Helical peptide structure improves conductivity and stability of solid electrolytes

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ABSTRACT

Ion transport is essential to energy storage, cellular signaling, and desalination. Polymers have been explored for decades as solid-state electrolytes by either adding salt to polar polymers or tethering ions to the backbone to create less flammable and more robust systems. New design paradigms are needed to advance the performance of solid polymer electrolytes beyond conventional systems. Here, the role of a helical secondary structure is shown to greatly enhance the conductivity of solvent-free polymer electrolytes using cationic polypeptides with a mobile anion. Longer helices lead to higher conductivity, and random coil peptides show substantially lower conductivity. The macrodipole of the helix increases with peptide length leading to larger dielectric constants. The hydrogen bonding of the helix also imparts thermal and electrochemical stability, while allowing for facile dissolution back to monomer in acid. Peptide polymer electrolytes present a promising platform for the design of next generation ion transporting materials.

Ion transport is central to energy storage[1-5] and signal transduction in cells[6,7]. Polyethylene oxide (PEO) has been used for decades to transport Li and provide safer alternatives to liquid electrolytes[8,9], and most strategies to improve conductivity and stability rely on tuning polymer architecture[10-16]. New concepts are needed to push the performance of solid polymer electrolytes beyond PEO. Bulky, delocalized ionic liquid groups have been tethered to polymer backbones (polymerized ionic liquids, PILs) to understand how ion attachment, dielectric constant, ion type, and segmental dynamics (the α-process) impact conductivity[17,18]. Such approaches show great promise, for example when both ions are attached (zwitterionic PIL) the conductivities of added Li salts is massively enhanced for a given rate of segmental dynamics leading to "superionic" behavior[19] and emphasizing the important role of ionic architecture.

The helix is ubiquitous in biology (e.g. DNA) and leads to unique chemical, physical and mechanical properties[20]. This structure is also of vital importance in drug and gene delivery[21], energy storage[22-25], and antimicrobials[26,27]. Recently, α-helical polypeptides with two redox active groups were developed as anode and cathode materials for electron conduction in all-organic, metal-free secondary batteries. These peptides showed excellent electrochemical stability and on-demand degradability[28], but the role of helical structure was not investigated. While PEO can form a helical structure, this only occurs in the crystalline state where conductivity is low[29]. Peptides, derived from the ring-opening polymerization (ROP) of *N*-carboxyanhydrides (NCAs), are ideal materials for understanding how helical architecture can lead to favorable pathways for ion transport in the molten state and stabilize polymers to external conditions by controlling secondary structure using NCAs with the same chemistry but different chirality (L and D) leading to analogous random coil or helical polypeptides[30]. This approach is distinct from inducing conformational transitions in peptides via pH which leads to changes in the charge of side groups and polarity which can affect ionic conductivity.

Helical polypeptide PILs (PPILs) were designed and synthesized to demonstrate how secondary structure improves the ionic conductivity and stability relative to analogous random coil electrolytes. Three PPILs (**X**-*DP*, where **X** and *DP* denotes the chirality and the degree of polymerization, respectively) were synthesized with the same chemical formula and *DP*, but either helical or random coil (Fig. 1a-d). The as-cast random coil PPIL exhibited a substantially higher glass transition (T_g) but annealing at 473 K disrupts unstable H-bonding and drops T_g. Helical PPILs show higher conductivity than the random coils and no change in conductivity or T_g due to the stability of the helix. The enhanced conductivity of helical PPILs can be further improved by increasing DP due to the persistent direction the helical backbone creating a macrodipole which directs ionic transport, increases the dielectric constant, and leads to substantially higher conductivity than random coils. All PPILs are stable over a 6V window, and can be degraded to the starting amino acid and other well-defined products, reducing the environmental impact of peptide electrolytes. This work demonstrates the key role of secondary structure on ionic conductivity and stability as a new design concept in solid polymer electrolytes.

