



Highly conductive, completely amorphous polymer electrolyte membranes fabricated through photo-polymerization of poly(ethylene glycol diacrylate) in mixtures of solid plasticizer and lithium salt

Mauricio Echeverri^a, Cosette Hamad^b, Thein Kyu^{a,*}

^a Department of Polymer Engineering, University of Akron, Akron, OH 44325, USA

^b Copley High School, Copley, OH 44321, USA

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ABSTRACT

Ternary phase diagram of prepolymer mixtures containing poly(ethylene glycol diacrylate) (PEGDA), succinonitrile (SCN) and lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) has been established in order to provide guidance for producing completely amorphous self-standing solid electrolyte membranes. The phase diagram of the precursor mixtures, thus obtained, consisted of a wide isotropic amorphous region, crystal + amorphous coexistence region at high lithium salt concentrations and plastic crystal + amorphous coexistence region at succinonitrile-rich compositions. Of particular interest is that upon photo-polymerization of isotropic compositions, the resulting networks remained completely amorphous without undergoing polymerization-induced phase separation or polymerization-induced crystallization. The ionic conductivity was mapped out as a function of composition within the isotropic region of the starting ternary phase diagram in conjunction with room temperature conductivities showing high ionic conductivities on the order of 10^{-3} S cm⁻¹ at several compositions. These solid state polymer electrolyte membranes are transparent, light weight, and flexible, which can be shaped in any forms with space saving attributes. More importantly, no solvent is required in the membrane fabrication as well as in the battery operation, thereby improving safety and cost effectiveness.

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1. Introduction

Over the past decades, the development of solid electrolytes for polymer lithium batteries has been a major challenge in the energy storage industry [1]. A common practice is the utilization of polymeric networks that entrap liquid solutions of lithium salts in organic solvents such as ethylene carbonate (EC), propyl carbonate (PC), dimethyl ether and acetonitrile in polymers such as poly(acrylonitrile) (PAN), poly(methylmethacrylate) (PMMA), or poly(vinylidene fluoride) (PVDF) matrices. The immobilization procedure varies from case to case, but it generally involves UV cross-linking, solvent casting, or physical gelation [2,3]. The effect of the plasticizer on conductivity enhancement could be profound; whereby the ionic conductivities of the PEO based networks changed from 9×10^{-7} S cm⁻¹ to 4×10^{-4} S cm⁻¹ depending on the physical characteristics of plasticizers such as permittivity and viscosity [4]. Other notable contributions include porous networks containing high concentrations of organic liquid solvents and lithium salts that can reach the conductivity level of 1×10^{-2} S/cm [5–8]. However, this type of material requires large amounts of organic solvent in the polymeric gel network, in some cases more than the total polymer weight.

An inevitable consequence is that the interaction of solvents with electrodes has led to contamination, which in turn reduces the battery

performance [9]. Another concern is the need for containment of organic solvents in metal or plastic containers of various shapes and thus such battery is heavy and bulky requiring sizable space in intended applications, for instance, in electric vehicles. Moreover, there is safety concern especially with damaged or leaky battery containers [10]. Several major efforts have been directed to fabrication of non-volatile conductive membranes, notably polymer gel based electrolytes. The conventional polymer electrolyte utilized poly(ethylene oxide) (PEO) as a matrix, but the room temperature ionic conductivity was orders of magnitude lower than the conventional lithium battery containing organic solvents. Recently, the feasibility of producing solvent-free solid electrolyte was demonstrated by doping with succinonitrile (SCN) plastic crystals for lithium ion transport [11,12]. It is intriguing to find that only small amount of lithium salt (1 mol%) such as lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) was needed to achieve reasonably high ionic conductivity in the order of 10^{-4} S cm⁻¹, despite the fact that SCN itself is a poor ionic conductor [13]. However, such plastic crystal matrix containing lithium salt is a waxy substance without sustainable mechanical strength and integrity thereby preventing its full utilization as solid electrolyte. Recently, a moderate room temperature ionic conductivity on the order of 10^{-4} S cm⁻¹ was achieved with the aid of SCN plastic crystal mixed with PEO. Upon combining with photo-curable poly(ethylene glycol) dimethacrylate (PEGDMA), the mechanical strength of the composite network improves while the SCN plastic crystal

