

**Development and Characterization of Advanced Polymer Electrolytes for Energy
Storage and Conversion**

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Development and Characterization of Advanced Polymer Electrolytes for Energy Storage and Conversion

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ABSTRACT (Academic)

Among the myriad energy storage technologies, polymer electrolytes have been widely employed in diverse applications such as fuel cell membranes, battery separators, mechanical actuators, reverse-osmosis membranes and solar cells. The polymer electrolytes used for these applications usually require a combination of properties, including anisotropic orientation, tunable modulus, high ionic conductivity, light weight, high thermal stability and low cost. These critical properties have motivated researchers to find next-generation polymer electrolytes, for example ion gels.

This dissertation aims to develop and characterize a new class of ion gel electrolytes based on ionic liquids and a rigid-rod polyelectrolyte. The rigid-rod polyelectrolyte poly(2,2'-disulfonyl-4,4'-benzidine terephthalamide) (PBDT) is a water-miscible system and forms a liquid crystal phase above a critical concentration. The diverse properties and broad applications of this rigid-rod polyelectrolyte may originate from the double helical conformation of PBDT molecular chains.

We primarily develop an ionic liquid-based polymer gel electrolyte that possesses the following exceptional combination of properties: transport anisotropy up to $3.5\times$, high ionic conductivity (up to 8 mS cm^{-1}), widely tunable modulus ($0.03 - 3\text{ GPa}$) and high thermal stability (up to 300°C). This unique platform that combines ionic liquid and polyelectrolyte is essential to develop more advanced materials for broader applications.

After we obtain the ion gels, we then mainly focus on modifying and then applying them in Li-metal batteries. As a next generation of Li batteries, the Li-metal battery offers higher energy capacity compared to the current Li-ion battery, thus satisfying our requirements in developing longer-lasting batteries for portable devices and even electric vehicles. However, Li dendrite growth on the Li metal anode has limited the practical application of Li-metal batteries. This unexpected Li dendrite growth can be suppressed by developing polymer separators with high modulus ($\sim$ GPa), while maintaining enough ionic conductivity ($\sim$ 1 mS/cm). Here, we describe an advanced solid-state electrolyte based on a sulfonated aramid rigid-rod polymer, an ionic liquid (IL), and a lithium salt, showing promise to make a breakthrough. This unique fabrication platform can be a milestone in discovering next-generation electrolyte materials.

ABSTRACT (Public)

Among the myriad energy storage technologies, polymer-based electrolytes have been widely employed in diverse applications such as fuel cell membranes, battery electrolytes, “artificial muscle” mechanical actuators, reverse-osmosis membranes and solar cells. The materials used for each of these applications usually require a specific combination of properties, which include anisotropic orientation, tunable mechanical stiffness (modulus), high ionic conductivity, light weight, high thermal stability and low cost. These critical properties have motivated researchers to find next-generation polymer-based electrolytes, for example “ion gels” that consist of a polymer combined with ionic liquids or salts.

This thesis describes development of an ion gel that possesses the following exceptional combination of properties: high ionic conductivity (up to 8 mS cm^{-1}), widely tunable modulus ($0.03 - 3 \text{ GPa}$), ion transport anisotropy up to $3.5\times$, and high thermal stability (up to 300°C). Thus, this unprecedented material shows liquid-like ion motions inside a matrix with solid-like stiffness, and in a material that can withstand extreme temperatures and will not burn.

After obtaining these ion gels, we are then mainly focusing on modifying them for application in safe and high density Li-metal batteries. As a next generation of Li batteries, the Li-metal battery offers higher energy capacity compared to the current Li-ion battery, thus satisfying our requirements in developing longer-lasting batteries for portable devices and even electric vehicles. However, Li dendrite growth on the Li metal anode has limited the practical application of Li-metal batteries. This unexpected Li dendrite growth can be suppressed by developing polymer electrolytes with high modulus

(~ GPa), while maintaining sufficient ionic conductivity (~ 1 mS/cm) for efficient battery operation.

In short, this thesis describes an advanced solid-state electrolyte based on a kevlar-like (sulfonated aramid) rigid-rod polymer, an ionic liquid (IL), and a lithium salt, showing promise to make a breakthrough and enable practical Li-metal batteries. Furthermore, the unique fabrication platform for these ion gels represents a new paradigm for discovering next-generation electrolyte materials for a wide variety of applications.