Polypeptides with different secondary structures

Three polypeptides were synthesized (Supplementary Scheme 1) by the controlled ROP of γ-(3-chloropropanyl)-**x**-glutamate NCA (ClP**X**G-NCA) made from L-, D-, and LD-glutamic acids (**X**Gs). Polypeptides with *DP* = 50 and low dispersity (*Đ* < 1.1) were confirmed by size exclusion chromatography (SEC) and ^{1}H NMR (Supplementary Fig. 1-6). PClP**L**G and PCIP**D**G adopted a right-handed and left-handed helix, respectively, as evidenced by the absorbance peaks of amide I at 1652 cm^{-1} and amide II at 1548 cm^{-1} in Fourier transform infrared spectra (FTIR) and the double minima/maxima at 208 nm and 222 nm via circular dichroism (CD). PCIP**LD**G adopted a random coil conformation based on the shift in the amide I absorption peak at 1661 cm^{-1} and negligible intensity in the CD spectra (Supplementary Fig. 7). Functionalization of the side chains provided the final PPILs (**X**-50s) with ammonium-bis(trifluoromethane)sulfonamide (TFSI) ion pairs, including azidation of the chloro group, copper-catalyzed azide−alkyne cycloaddition (CuAAC) click reaction to incorporate charged groups, and finally ion exchange (Supplementary Table 1). The resulting polymers have tethered ammonium groups and mobile TFSI groups which are responsible for the conductivity. PPILs were freeze-dried and then vacuum dried at 393 K for at least 2 days to remove water, and *DP* was unchanged from the starting peptides (Supplementary Fig. 8-10).

The secondary structures of **L**, **D**, and **LD**-50 PPILs were maintained based on FTIR (Supplementary Fig. 11) and CD spectra in methanol (Fig. 1e, left). Secondary structure differences in the solid state were confirmed by ATR-FTIR, CD and cross polarization magic angle spinning (CP/MAS) solid-state ^{13}C NMR spectroscopy. Films (~100 μm) were hot-pressed at 80 °C, and FTIR spectra show amine I at 1653 cm^{-1} and amine II at 1548 cm^{-1} for **L**-50 and **D**-50 indicating the helix is maintained in the solid state (Fig. 1f). **LD**-50 adopted a random coil conformation (amide I peak at 1661 cm^{-1}). No peak is observed for LD-50 in the CD spectra (Fig. 1e), while mirror peaks appeared between 240 nm to 250 nm for L-50 and D-50 indicating opposite handed helices. The conformation-dependent ^{13}C chemical shift of C$_{\alpha}$ and amide C=O was measured by CP/MAS solid-state

^{13}C NMR[31] (Fig. 1g), and both **L**-50 and **D**-50 have a carbonyl signal at 176 ppm and C_α at 57 ppm corresponding to a helical conformation. These two signals shift downfield by 3 and 4 ppm in **LD**-50, respectively, indicating a random coil conformation.[32] The width of these two peaks was broadened in **LD**-50 corresponding to more heterogeneity in the local environment. Thus, the **L**-50 and **D**-50 are helical while **LD**-50 is a random coil from a combination of FTIR, CD, and NMR. An equimolar mixture of 50% **L-50** + 50% **D**-50 (Supplementary Fig. 12) was prepared as a comparison by physical mixing and dissolution, followed by casting and drying. The only difference in the various PPILs is the secondary structure, and thus its role on ion transport can be elucidated.