* Corresponding author.

promotes lithium ion transport [14]. Other authors have used SCN as plasticizer to crosslinkable systems [15–18]. Although the aforementioned approaches are promising, there is little or no in-depth understanding of the phase behavior of these mixtures, e.g., the effect of different coexistent regions on ionic conductivity and mechanical properties.

We have demonstrated recently that completely amorphous mixtures of PEO/SCN/LiTFSI, optimized within the isotropic region of the ternary phase diagram, exhibited higher room temperature ionic conductivity relative to the plastic crystalline phase of the SCN constituent [19]. Furthermore, we have shown that the ionic conductivity can be enhanced upon melting the PEO crystals, i.e., the completely amorphous mixtures of PEO/SCN/LiTFSI out-performed the crystalline or plastic crystalline mixtures. One short coming was that the mechanical strengths of the highly conductive PEO/SCN/LiTFSI electrolyte compositions were low, forming only viscous paste. On the contrary, high PEO contents show greater mechanical strength, but lower ionic conductivities [19].

In an effort to improve mechanical strength, photo-crosslinkable oligomeric thermosets such as poly(ethylene glycol diacrylate) (PEGDA) were used in lieu of poly(ethylene oxide) thermoplastic in the present work. A ternary phase diagram of PEGDA/SCN/LiTFSI mixture was constructed in order to establish a processing window for fabricating completely amorphous transparent polymer electrolyte films. Photopolymerization of PEGDA was carried out in the single phase region of the ternary mixtures. Although the starting ternary prepolymer mixtures are in the single isotropic phase, there is always a possibility of either polymerization induced phase separation or phase transition taking place. It was found that the photo-cured polymer electrolyte remained in the single phase and formed a homogeneous transparent film. Subsequently, AC impedance spectroscopy measurement was performed as a function of composition and temperature. The observed conductivity behavior was analyzed in relation to the apparent activation energy of the ion transport as well as the tensile properties of the photo-polymerized electrolyte mixture.

2. Experimental

2.1. Materials

Poly(ethylene glycol) diacrylate (PEGDA) with a number averaged molecular weight, M_n of 700 g/mol was purchased from Sigma-Aldrich. Photo initiator, Irgacure® 651, was bought from CIBA. Lithium bis(trifluoromethane) sulfonimide (purity of 99.9%) and succinonitrile (>99%) were obtained from Aldrich. Methylene chloride (99.9%) and acetone (99.9%), were bought from Fisher Scientific and Mallinckrodt, respectively.

For the determination of phase diagram, the ternary mixtures of PEGDA/SCN/LiTFSI were prepared in a glove box under nitrogen flow by co-dissolving in solution mixture of methylene chloride and acetone at 40:1 weight ratios. Solvent was evaporated during casting of a thin film in a hot stage at 80 °C under nitrogen flow. To avoid potential loss of SCN during prolong exposure to elevated temperatures, the thermal treatment for all blends containing SCN was limited to 80 °C. It should be emphasized that the solvents were used only in the preparation of the binary and ternary PEGDA/SCN/LiTFSI mixtures.

2.2. Melt-blending method

Various PEGDA/SCN binary mixtures were melt-blended in the isotropic region by mechanical stirring at 60 °C for 15 min to assure complete mixing. The samples were then kept in amber vials in a refrigerator at 4 °C. LiTFSI was predried at 170 °C in a vacuum oven for 24 h. Various concentrations of binary PEGDA/LiTFSI mixtures were prepared in a glove box under dry nitrogen atmosphere by dissolving these materials in solution mixture of methylene chloride/acetone at 40:1 weight ratio. Solution casting was carried out under continuous nitrogen gas flow at 100 °C for 1 h. Finally, the blend samples were placed in a high vacuum

chamber at room temperature for 24 h to further remove residual solvent or moisture, if any.

