Semi-interpenetrating polymer networks as solid polymer electrolytes: Effects of ion-dissociation, crosslink density and oligomeric entanglements on the conductivity behavior in poly(ethylene oxide)–polyurethane/poly(acrylonitrile) matrix

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HIGHLIGHTS

► Aspects of structural modifications on a promising semi-IPN electrolyte are reported.
► Dependence of ion-dissociation and matrix conductivity on the nature of salt used.
► Network crosslink density depends on PEG chain length and affects ion conductivity.
► Use of an entangled oligomer to effectively plasticize and create a ternary system.
► Results demonstrate versatility of these semi-IPNs to be custom designed as SPEs.

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ABSTRACT

The present study investigates into three aspects of tailoring and simple structural modifications on a promising solid polymer electrolyte system of poly(ethylene oxide)–polyurethane/poly(acrylonitrile) semi-interpenetrating polymer networks. Influence of the nature of salt solvated, cation/anion mobility, ion–polymer interaction and transient crosslink formation is evaluated using different solvated electrolytes and the conductivity achieved varied as $LiClO_4 \geq LiCF_3SO_3 > NaBF_4 > NaClO_4 > KI$. The role of optimum chain length between the crosslinks (crosslink density) necessary to attain better conductivity levels is appraised using PEG of different molecular weights (400, 2000, 4000, 10,000 and 35,000) for synthesis and the maximum conductivity was obtained for PEG-4000. The temperature dependence of ion conductivity shows an Arrhenius to VTF transition at ∼323 K in these semi-IPNs, a general behavior independent of the nature of salt and the poly(ethylene glycol) chain length. Ternary composition of semi-IPN containing 30 wt% PEGDME MW 500 yields a conductivity of $\sim 2 \times 10^{-5}\,S\,cm^{-1}$ at 35 °C, an order of magnitude higher than that obtained without plasticizing component. VTF behavior is witnessed throughout the temperature window in the study for samples with oligomeric plasticization. Linear sweep voltammetry indicates significantly good electrochemical stability (∼4.6 V) of the semi-IPN electrolyte matrix.

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1. Introduction

The goal of achieving an ideal polymer electrolyte (PE) suitable for realizing practical application is still elusive and several gaps and bottlenecks remain to be addressed. Structural modification of PEO based systems to improve their physical properties and conductivity behavior is still an open challenge in the field of solid polymer electrolytes. Redesigning the polymer architecture to incorporate optimal distribution of solvating groups for cation coordination, minimization of chain regularity to reduce crystallinity and enhancing chain flexibility have been identified as some of the most suitable strategies to develop superior SPEs. In this direction, various classes of polymeric materials such as random copolymers [1–8], block copolymers [9–11], comb polymers [12–14] and crosslinked networks [15–18] have been explored and documented. The nature (cation/anion) and concentration of the

incorporated salt used can affect the conductivity by influencing the formation of crystalline domains, intermolecular crosslinking and phase composition. Thus, the electrolyte properties can be suitably modified by incorporating different salts into the matrix [11,19]. For network systems, the crosslink density i.e. the molecular weight of the polymeric chains between the crosslinks, too plays a significant role in the ion conducting behavior of the electrolyte matrix.

In combination with these simple structural modifications, further plasticization of the polymer matrix is a widely employed approach to improve the overall performance of the polymer electrolytes [20–39]. Plasticizers used in 'gel' polymer electrolytes are usually low molar mass organics, preferably having a high dielectric constant to ensure strong charge dissociation and provide a liquid-like environment within the polymer matrix, which facilitates ion transport. Propylene carbonate (PC) [20–23], ethylene carbonate (EC) [38,39], dimethyl carbonate (DMC) [35], diethyl carbonate (DEC), γ-butyrrolactone and the likes, are some of the conventional organic liquids commonly used for the purpose. Low molecular weight glycols, such as diglyme, tetraglyme (TGME) and polyethylene glycol dimethylether (PEGDME) have also been exploited [28–33]. Ideally, the system behaves like a liquid with high ionic conductivity, while preserving the dimensional stability of the solids.

The feasibility of using poly(ethylene oxide)–polyurethane/poly(acrylonitrile) (PEO–PU/PAN) semi-interpenetrating polymer networks (semi-IPNs) and its nano-composites as solid polymer electrolytes have been demonstrated by our group in recent years [40–44]. The attempts have resulted in a promising SPE with room temperature ionic conductivity of $\sim 10^{-6}$ S cm^{-1}, while retaining the necessary dimensional and thermal stability required for a polymer electrolyte. Useful insights into the various aspects of the electrochemical behavior of these systems and their dependence on the physico-chemical properties gained from these studies provided reasonable grounds for tailoring the system further.

In continuation with our efforts to enhance the ionic conductivity whilst creating an effective library of these semi-IPN matrices, the present paper, reports some of the interesting findings pertaining to various simple structural modifications that have generated important leads toward developing an ideal SPE for practical purposes. This endeavor investigates into three aspects of structural modifications on the PEO–PU/PAN semi-IPN system and their impact on the ionic conductivity behavior: viz., i) the nature of salt (ion-dissociation), ii) crosslink density of the PEO–PU network (PEG chain length) and iii) creating a ternary system using an entangled oligomer within the semi-IPN matrix (oligomeric plasticization) have been assessed. The results presented herein, provide a more comprehensive understanding of the complex matrix behavior for the PEO–PU/PAN semi-IPNs and affirm our contention of the potential use of such systems as solid polymer electrolytes.

