

A New Poly(amide urethane) Solid State Electrolyte Containing Supramolecular Structure

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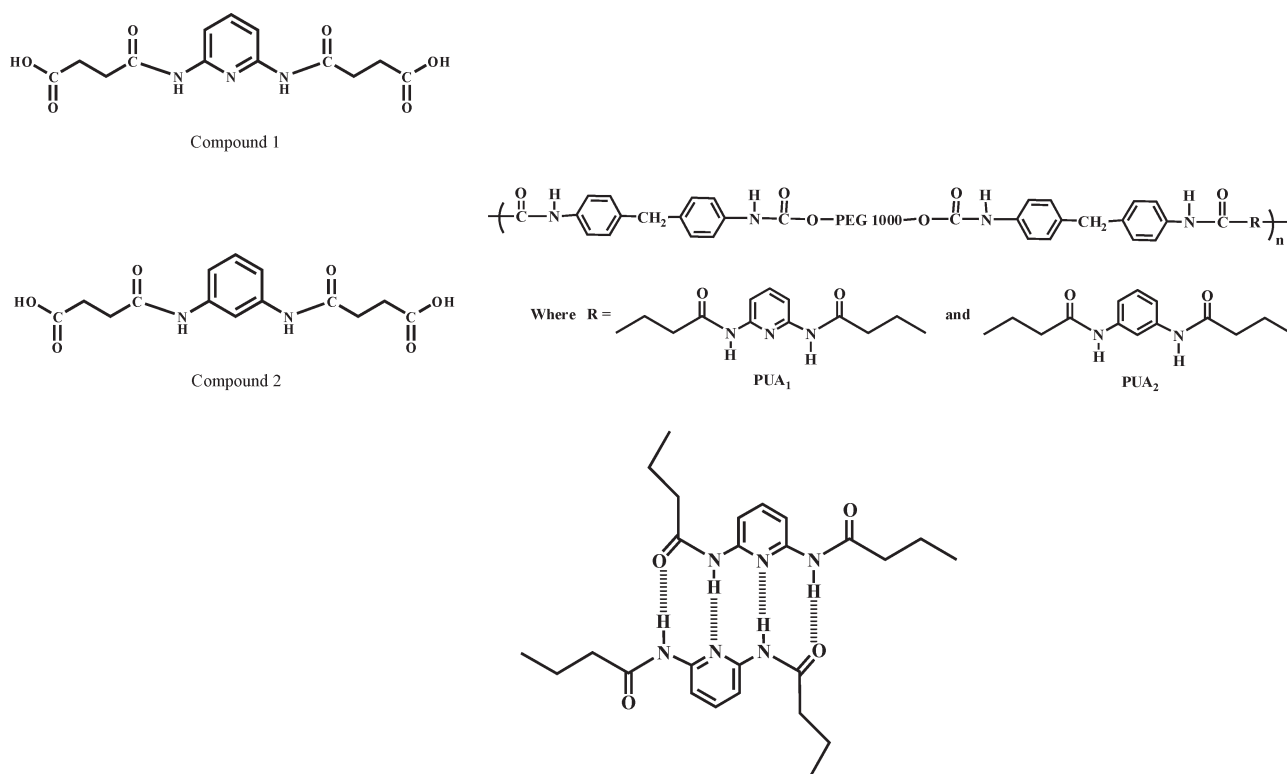
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Polymer electrolytes formed through dissolving salts into polar and high-molecular-weight macromolecules are the subject of intensive research because of their potential for use as the solid polymer electrolytes (SPEs) in rechargeable lithium batteries.¹ The use of these electrolytes for high-energy-density batteries and other solid state electrochemical devices has spurred considerable interest in the ion-transport properties of these materials. The goal for the SPE research is the development of highly ionic conductive (ca. 10^{-4} S cm^{-1}), dimensionally stable, and flexible materials under ambient conditions. Since Wright reported that poly(ethylene oxide) (PEO) can be the candidate for use in SPEs

derivatives have been prepared through numerous physical and chemical procedures, including covalent copolymerization,^{3c–e} dendrimerization,^{3f} grafting,^{3g} and radiation^{3h} in studying their interaction mechanisms and chemical and physical properties. In our previous studies, interaction mechanisms have been proposed on SPEs including copolymers,^{4a,b} polyhedral oligomeric silsesquioxane (POSS),^{4c,d} clay,^{4e} and salts. However, the development of the highly conductive SPE materials still remains an important challenge. Recently, Gadjourova et al.⁵ reported that a crystalline polymer electrolyte with ordered structure offers ion conductive paths and exhibits even higher ionic conductivity than an