Helical structure stabilizes PPILs

The degradation temperatures (T_d) and T_g were measured by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC), respectively (Supplementary Table 2). Helical **L**-50 and **D**-50 showed high T_d = 591 K and 598K, respectively, while **LD**-50 is less stable with T_d = 556 K (Supplementary Fig. 13). The as-cast helical PPILs showed the same T_g (297-298 K) since the direction of the helix does not affect segmental dynamics, while the as-cast random coil PPIL exhibited a higher T_g = 332K (Fig. 2a). The origin of T_g in peptides is attributed to the motion of side chains, as the helix is relatively static[31,33]. After annealing at 473 K, no change occurred in the stable helical peptides, while T_g dropped by 40 K to 292 K in the random coil and became broader (Fig. 2d). No degradation was detected by NMR and FTIR (Supplementary Fig. 14). Helices are formed and stabilized through intramolecular H-bonding between C=O and N–H groups on the same backbone, but random coils do not have regular H-bonding patterns and are less stable (Fig. 2i). Five DSC heating cycles (Supplementary Fig. 15) were used to analyze the stability of **LD**-50, and at 473 K an endotherm is observed only on the first heating and attributed to the disruption and restructuring of H-bonds leading to a T_g drop with subsequent heating cycles. Helical PPILs do not show any additional thermal transitions or shifts in T_g with heating up to 473K. ATR-FTIR spectroscopy of **LD**-50 after annealing (Supplementary Fig. 16) revealed that amide I peak is broadened, but can be reversed to the original state by re-dissolving and then drying, and the changes are not due to thermal degradation which occurs at 513 K. Helical peptides show no change in ATR-FTIR upon annealing. Peptides made via solid phase synthesis would provide key insights into the potential role of short chains on the metastable H-bonding in **LD**-50, as would mixtures of random coil and helical PPILs.

Helical structure promotes ionic conductivity

Electrochemical impedance spectroscopy (EIS) was used to measure ionic conductivity from 298 K to 408 K with all samples measured in triplicate, and errors determined from the standard deviation of Vogel-Fulcher-Tammann (VFT) fit parameters from three independent samples (Supplementary Table 2 and Fig. S17-18). FTIR spectroscopy indicates the stability of both helix and random coil conformations at the measurement temperatures (Fig. 1e, Supplementary Fig. 19). A non-Arrhenius conductivity was observed for all PPILs as expected for ionic polymers. Conductivities are shown in Fig. 2 (Supplementary Fig. 20-22), and as-cast and annealed helical PPILs exhibited higher ionic conductivity at fixed temperature compared to random coils with the same thermal history (Fig. 2b and 2e). To confirm that helical peptides are single ion conductors, a Li conducting analogue was synthesized (Supplementary Scheme 2-3) and the transference number was measured as t^{+}_{ss} = 0.93 ± 0.05 (Supplementary Fig. 23-25).

The T_g-normalized ionic conductivity of as-cast **LD**-50 (Fig. 2c) is higher than that of the helices due to the initially higher T_g of the sample which drops upon annealing due to unstable H-bonding. Annealed helical PPILs (Fig. 2f) are ultimately more conductive at a given temperature, before and after T_g-normalization, and are stable when annealed. This points to the critical role of thermal history when considering peptides for energy applications.

To better understand the conductivity of PPILs, data at T_g + 10 K and above was fit with the VFT equation:

$$\sigma(\mathrm{T}) = \sigma_{\infty}\exp\left(-\frac{DT_0}{T-T_0}\right) \qquad \text{(Eq 1)}$$

where σ_{∞} is the theoretical limiting ionic conductivity at high temperature, D is the strength parameter (describing non-Arrhenius character), and T_0 is the Vogel temperature where the ionic conductivity hypothetically diverges to zero.[34,35] Fit parameters are summarized in Supplementary Table 2. As-cast and annealed **L**-50s and **D**-50s (entries 1-4) indicate conductivity is independent of helical direction, and the helix is stable up to 473 K. Obvious differences between helical and random coil PPILs (entries 1-7) indicate the major role of thermal history on unstable random coil H-bonding (entries 5-6).