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Chapter 6: Ionid Liquid Based Polymer Electrolytes with Tunable Modulus for Long-lasting and Dendrite-free Li-metal Battery

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Chapter 1

Overview of Polymer Electrolytes and Ion Gels

1.1 Motivation and Research Goals

Over the previous few decades, ion-containing polymers have received a great deal of attention for diverse applications including fuel cell membranes,^[1-3] electro-responsive materials,^[4] ion battery electrolytes,^[5] artificial muscles,^[4] gas separation membranes^[6] and solar cells.^[7] As important sources of fuel cell membranes, ion-containing polymers, such as Nafion[®],^[8] sulfonated aromatic polymers,^[9] and sulfonated block copolymers,^[9] are usually composed of fluorinated or aromatic backbones with sulfonic acid pendant groups. Nafion[®] is the benchmark material used for polymer electrolyte membranes in fuel cells, and it possesses high ionic conductivity as well as excellent mechanical, thermal, and chemical properties.^[10] However, Nafion requires significant water swelling to deliver high conductivity. This water content is unstable at temperatures above $\sim 80^{\circ}\text{C}$, and water is incompatible with many electrochemical devices, such as rechargeable Li-ion or Li-metal batteries. In general, development of polymeric materials for various electrochemical devices should target low cost, high thermal stability, tunable modulus, adjustable chemical stability, the ability to macroscopically align the material for directional properties, and high ionic mobility. These are still substantial challenges for current polymer-based electrolyte materials.^[11,12] Also, different device applications have their own special challenges and requirements. The goal of this project is to develop advanced polymer electrolytes possessing a combination of properties mentioned above so as to suit specific applications.

Ionic liquids (ILs) are room temperature molten salts with unique properties including low vapor pressure, high thermal stability, wide electrochemical window, and high ionic conductivity.^[13] Numerous studies have shown that ILs can be fruitfully combined with polymeric systems to produce fast ion conduction and material stability in electrochemical devices such as mechanical actuators,^[14,15] fuel cell membranes^[16] and battery separators.^[17] The combination of ionic liquids with polymers promises to allow greater freedom of design and enhanced properties for polymer-based materials, thus enabling wider and more efficient applications.

Recently, in order to combine properties of ILs and polymers, researchers have developed “ion gels” as promising candidates for applications including fuel cell membranes, battery separators, and artificial muscles.^[11,18-20] Ion gels are polymeric networks swollen with a large volume fraction of ILs. As a perfect combination of traditional solid-state and liquid-state electrolytes, ion gels exhibit high ionic mobility, excellent thermal stability, mechanical integrity, and conformable electrode-electrolyte contact.^[11] By elaborate design and construction of polymeric networks, ion gels can not only ensure high ionic conductivity, but also offer the opportunity to control pathways for ion transport.^[11,17]

In order to achieve oriented conducting pathways in polymer electrolytes, researchers have used mechanical stretching (drawing),^[1,21] solution casting schemes,^[22] and magnetic or electric fields^[23,24] on various systems such as nanophase-separated polymers,^[24] liquid crystal (LC) polymers^[21] and block copolymers.^[22] For example, Nafion[®] membrane, after mechanical stretching along the in-plane direction, exhibits

elevated diffusion rate of absorbed water along the stretch direction.^[1] However, electrolyte membranes with faster diffusion rate along the desired through-plane direction are rarely reported.^[11,25,26] To provide ease of material alignment in polymer electrolyte composites, the liquid crystal phase has been widely employed as an assembly template. Rigid-rod polyelectrolytes possessing an anisotropic LC phase form the basis of a variety of natural biopolymers such as DNA,^[27] polypeptides,^[28] tobacco mosaic virus,^[29] and cationic liposomes,^[29] and also comprise a range of synthetic ion functionalized polymers.^[17,30] Furthermore, LC phases can display monodomain alignment when placed in a magnetic field (B_0). Such magnetically aligned LC phases can thus be employed as assembly templates for developing long range ordered structures. In order to promote the delivery of mobile counterions, such as Na^+ , Li^+ , or IL ions, in LC systems, one can add a high density of charged side groups along a rigid LC polymer backbone.^[30] Understanding ion transport, phase behavior, and self-assembled morphology in rigid-rod polyelectrolytes will not only enhance the fundamental understanding of self-assembly, but also provide opportunities to discover next-generation electrolyte materials with wider practical applications.