Scheme 1. Chemical Structures of Compound 1, Compound 2, PUA₁, and PUA₂



in 1975, it has become one of the most studied SPE materials.² The transport mechanism within SPEs based on PEO and salts has been proposed in several studies.^{3a,b} In addition, the PEO

amorphous one, which provides new insight into the research for highly ionic conductive SPEs.

Self-assembled polymers such as block copolymers are usually formed through covalent linkages in traditional polymer chemistry, including bonds connecting monomer units and attaching

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Table 1. Compositions of PUA₁ and PUA₂ SPEs

PUA ₁ SPEs ^b	Li ⁺ /O ^a	PUA ₂ SPEs	Li ⁺ /O
PUA _{1A}	1/20	PUA _{2A}	1/20
PUA _{1B}	1/16	PUA _{2B}	1/16
PUA _{1C}	1/12	PUA _{2C}	1/12
PUA _{1D}	1/8	PUA _{2D}	1/8
PUA _{1E}	1/3	PUA _{2E}	1/3

^a Molar fraction. ^b The preparation of these SPEs was described in the Supporting Information, S1.

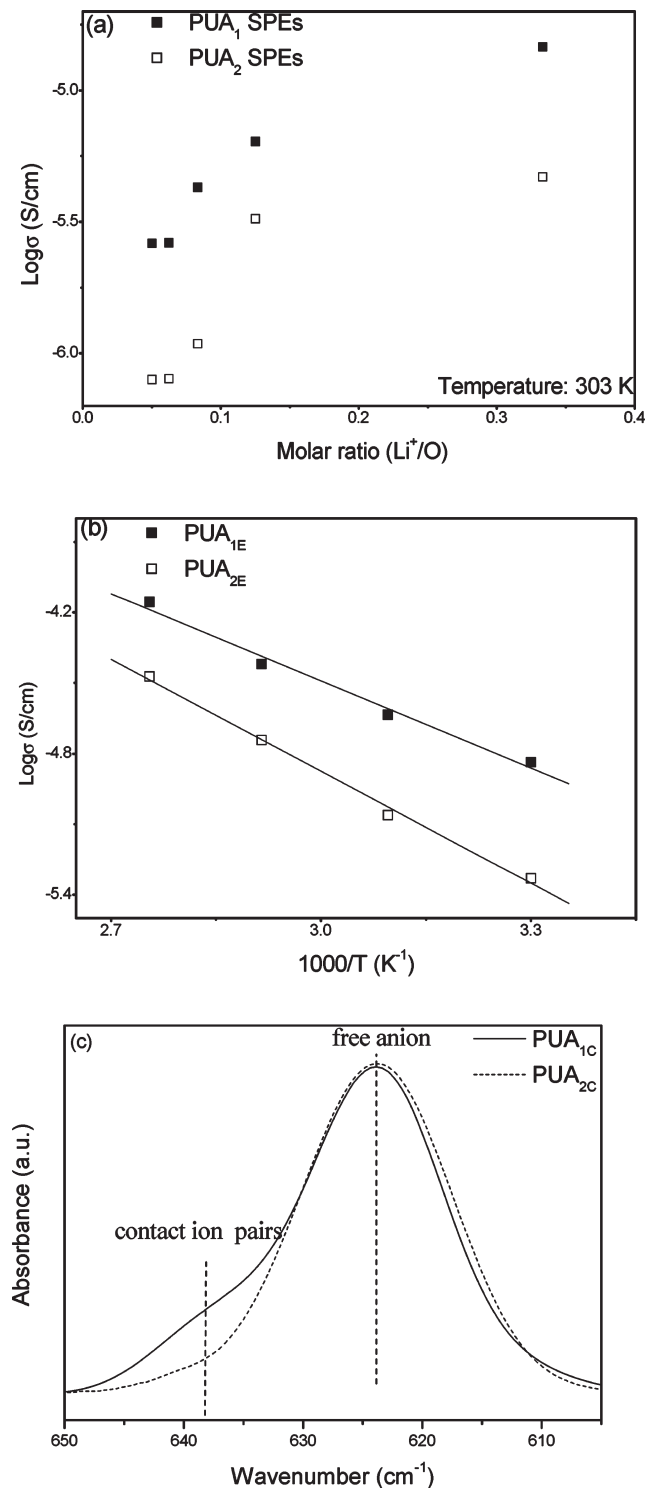


Figure 1. (a) Ionic conductivity of these PUA₁ and PUA₂ SPEs plotted with respect to the LiClO₄ content. (b) Arrhenius ionic conductivities plotted with respect to temperature. (c) IR spectra ranged from 610 to 650 cm⁻¹ displaying the $\nu(\text{ClO}_4^-)$ internal vibration modes of the PUA₁ and PUA₂ SPEs.

functional groups to the polymer backbone. Recently, novel structural organizations of self-assembled polymers formed through highly directional and sufficiently strong noncovalent host–guest pairs have attracted great attention.^{6,7} During the past few years, several reports regarding the incorporation of nucleobase functionality into main- and side-chain polymers mediated by complementary hydrogen bonds (arrays of hydrogen bonds) have been explored.⁸ This concept stemmed from the direct observation of complementary materials where the complexity and molecular functionality can form noncovalent bonds to construct materials exhibiting specific structures such as proteins.