Nanoscale morphology of PPILs

Small-angle and wide-angle X-ray scattering (SAXS/WAXS) were used to investigate the morphology of the PPILs (Figure 2g-h). No long-range order was observed (Supplementary Fig. 26), and no peaks associated with the secondary structure are discernable from the amorphous halo. However, FTIR, CD and ^{13}C NMR are sufficient to demonstrate secondary structure is different (Fig. 1). Thermal annealing has no impact on helical L-50 and D-50, but a noticeable effect on LD-50. Based on prior PIL studies[36-

[38], the highest peak (q_1) was assigned as the amorphous halo, the intermediate peak (q_2) reflects ion-ion correlations, and the lowest peak (q_3) corresponds to backbone-backbone correlations. Helical PPILs showed a broad amorphous halo at q_1 ~13.5 nm^{-1}, while LD-50 exhibited a significant shift to q_1 ~13.0 nm^{-1}. As-cast **LD**-50 showed $q_2 = 8.5\ nm^{-1}$, lower than **L**-50 and **D**-50 with $q_2 = 9.4\ nm^{-1}$ indicating the initial H-bonding of **LD**-50 can lead to longer ranger ionic correlations of the TFSI anions, an increase in T_g, and greater decoupling of conductivity from segmental dynamics prior to annealing. Peak q_3 is also lower in as-cast **LD**-50, indicating longer range correlations for ion transport. After annealing, the H-bonding was disrupted and the intensity of q_2 and q_3 peaks in **LD**-50 decreased, corresponding to a decrease in ionic conductivity. The changes in peak intensity are only discussed qualitatively as many factors affect the scattering, but all systems possess the same backbone and ions making qualitative changes meaningful.

Synthesis and characterization of helical PPILs with increasing lengths

The role of the helix on efficient ion transport was further investigated by increasing the length of right-handed PPILs. The hypothesis is that increasing the macrodipole will direct ion transport over longer length scales and increase the dielectric constant. Crown ether catalyzed ROP method allows polypeptides with extremely high molecular weights (MWs)[39]. A helical macroinitiator $PClPLG_{50}\text{-}NH_2$ (Fig. 3a, Supplementary Fig. 27) was synthesized by hexylamine-initiation at 4 °C to maintain the end amine group fidelity. A second ROP in a dichloromethane/phosphate buffer emulsion system ($V_{DCM}/V_{pH=7\ phosphate\ buffer}$= 95%/5%) was then performed with monomer to macroinitiator ratio $[M]_0/[I]_0$ varied from 200 to 950, and the obtained MWs matched the expected MW with $Đ < 1.05$ (Fig. 3b, Supplementary Fig. 28). Post-modification to PPILs (Supplementary Scheme 3) was confirmed by NMR (Supplementary Fig. 29-32). The right-handed α-helix was intact after functionalization based on ATR-FTIR and CD spectra (Supplementary Fig. 33). Five helical polymers (Fig. 3c, **L**-50, **L**-233, **L**-498, **L**-768, **L**-925) showed similar $T_{d,\,5\%}$ and T_g increased modestly from 297 K to 304 K with increasing MW (Supplementary Fig. 34-35).

Longer helices promote higher conductivity

In contrast to random coil PILs[36,40-43], the ionic conductivity of helical PPILs increased with increasing of DP (Fig. 3d-e, Supplementary Fig. 36-39, Supplementary Table 1-3) despite a 5 K T_g increase relative to **L**-50. The T_g -normalized ionic conductivity of the longest **L**-925 was 5 to 50 times higher than **L**-50 going from 0.75 to 1.0 T_g/T (Fig. 3f). **L**-925 was ultimately 65 times more conductive than **LD**-50 illustrating the combined effect of secondary structure and peptide length, where longer helices more efficiently transport ions along the backbone. The longest helix exceeds 10^{-3} S/cm at high temperature which is comparable to salt-in-polymer systems[43], despite being a single ion conductor. Future approaches to reduce T_g through copolymerization or achieve synergistic effects of sequence[44] can increase the room temperature conductivity.