In this dissertation, we mainly explore a synthetic sulfonated aramid polyanion, poly (2,2'-disulfonyl-4,4'-benzidine terephthalamide) (PBDT), shown in **Figure 1.1**. Above a critical concentration C^* , this water-miscible system forms a lyotropic nematic LC phase and has a high ion density along the polymer backbone.^[30] PBDT is a rigid rod polyamide with multicomponent molecular interactions, including π - π interactions of the rigid aromatic rings, intermolecular H-bonding of the amide groups, and electrostatic interactions of the ionogenic sulfonate groups, all of which contribute to the anisotropic

interactions underlying the aligned rigid rod structure in aqueous solution.^[30] In a uniform B_0 , this lyotropic LC phase reorganizes from a randomly distributed polydomain nematic to a monodomain nematic with the alignment axis (director) parallel to B_0 .^[30] By investigating molecular conformation and crystalline packing in the aqueous solutions, we seek to understand how the anisotropic morphology of PBDT relates to the transport of the mobile species in the aqueous solutions, for example Na^+ counterions and H_2O molecules.

By combining the PBDT aqueous solutions (highly oriented template) with specified ionic liquids (shown in **Figure 1.1**) in an external magnetic field B_0 , we create a series of ion gels that provides an unprecedented combination of properties that can be tailored to a variety of electrochemical devices.^[17] We investigate properties of the newly developed ion gels, such as multi-scale morphology, diffusion rate, ionic conductivity, and thermal and mechanical stabilities by applying a variety of characterization methods. Additionally, we hope to extend this new platform to generate more advanced polymer electrolytes with a comprehensive array of tunable properties for practical applications such as battery electrolytes, fuel cell membranes, mechanical actuators and optical sensors.

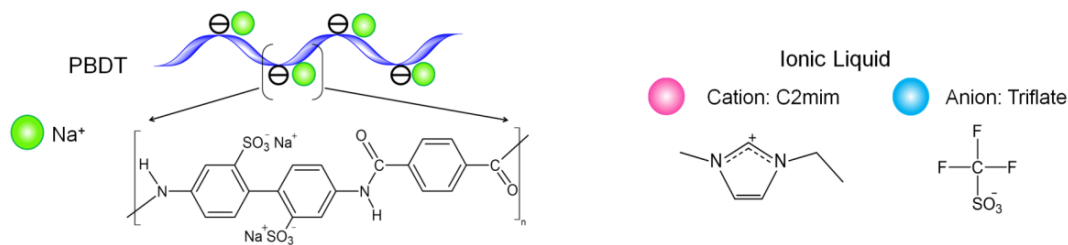


Figure 1.1. The chemical structure of PBDT and C2mimTfO. The chemical structure at left is poly (2,2'-disulfonyl-4,4'-benzidine terephthalamide) (PBDT), a rigid rod liquid

crystalline polyelectrolyte. The IL shown at right contains the cation 1-ethyl-3-methyl imidazolium $[\text{C}_2\text{mim}]^+$ and the anion trifluoromethanesulfonate $[\text{TfO}]^-$. These two materials can be combined to form an ion gel with a surprising combination of properties that include high ionic conductivity, high modulus, and high thermal stability.

1.2 Rigid-rod Polyelectrolytes

Rigid-rod polyelectrolytes are charged polymers with rod-like chain conformation, which usually possesses the properties of not only liquid crystal polymers, but also polyelectrolytes.^[31] Here, I will briefly and separately introduce the concepts associated with liquid crystal polymers and polyelectrolytes.

1.2.1 Liquid Crystal Polymers

A liquid crystal (LC) is a fourth state of matter, besides the three common states: gas, liquid, and solid.^[32,33] The first liquid crystalline macromolecular system was discovered by Bawden (1937) in tobacco mosaic virus.^[33,34] Then, Onsager (1949), Flory (1956) and co-workers proposed different rigid-rod models for LC polymer (LCP) materials.^[33,34]

In terms of orientation and assembly, LCs can be classified into three categories, nematic, smectic and cholesteric, as shown in **Figure 1.2a, b, and c**, respectively.^[34] The most common LC phase is nematic, where the long axes of the rigid-rod molecules lie parallel to what is known as the phase *director*. The smectic phase possesses two-dimensional ordering, where the molecular interactions among the neighboring mesogenic groups contribute to the alignment in not only the main director of the phase but also in the perpendicular direction. The resulting layers can slide over one another.^[33]