⁹ The hydrogen-bonding interactions in terms of complementary recognition can be broadly classified into self-complementary and heterodimer recognition. Generally, in a self-complementary system, the hydrogen bonded units are attached covalently to the polymer backbone and exhibit a strong tendency for self-association resulting in interchain association.¹⁰ In our previous study, we reported the heterodimer recognition [thymine–adenine (T–A) base pair] between the DNA-like side chains on different polymers.¹¹ In this study, the self-complementary interaction (Scheme 1) was employed to prepare SPE materials to possess enhanced properties due to novel structural organization. A new SPE with self-complementary material has been successfully synthesized as shown in Scheme 1.^{8j} The self-complementary behavior of the synthesized SPE material provides a strategy to investigate the effect of the self-complementary interactions on SPE properties.

A new amorphous SPE (PUA₁) (shown in Scheme 1) possessing both self-complementary interaction ($K_a \approx 170 \text{ M}^{-1}$) and ion conductive behavior was synthesized through a new self-complementary compound, compound **1**, and PEG1000 prepolymer (Supporting Information, S2).^{8j} A control group (PUA₂) representing a conventional SPE was also synthesized. As compared with PUA₁, PUA₂ only possessed nonspecific hydrogen-bonding interaction. Poly(amide urethane) was chosen as the polymer matrix of these SPEs because of its well-known microphase-separated behavior and diversity of functionality, and it was previously employed as SPE.¹² The reaction schemes are illustrated in the Supporting Information, S2 and S3. Compositions of PUA₁ and PUA₂ SPEs are summarized in Table 1.