The helix macrodipole increases with DP[45], which increases the dielectrics constant beyond prior PILs[46] to create a more favorable environment for ion solvation and conduction (Fig. 4a,b). Helices oriented in the direction of the field will show enhanced transport while those perpendicular to the field will show no effect. The persistence length (l_p) of α-helical peptides is substantially higher than that of random coil polymers in solution, for example α-helical poly-L-lysine has l_p ~15-20 nm compared to random coil polymers which are ~ 1 nm or less[47]. Separate simulations indicate l_p of helical peptides around 100 nm[48]. The l_p for poly(γ-benzyl-l-glutamate) (PBLG) in the melt was reported as 1-2 nm through dielectric analysis of the dipole moment of the helix, but was not compared to an analogous random coil[49]. Charge, solvent and side chain will dictate the precise value of l_p in helical PILs, but it is still expected to be higher than for an analogous random coil. Even with defects or bending along a helical backbone, the macrodipole will still increase the dielectric constant and direct transport in a more efficient manner. Techniques such as neutron scattering will be critical to probe solid state l_p or correlation lengths of PPILs.

The five **L**-*DP* materials have identical chemical formula, charge and secondary structure, thus the increased ionic conductivity is due to 1) the presence of a helix and 2) increasing the helix length. The **LD**-50 has a similar conductivity to prior random coil ammonium PILs of various *DP* (Figure 4c)[40,50]. SAXS/WAXS measurements (Figure 4d, Supplementary Fig. 40) show an invariance in the amorphous halo (q_1, ~13.5 nm^{-1}), while the intensity and *d*-spacing of q_2 increased with increasing *DP* as the ions are correlated over longer length scales leading to enhanced scattering and higher conductivity.

Liquid Crystallinity at PPIL surfaces

Helical peptides can form liquid crystalline (LC) phases which would impact conductivity. Polarized optical microscopy (POM) and grazing incidence X-ray scattering (GISAXS and GIWAXS) were performed, and POM showed no LC order for the random coils or the shortest L-50 helical sample (Fig. 6a). Longer helices show LC textures and for **L**-233 and **L**-498, a non-reversible transition to isotropic is observed above 120 °C (Supplementary Fig. 41-42) indicating the order is induced by hot-pressing. **L**-768 and **L**-925 show stable LC texture up to 150 °C supporting the picture of rigid helices that persist and drive LC assembly. GISAXS shows a scattering peak at ~ $q = 0.2\ \text{nm}^{-1}$ for L-233 to

L-925, but not L-50 or LD-50 consistent with POM (Fig. 6b, Supplementary Fig. 43-44). WAXS and GIWAXS show no discernable differences (Supplementary Fig. 45) and indicate no crystallinity. Calorimetry reveals no LC transition in any of the samples, indicating that order is present only at the surface of the films which are transparent (Fig 1a). Future work optimizing LC orientation will lead to further enhancements in the ionic conductivity along the helix direction.

On-demand Degradation of PPILs

Polymers are difficult to degrade, but PPILs possess amide and ester bonds which are acid, base and enzyme-degradable. In 6 M HCl at 110 °C, PPILs completely degraded after 1 day to four degradation products detected by liquid chromatography–mass spectrometry (LC-MS, Fig. 5) and ^{1}H NMR (Supplementary Fig. 46-49), including protonated hexylamine and glutamic acid from the side chains. Future work will investigate milder pathways, including enzyme degradation. All samples are stable over a 6 V window (Supplementary Fig. 50-51).

Helical ionic peptides are a powerful new platform for solid electrolytes with improved conductivity and stability. The helices resist conformational changes up to 200 °C, allowing for higher conductivity than unstable random coil analogues, and are stable over a 6V window. Conductivity can be further enhanced by increasing the helix length which increases the macrodipole, dielectric constant, and ion-ion correlations. PPILs are readily degraded in acid for recyclability. The PPIL approach is readily generalizable to other ion pairs and functional groups via click chemistry. This work not only paves the way for future mechanistic studies but also the design of next-generation stable, recyclable, and high-performance electrolytes.

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Author Contributions C.M.E conceived of using the helix to enhance conductivity, and Y.C and T. X conceived of the polymer electrolyte design and synthesis. Solid ^{13}C NMR was conducted by S.J. Dielectric spectroscopy was conducted by C.C. Y.C. and C.M.E. wrote the manuscript with contributions from all authors. All authors discussed the results and commented on the manuscript.

Competing Interests

The authors declare no competing interests.