A cholesteric liquid crystal exhibits a chiral LC phase with a helical director structure. Alignment is achieved in each layer, and the director of each layer is varying with periodic tilt angles. The half periodic pitch length $p/2$, shown in Figure 3c, corresponds to the thickness of the layers with a 180° variation of the director. Hydroxypropyl cellulose and cholesteryl benzoate are examples of the cholesteric liquid crystal phase.^[33]

In the mid-1960s, DuPont® initially developed the LCP “Kevlar” (poly paraphenylene terephthalamide), shown in **Figure 1.3**, which possesses extremely strong and stiff mechanical properties. Meanwhile, Twaron, another commercialized fiber product developed by Teijin® and Akzo Nobel®, shares a similar aramid structure and the excellent mechanical properties of Kevlar. Following such aramids, a series of polyesters were generated that also showed liquid crystalline properties.^[35-39]

Furthermore, LCPs can be classified into lyotropic liquid crystal^[40,41] and thermotropic liquid crystal^[37] according to the forming condition of the LC phases.^[34] The two forming conditions are dissolution and fusion, respectively. Lyotropic liquid crystal polymers usually display LC phases after being dissolved in a certain solvent above a critical concentration. These LCPs possess higher melting temperature as compared to the decomposition temperature, for example, poly(p-phenylene terephthalamide) (PPTA) and PBDT.^[34] However, thermotropic liquid crystal polymers exhibit LC phases after being melted above the polymer melting temperature. The majority of LCPs are thermotropic polyesters.^[34,36-39] LCPs are widely employed to form polymeric fibers with excellent modulus and mechanical strength, because of some unique properties, including low processing viscosity and high orientational order.^[34] In

our proposal, PBDT aqueous solution also displays a lyotropic LC phase above a critical concentration (≈ 1.8 wt%). We will describe the significance of this by employing the LC phase of PBDT to form a long range ordered template. This LCP template promises to enable new functional materials with elaborate construction of the polymeric network. For example, we will introduce a new PBDT ion gel in Chapter 5.

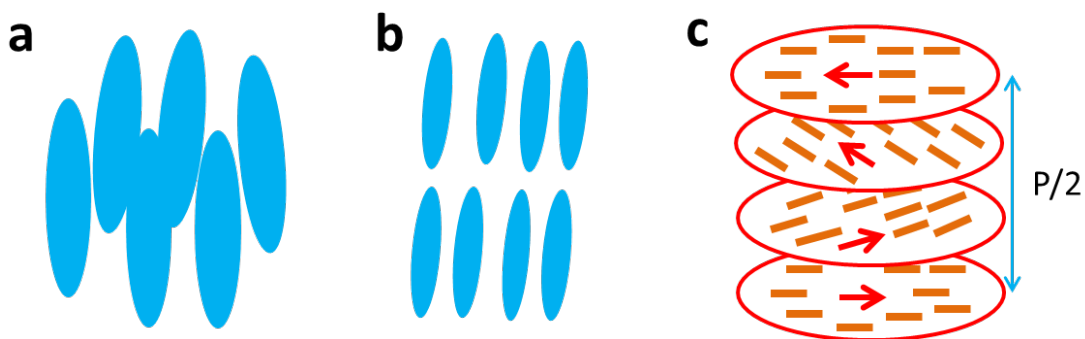


Figure 1.2. Three different liquid crystal phases. (a) Nematic (b) Smectic (c) Cholesteric.

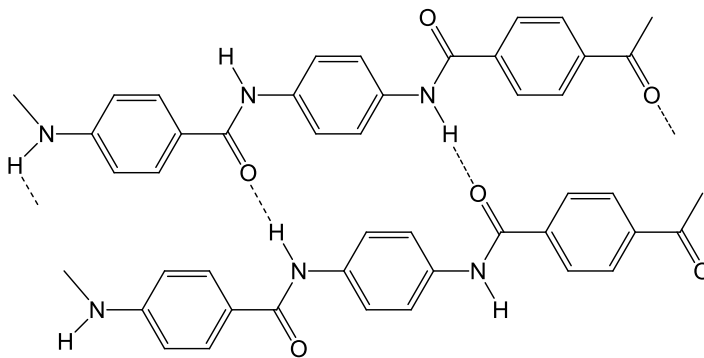


Figure 1.3. The chemical structure of poly(paraphenylene terephthalamide), also known as Kevlar or Twaron.