Figure 1a displays the ionic conductivities of PUA₁ and PUA₂ SPEs plotted against LiClO₄ content measured through an Autolab designed by Eco Chemie. All these PUA₁ SPEs exhibit about half-order higher ionic conductivity than the control PUA₂ SPEs, indicating that the incorporation of the self-complementary material (compound **1**) indeed results in improved ionic conductivity. In addition, the relatively lower E_a of PUA_{1E} (Li⁺/O = 1/3) obtained from the Arrhenius ionic conductivities plotted with respect to temperature (Figure 1b) implies that the ionic conductivity of PUA_{1E} is less sensitive to temperature. The ionic conductivity measurement, preparation, and compositions of these SPEs are summarized in the Supporting Information, S1. Figure 1c presents IR spectra ranged from 610 to 650 cm⁻¹ displaying the $\nu(\text{ClO}_4^-)$ internal vibration modes of these SPEs where bands centered at 624 and 638 cm⁻¹ correspond to the free anion and contact ion pair, respectively.^{4c} The PUA_{1C} (Li⁺/O = 1/12) possesses a greater fraction of contact ion pair relative to the PUA_{2C} (Li⁺/O = 1/12) but exhibits higher ionic conductivity. This is unexpected because electrolytes with more free ions usually possess higher ionic conductivity.³ Figure 2 presents IR spectra ranging from 1620 to 1750 cm⁻¹ of PUA₁ and PUA₂ SPEs (Supporting Information, S1). In Figure 2a, the pristine PUA₁ exhibits several characteristic bands, including 1728 cm⁻¹ (free C=O of urethane), 1704 cm⁻¹ (hydrogen-bonded C=O of urethane), 1673 cm⁻¹ (free amide I), and 1650 cm⁻¹ (hydrogen-bonded amide I), revealing that fraction of these urethane and amide I groups are hydrogen-bonded.¹³ In addition, the fraction

of the hydrogen-bonded C=O of urethane within the pristine PUA₁ is relatively less than that of the pristine PUA₂ because the self-complementary interaction within PUA₁ dominates over the formation of hydrogen bonds between urethane groups. Upon adding LiClO₄ to the PUA₁ polymer, the intensities of the urethane hydrogen-bonded C=O (1704 cm⁻¹) and amide I (1650 cm⁻¹) groups of PUA₁ SPEs increase with the disappearance

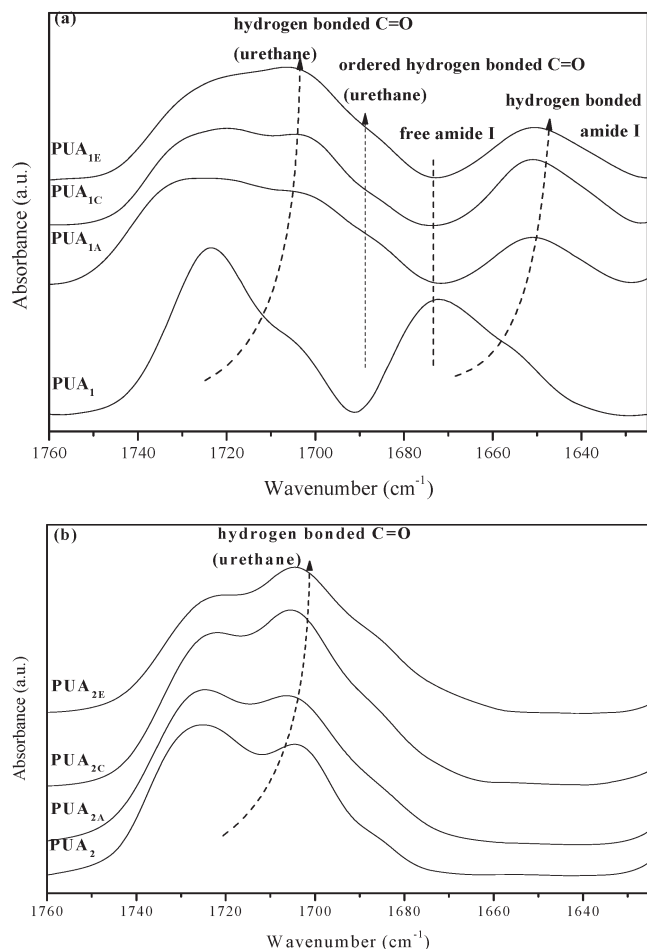


Figure 2. IR spectra ranging from 1620 to 1750 cm⁻¹ of (a) PUA₁ and (b) PUA₂ SPEs.

