker J M and Wright P V 1973 *Polymer* **14** 589; (b) Wright P V 1975 *Br. Polym. J.* **7** 319; (c) Wright P V 1976 *J. Polym. Sci. Polym. Phys. Ed.* **14** 955
5. (a) Stoeva Z, Litas I M, Staunton E, Andeev Y G and Bruce P G 2003 *J. Am. Chem. Soc.* **125** 4619; (b) Bruce P G, Campbell S A, Lightfoot P and Mehta M A 1995 *Solid State Ionics* **78** 191
6. Ellis J W, Harrison K N, Hoyer P A T, Orpen A G, Pringle P G and Smith M B 1992 *Inorg. Chem.* **31** 3026
7. Behera G and Ramakrishnan S 2004 *J. Polym. Sci. Part A: Polym. Chem.* **42** 102
8. (a) Wessig P and Mollnitz K 2008 *J. Org. Chem.* **73** 4452; (b) Mlochowski L S J and Klock 1983 *Tetrahedron* **39** 781
9. (a) Kumar J, Rodrigues S J and Kumar B 2010 *J. Power Sources* **195** 327; (b) Lee K-H, Park J-K and Kim W-J 2000 *Electrochim. Acta* **45** 1301; (c) Morales E and Acosta J L 1999 *Electrochim. Acta* **45** 1049
10. (a) Peckham T J, Massey J A, Honeyman C H and Manners I 1999 *Macromolecules* **32** 2830; (b) Allcock H R 2003 In *Chemistry and applications of polyphosphazenes* (Hoboken: Wiley Interscience); (c) Chandrasekhar V 2005 In *Inorganic and Organometallic Polymers* (Heidelberg: Springer); (d) Sato M, Tada Y and Yokoyama M 1980 *Eur. Polym. J.* **16** 671; (e) Vlad-Bubulac T and Hamciuc C 2009 *Polymer* **50** 2220; (f) Bourbigot S and Duquesne S 2007 *J. Mater. Chem.* **17** 2283; (g) Lu S Y and Hamerton I 2002 *Prog. Polym. Sci.* **27** 1661
11. (a) Muralidharan K, Reddy N D and Elias A J 2000 *Inorg. Chem.* **39** 3988; (b) Ramakrishna T V V and Elias A J 2001 *J. Organomet. Chem.* **637** 382; (c) Reddy N D, Elias A J and Vij A 2000 *Inorg. Chem. Commun.* **3** 29
12. Chen X-T, Sun H, Tang X-D and Wang C-Y 2008 *J. Appl. Polym. Sci.* **110** 1304
13. (a) Abraham K M, Jiang Z and Carroll B 1997 *Chem. Mater.* **9** 1978; (b) Yoshida K, Nakamura M, Kazue Y, Tachikawa N, Tsuzuki S, Seki S, Dokko K and Watanabe M 2011 *J. Am. Chem. Soc.* **133** 13121; (c) Britz J, Meyer W H and Wegner G 2007 *Macromolecules* **40** 7558