Some primary methods to characterize orientational order in LCPs include polarized optical microscopy (POM), dynamic scanning calorimetry (DSC), X-ray scattering, and

nuclear magnetic resonance (NMR). These methods will be introduced in detail in Chapter 2, with POM in Section 2.1, ^1H , ^2H , ^{23}Na NMR and pulsed-field-gradient (PFG) NMR diffusometry in Sections 2.2 and 2.3, and X-ray scattering techniques in Section 2.4. By investigating the fundamental properties of LC phases, we can gain a comprehensive understanding of these systems and make better use of the self-assembly templates made available by the use of rigid-rod polymers.

1.2.2 Polyelectrolytes

Polyelectrolytes, including polycations and polyanions, are polymers containing ionogenic groups in the chemical repeat units.^[31] Polyanions usually contain acid groups such as $-\text{COOH}$, $-\text{SO}_3\text{H}$, or $-\text{PO}_3\text{H}_2$, while polycations contain ionogenic groups that include $-\text{N}^+\text{R}_3$, pyridinium, imidazolium. Polyelectrolyte solutions have been widely investigated because of their abnormal properties, such as nonlinear flow dynamics, osmotic pressure, counterion condensation and unusual self-assembled molecular conformations. These properties are highly correlated with concentration, solvents, added salts and temperature in the polyelectrolyte solutions.^[31] In terms of application, polyelectrolytes are widely used in viscosity modifiers (e.g., thickeners), emulsifiers, conditioners, water purifiers, and clarifying agents. In addition, some water-soluble and biocompatible polyelectrolytes are promising candidates for implant coating and site specific drug release.^[31,42-44]

As we are familiar, polymer conformations are strongly correlated with morphology and the resulting properties of polymeric materials. Similarly, the association behaviors of the counterions in polyelectrolyte solutions are also influenced by the molecular

conformations of polyelectrolytes. Two analytical theories, Manning counterion condensation theory^[45-48] and the Poisson-Boltzmann equation,^[49] have been developed to describe the distribution of counterions in dilute solutions of polyelectrolytes. To illustrate counterion condensation behaviors, the two theories similarly propose an ideal model that describes a rigid-rod polyelectrolyte with equally spaced charges that smear out continuously along the polymer chain. The charge parameter can be expressed as

$$\xi = \frac{\sigma^2 \alpha}{4\pi\epsilon_0\epsilon_r kTl} \quad (1.1)$$

where σ is the charge value and α is the number of ionogenic sites per chemical repeat unit, ϵ_0 and ϵ_r are absolute and relative dielectric constants, l is the length of the chemical repeat unit, and k is the Boltzmann constant.^[47]

According to the counterion condensation theory by Manning et al,^[47] in dilute polyelectrolyte solutions, the counterions tend to tightly associate with the ionogenic groups of the polymer when the charge parameter ξ of the polyelectrolyte molecular chain is > 1 . Following this, the fraction of neutralized groups along the polymer chain is $1 - \xi^{-1}$. For example, if the ξ of double-helical DNA in water at 25°C is 4.2, then the neutralized fraction is 0.76.^[27]

The Poisson-Boltzmann equation alternately describes the concentration of counterions surrounding rigid-rod polymer chains. The counterion concentration will radially decay with increasing distance away from the surface of rigid-rod polymer chains. In addition, the fraction of associated counterions is closely correlated with the salt concentration in polyelectrolyte solutions.^[27]

From an experimental angle, by using ^{23}Na NMR diffusometry, we investigate diffusion coefficients of Na^+ counterions in PBDT aqueous solutions with varying polymer weight percentage, as introduced in Chapter 3. According to the calculated results from the above theories, we can get a preliminary understanding of transport and association behaviors of the Na^+ counterions in PBDT aqueous solutions. Meanwhile, we also propose a simple lattice model to mimic the conformation and morphology in PBDT aqueous solutions in Chapter 3 and 4.