Figure Legends/Captions

Figure 1. Synthesis and confirmation of helix in the solid state. (a) Schematic illustration of coin cell assembly and image of a transparent PPIL hot-pressed film. Illustration of the secondary structure and chemical structure of PPILs (**X**-50s, **X** denotes the chirality of amino acids): (b) **L**-50 adopted right-handed α-helical conformation; (c) **D**-50 exhibited left-handed helical conformation and (d) **LD**-50 displayed random coil conformation. (e) CD spectra of **X**-50s in solution (0.5 mg/mL in methanol) and solid films. (f) ATR-FTIR spectra of **X**-50s at different temperatures with equilibration times of 10 min. (f) (g) CP-MAS ^{13}C NMR spectra of **X**-50s. Different color curves correspond to **L**-50 (orange), **D**-50 (green) and **LD**-50 (purple).

Figure 2. Temperature and thermal history effects on conductivity and stability. (a) Second heat cycle DSC curves of as-cast **X**-50s under N_2 flow from -60 to 150 °C at a heating and cooling rate of 10 °C/min. Ionic conductivities of as-cast **X**-50s (b) as a function of temperature and (c) as a function of T_g/T. (d) Second heat cycle DSC curves of 473 K-annealed **X**-50s. Ionic conductivities of 473 K-annealed **X**-50s (e) as a function of temperature and (f) as a function of T_g/T. (g) WAXS profiles of as-cast (bottom, solid lines) and 473 K-annealed (upper, dashed lines) **X**-50s. (h) 2D WAXS patterns of as-cast and 473 K-annealed **L**-50 and **LD**-50. (i) Schematic showing a proposed mechanism for hydrogen bonding stability during thermal processing.

Figure 3. Role of increasing helix length on increased conductivity. (a) Construction of polypeptide backbones with higher helical length using 2-step: hexylamine-initiated ROP to synthesize the α-helical macroinitiator PCIPLG$_{50}$-NH$_2$, followed by a second ROP in a dichloromethane/phosphate buffer emulsion ($V_{DCM}/V_{pH=7\ phosphate\ buffer}$= 95%/5%) with different feeding ratios $[M]_0/[I]_0$. (b) Comparison of the expected MWs, obtained MWs and *Đ* of polypeptide backbone PCIP**L**G-(50+m) initiated by PCIPLG$_{50}$-NH$_2$. (c) Schematic representation of the growth of helical length with increasing DP. Ionic conductivities of **L**-DPs as a function of (d) temperature and (e) T_g/T. Solid curves are VFT fits. (f) Enhancement of conductivity due to the helix as various temperatures above (left) and equal to (right) T_g. Data are means ± s.d., n = 3 independently prepared replicates. The effect grows from an order of magnitude to a factor of 65 at lower temperatures.

Figure 4. **Longer helices increase macrodipole, dielectric constant, and conductivity.** (a) Scheme showing the macrodipole of a helix. (b) The dielectric spectra ε' of L-DPs at 243 K. (c) Comparison of the T_g-normalized ionic conductivity of the helical and random coil PPILs (**L**-925 and **LD**-50), as well as previously studied random coil PILs with similar ion pairs from Zhao et al.[50] (green) and Fan et al.[40] (blue). (d) Normalized WAXS profiles of **L**-DPs.

Figure 5. Acid degradation of PPILs. Degradation analysis of PPILs using LC-MS (positive ESI). (a) Trace map and (b) chemical structures for observed products.

Figure 6. Liquid crystallinity at PPIL surfaces. (a) POM images of precursor PClPLG and **X**-DP hot-pressed films. (b) GISAXS profiles of L-DPs and LD-50 hot-pressed films at angle of incidence 0.15°.

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Methods

All detailed experimental procedures and characterization of compounds can be found in the Supplementary Information.

Data availability

The authors declare that all data supporting the findings of this study are available within the paper and Supplementary Information files. The raw numbers for charts and graphs are available in the provided Source Data file whenever possible. Additional images are available from the corresponding authors upon reasonable request. Source data are provided with this paper.