of the free amide I band (1673 cm⁻¹) and the appearance of a band centered at 1689 cm⁻¹ corresponding to the ordered hydrogen-bonded C=O.^{13b,c} In contrast, these bands within PUA₂ remain nearly unchanged except that of the hydrogen-bonded C=O as shown in Figure 2b. The PUA₁ SPEs exhibit both highly hydrogen-bonded amide I groups (highly interacted self-complementary sites) and ordered hydrogen-bonded C=O upon the presence of LiClO₄. Based on the above, PUA₁ SPEs possess relatively ordered structure as compared with PUA₂ SPEs, and thus they are able to provide more free-flowing ion conductive paths and exhibit ca. 5 times the ionic conductivity of PUA₂ SPEs.⁵

In order to further understand the interdependence of LiClO₄ on hydrogen-bonding interactions within PUA₁ SPEs, two-dimensional (2D) FT-IR and solid state ⁷Li NMR measurements were employed. The added lithium cations are able to interact with both ethylene oxide segments and urethane groups without affecting the self-complement and result in relatively ordered structure (Supporting Information, S4).^{14–16} For these PUA₁ SPEs, the lithium cation interacts relatively less with the self-complementary sites due to the highly self-complementary interaction. The PUA₂ SPEs possess relatively more interacting sites for forming ion-dipole interaction with LiClO₄; thus, PUA₂ SPEs exhibit a relatively higher fraction of free anion. As shown in Figure 3, the relatively ordered structure of the PUA₁ SPEs (as confirmed through the FTIR spectra and small-angle X-ray scattering (SAXS) patterns shown in the Supporting Information, S5) resulted from the incorporation of self-complementary material is able to provide more free-flowing ion conductive paths for lithium cation transport and thus enhances the ionic conductivity.

In summary, a new SPE composed of PUA₁ and LiClO₄ possessing self-complementary material was successfully synthesized. The presence of the highly hydrogen-bonded amide I groups (highly interacted self-complementary sites) induces these PUA₁ SPEs to exhibit more ordered structure as compared with a conventional poly(urethane amide)/LiClO₄ SPE. Although the PUA₁ SPE possesses relatively lower fraction of free anion, its relatively ordered structure provides more free-flowing ion conductive paths and thus results in enhanced ionic conductivity. In this study, the self-complementary material incorporated into SPE has the potential for the SPE application. A new concept of SPE preparation exhibiting distinctive properties is proposed.

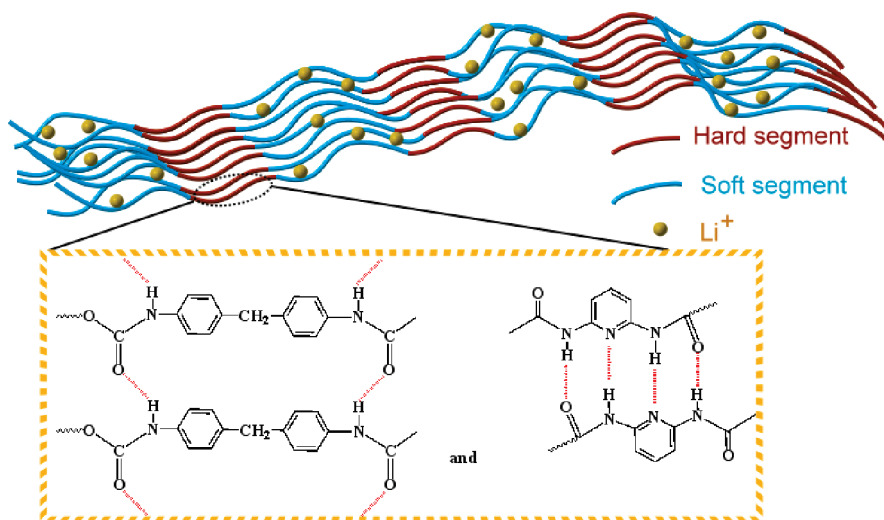


Figure 3. Graphical representation of the structure formed from the self-complementary material.

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Supporting Information Available: All experimental procedures and the NMR spectra, elementary analysis data, GPC data, intrinsic viscosity, DSC curves, two-dimensional IR, and SAXS data concerning the present investigation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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