1.3 Room Temperature Ionic Liquids

Room temperature ionic liquids (RTIL) are molten salts with unique and adjustable properties that usually include low vapor pressure, high thermal stability, wide electrochemical window, and high ionic conductivity at room temperature.^[13] The formation mechanism of an IL is illustrated in **Figure 1.4**. For ionic solids, symmetric cations and anions form highly ordered crystalline structure, e.g., NaCl. However, by incorporating asymmetric and/or bulky (low charge density) cations or anions, the crystalline structure is disrupted, giving rise to a lower order liquid state.^[13] Ionic liquids are outstanding solvents for many polymers, such as cellulose.^[50] Some common cations and anions used to form ionic liquids are separately shown in **Figure 1.5** and **Figure 1.6**.^[13]

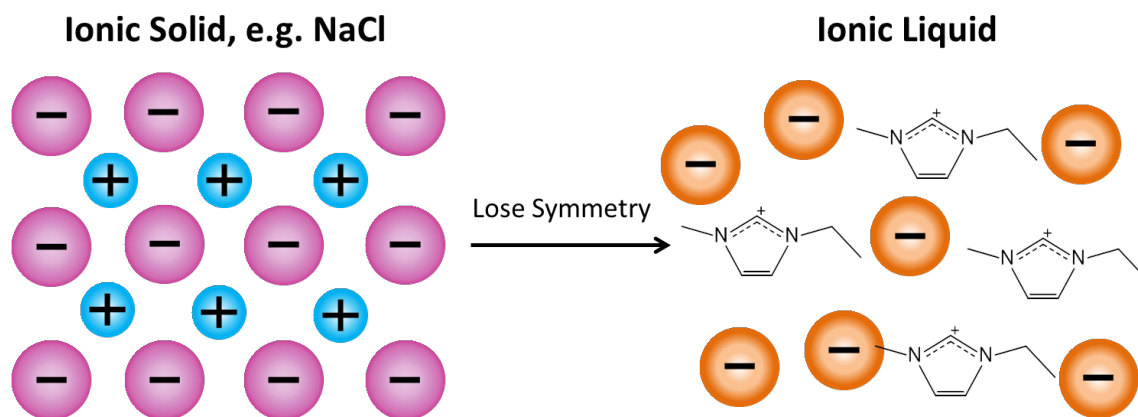


Figure 1.4. From ionic solid to ionic liquid. The structure at left shows the crystalline packing of ionic solids, for example, NaCl. After replacing the cations in ionic solids with asymmetric cations, we obtain the lower order ionic liquid shown at right.

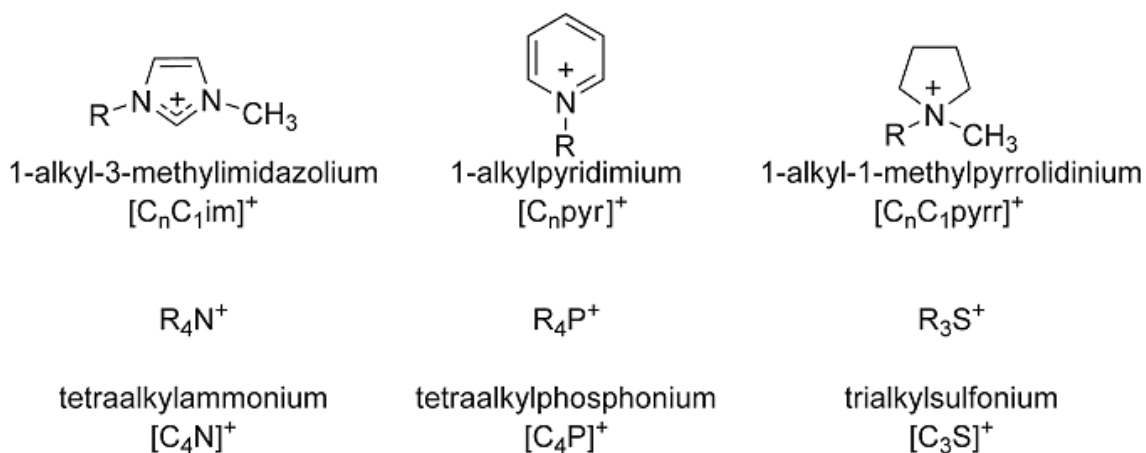


Figure 1.5. Common cations found in ionic liquids. Figure reproduced from ref. 13.