2.3. Miscibility characterization

Differential scanning calorimetry, DSC (TA Instruments, Model Q200), was employed to determine the melting points of various blend pairs. Samples weighing 5–10 mg were hermetically sealed in aluminum pans covered with lids by crimping. An empty crimped pan with lid was used as a reference. In the case of PEGDA/SCN mixtures, the blend samples were rapidly cooled to –50 °C, equilibrated at this temperature for 15 min, and then ramped up to 70 °C at a heating rate of 10 °C min⁻¹. In the case of PEGDA/LiTFSI mixtures, the samples were hermetically sealed inside a glove box under nitrogen gas circulation. For this mixture, the DSC analysis was performed by cooling the samples to –50 °C, keeping the samples at this temperature for 15 min, and then heating up to 250 °C at 10 °C cm⁻¹. Likewise, the ternary mixtures were sealed in aluminum pans in a glove box under nitrogen gas and the DSC scans were carried out between –50 and 80 °C at 10 °C cm⁻¹. All DSC scans were ramped twice; the first cycle was performed to provide the same thermal history to all samples and only the data from the second run was used in the analysis. The peaks of the endothermic signals were regarded as the phase transition points and plotted as a function of composition.

In order to corroborate the DSC melting transitions and the morphology of the samples at different temperatures, microscopic characterization was performed using a polarized optical microscope (POM, Olympus BX60). Samples were placed between glass slides right after drying. A heating/cooling chamber (TMS93 Linkam) was used under constant nitrogen gas flow to prevent moisture absorption. POM micrographs were taken using a 35 mm digital camera (EOS 300D, Canon).

2.4. Membrane fabrication

To fabricate self-standing conductive membranes, appropriate compositions of PEGDA/SCN/LiTFSI corresponding to the isotropic region of the ternary phase diagram were selected and then melt-blended at room temperature. These mixtures were added with 2 wt.% Irgacure 819® relative to the PEGDA amount. The homogeneous mixture thus obtained was placed on a Teflon® sheet with a Teflon frame spacer having a rectangular or square shape with a dimension of 20 × 10 mm² for tensile tests and 12 × 12 mm² for the AC impedance measurements and then covered with a transparent PET film. Subsequently, UV polymerization was performed at 25 °C by illuminating with a UV Cure Lamp (Bondwand 350 nm) at an intensity of 5 mW cm⁻² for 15 min in a glove box under nitrogen atmosphere. The thickness of the photo-cured film was approximately 0.6 mm.

2.5. Membrane characterization

Fourier Transform Infrared (FTIR) spectroscopy experiments were conducted using a FTIR Nicolet 380 Thermo Scientific. A liquid isotropic sample containing PEGDA/SCN/LiTFSI was placed in between KBr disks in a glove box under nitrogen atmosphere. The photo-curing was carried out by exposing to UV light using a Bondwand lamp at 350 nm and an intensity of 5 mW cm⁻² for 15 min in a glove box under nitrogen atmosphere. The IR spectra of these mixtures before and after curing were analyzed as a function of composition and curing time. Note that the acquired spectra were the average of 32 scans with a resolution of 4 cm⁻¹ in transmission mode.

The UV cured PEGDA/SCN/LiTFSI network was homogeneous, transparent, and flexible. These flexible films were placed between polished stainless steel electrodes in a glove box under dry nitrogen gas. The assembly of the sample and electrodes was sealed in plastic bags to prevent moisture absorption during the AC impedance test. To avoid potential current leakage from the edges, the films were cut into a slightly larger dimension (12 mm × 12 mm) relative to the dimension of

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