2. Experimental

2.1. Materials

Castor oil (BSS Grade), diphenylmethane diisocyanate (MDI) (Ind-ital Chem. Ltd.), polyethylene glycol (PEG), (MW = 400, 2000, 4000 from SD Fine Chemicals and MW = 10,000, 35,000 from Fluka), N,N-dimethylaniline (DMA) (SD Fine Chemicals), acrylonitrile (SRL), benzoyl peroxide and tetrahydrofuran (THF) (Ranbaxy), lithium perchlorate (LiClO₄) (Aldrich), lithium trifluoromethanesulfonate (LiCF₃SO₃) (Aldrich), sodium perchlorate (NaClO₄) (Aldrich), sodium tetrafluoroborate (NaBF₄) (Merck), potassium iodide (KI) (SD Fine Chemicals), polyethylene glycol dimethylether (PEGDME, MW = 500) (Aldrich) were used as obtained.

2.2. Synthesis of PEO–PU/PAN (60/40) semi-IPNs

2.2.1. Variation of salt

In a typical reaction, the isocyanate terminated urethane pre-polymer is synthesized by reacting castor oil with excess of MDI in THF for 1 h at room temperature under nitrogen atmosphere as reported elsewhere [40–43, see Supporting information]. The desired amount of various salts to be added for each composition is calculated from the EO/M$^+$ mole ratio (M$^+$ = Li$^+$, Na$^+$, K$^+$). The EO/M$^+$ mole ratios (salt concentration) used in the present study are 30, 20, 15 and 10 (Table 1). The required amount of salt is mixed with PEG and dissolved in acetonitrile/THF (2:1) prior to its addition to the prepolymer. The PEG containing the desired amount of salt, the second monomer acrylonitrile (40 wt%), benzoyl peroxide (initiator) and N,N-dimethylaniline (catalyst) is then added to the prepolymer. For the synthesis of the poly(ethylene oxide)–polyurethane networks a −OH/−NCO ratio of 1:1.25 is maintained. The mixture is again degassed and stirred under nitrogen atmosphere at room temperature for 30 min. The viscous solution is then cast in

Table 1
Electrolyte compositions of PEO–PU/PAN (60/40) semi-IPNs studied with respect to the molecular weight of PEG used, type of salt, weight % of oligomer PEGDME 500, the EO/M$^+$ mole ratio, the Arrhenius activation energy (ΔE_a) and the Vogel–Tammann–Fulcher (VTF) fitting parameters (T_0, A and B).

No.	PEG mol. wt	Salt	PEGDME (wt%)	EO/M$^+$	ΔE_a (eV)	T_0 (K)	A (S cm^{-1})	B (eV)
1	4000	NaClO₄	–	30	0.66	286.7	0.035	0.014
				20	0.67	281.3	0.034	0.020
				15	0.64	298.7	0.044	0.019
				10	0.54	281	0.086	0.017
2	4000	NaBF₄	–	30	0.65	284.2	0.041	0.056
				20	0.69	300.3	0.043	0.053
				15	0.74	299.7	0.014	0.066
				10	0.63	281.9	0.053	0.064
3	4000	KI	–	30	0.70	211.1	0.144	0.080
				20	0.73	208.6	0.178	0.085
				15	0.81	246.9	0.167	0.045
4[b]	4000	LiCF₃SO₃	–	30	0.59	180.5	0.0227	0.076
				20	0.52	181.4	0.0423	0.079
				15	0.57	186.3	0.0955	0.094
				10	0.52	187.5	0.1435	0.101
5[a]	4000	LiClO₄	–	30	0.58	188.6	0.0070	0.066
				20	0.55	187.7	0.0049	0.055
				15	0.53	190.9	0.0013	0.027
				10	0.52	195.2	0.0008	0.015
6	400	LiClO₄	–	30	0.54	244.4	0.016	0.024
				20	0.80	179.2	0.086	0.097
				15	0.78	220.2	0.032	0.050
				10	0.78	251.1	0.048	0.043
7	2000	LiClO₄	–	30	0.68	263.1	0.047	0.023
				20	0.55	195.4	0.119	0.085
				15	0.70	245.9	0.091	0.037
				10	0.78	256.5	0.093	0.031
8	10,000	LiClO₄	–	30	0.59	248.7	0.031	0.027
				20	0.43	216.1	0.042	0.045
				15	0.45	274.4	0.017	0.014
				10	0.47	216.8	0.066	0.061
9	35,000	LiClO₄	–	30	0.52	262.9	0.020	0.019
				20	0.54	207.2	0.076	0.066
				15	0.59	187.8	0.116	0.092
				10	0.64	237.3	0.038	0.041
10	4000	LiClO₄	10	20	–	166.6	0.874	0.116
				15	–	229.1	0.203	0.042
				10	–	184.6	0.816	0.102
11	4000	LiClO₄	20	20	–	259.2	0.111	0.017
				15	–	247.9	0.153	0.022
				10	–	242.1	0.210	0.025
12	4000	LiClO₄	30	20	–	238.6	0.428	0.040
				15	–	234.9	0.303	0.033
				10	–	252.9	0.216	0.021

[a] Data from Ref. [40].
[b] Data from Ref. [41].