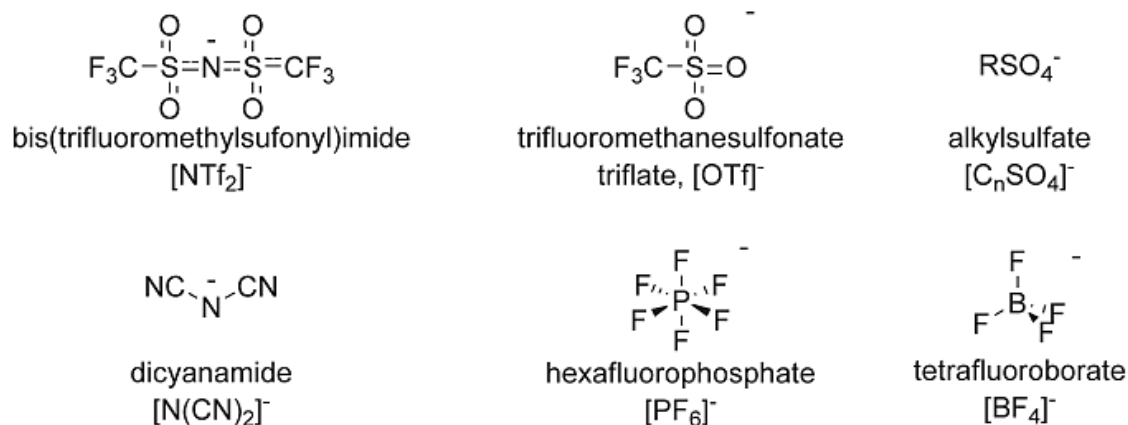


Figure 1.6. Common anions found in ionic liquids. Figure reproduced from ref. 13.

Ionic liquids enable a wide array of applications such as processing technology, functional fluids, synthetic catalysts and electrochemical devices.^[50] ILs can modify and improve the surface of different substrates, thus contributing to tunable interfacial properties such as wettability, lubrication, separation efficiency and electrochemical responses. ILs can form an ultrathin film on various substrates, thus enabling associated applications in synthetic catalysts and surface modifications. Furthermore, ILs can exhibit preferred arrangement, surface wettability, and unique layer growth behavior on specific substrates, based on electrostatic interactions between solid surfaces and ILs, as shown in **Figure 1.7**. Supported ILs (SILs) obtained by coating ILs on various particle substrates have received a great deal of attention.^[51] This modification process offers an opportunity to transfer desired properties of ILs to the particles, thus contributing to a wide array of applications, such as catalytic reactions, surface modification, separation technologies and electrochemical devices.^[51]

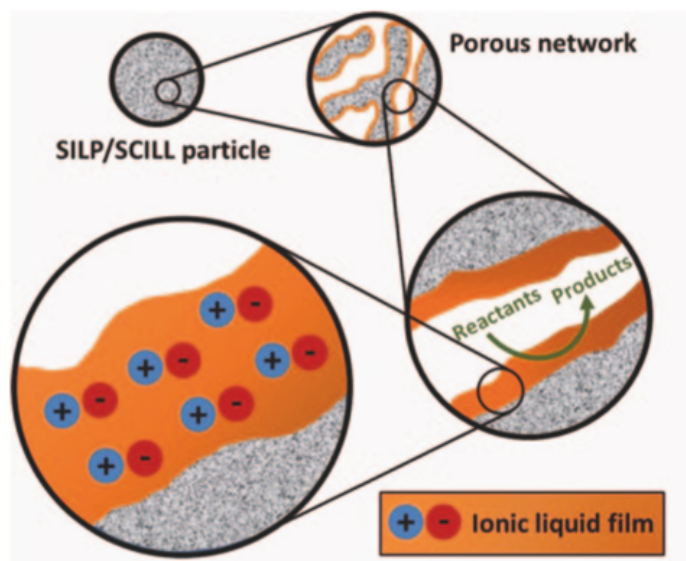


Figure 1.7. The ultrathin IL film formed on porous substrate and the corresponding application in a catalyst. The grey parts represent the inorganic particles, serving as the substrates. The porous network surface can act as the interfacial platform for various reactions. Figure reproduced from ref. 51.

As a unique platform for designing ion gel materials, the combination of ionic liquids and polymeric networks provide more possibilities in creating advanced materials. Thus, it is significant for us to gain more fundamental understanding of interactions between ILs and polymeric networks as well as some physical properties of ILs. Herein, I briefly introduce the interaction between ILs and some solid surfaces from two aspects: (1) The surface tension,^[52] and (2) the contact angle.^[53]

Surface tension (γ) measures the surface cohesive energy in liquids. Surface tension arises from various molecular interactions, including columbic forces, H-bonding and Van der Waals forces. It is believed that H-bonding is an important interaction in ionic liquids. The surface tension values of ILs are usually higher than those of conventional

organic solvents, such as methanol (22.07 mN m⁻¹) and acetone (23.5 mN m⁻¹), but lower than that of water (71.98 mN m⁻¹). **Table 1** presents surface tension values for various ILs at different temperatures.^[52] Both cation and anion can be carefully selected to tune the properties of the IL.^[52] The anion can be used to control the water miscibility, whereas the cation can be used to modify hydrophobicity and H-bonding in ILs. ILs are generally considered to be highly polar and yet can vary from moderately to strongly hydrophilic in solvent quality. In addition, both cation and anion affect surface tension of ILs.^[52] For the imidazolium family of ILs, the surface tension decreases with increasing alkyl chain length. However, in organic solvents, the surface tension is enhanced with increasing molecular size because of increased Van der Waals forces. The explanation for these contradictory phenomena between ILs and organic solvents is that although the increase in size of molecule leads to increasing Van der Waals forces, it contributes to a dispersion of charged ions and a diminution of H-bonding interactions. Here, I rank ILs having different anions according to the strength of H-bonding interactions and the associated surface tensions. An increase in the size of anion leads to a decrease in the surface tension, shown as the following sequence: $\gamma[\text{BF}_4] > \gamma[\text{PF}_6] > \gamma[\text{CF}_3\text{SO}_3] > \gamma[\text{Tf}_2\text{N}]$. The larger anion leads to a more delocalized charge as well as decreased capability to form H-bonding. The surface tension will thus be diminished because of the weakened H-bonding.^[52]

Table 1. The surface tension (γ) values of different ILs at varying temperature. Table reproduced from ref. 52.

[bmim][BF ₄]		[bmim][PF ₆]		[bmim][Tf ₂ N]		[bmim][CF ₃ SO ₃]	
T (K)	$\gamma \pm \sigma^a$ (mN m ⁻¹)	T (K)	$\gamma \pm \sigma^a$ (mN m ⁻¹)	T (K)	$\gamma \pm \sigma^a$ (mN m ⁻¹)	T (K)	$\gamma \pm \sigma^a$ (mN m ⁻¹)
293.15	44.81 $\pm$ 0.02	293.15	44.10 $\pm$ 0.02	293.15	33.60 $\pm$ 0.01	293.20	35.52 $\pm$ 0.03
303.15	44.18 $\pm$ 0.02	303.15	43.52 $\pm$ 0.04	303.15	33.09 $\pm$ 0.02	303.20	35.05 $\pm$ 0.03
312.65	43.58 $\pm$ 0.02	313.15	42.90 $\pm$ 0.03	313.15	32.50 $\pm$ 0.01	313.20	34.62 $\pm$ 0.02
322.15	42.90 $\pm$ 0.02	323.15	42.21 $\pm$ 0.03	323.15	31.92 $\pm$ 0.01	323.20	34.19 $\pm$ 0.02
331.45	42.27 $\pm$ 0.03	333.15	41.53 $\pm$ 0.03	333.15	31.35 $\pm$ 0.02	333.20	33.71 $\pm$ 0.02
341.35	41.64 $\pm$ 0.02	343.15	41.07 $\pm$ 0.01	343.15	30.90 $\pm$ 0.02	343.20	33.30 $\pm$ 0.03
[omim][PF ₆]		[bmmim][PF ₆]		[omim][BF ₄]		[hmim][PF ₆]	
293.15	35.16 $\pm$ 0.01	303.15	44.80 $\pm$ 0.03	288.15	34.15 $\pm$ 0.03	293.15	39.02 $\pm$ 0.02
303.15	34.60 $\pm$ 0.02	313.15	44.07 $\pm$ 0.01	293.15	33.62 $\pm$ 0.02	303.15	38.35 $\pm$ 0.02
313.15	33.89 $\pm$ 0.02	323.15	43.52 $\pm$ 0.04	303.15	33.04 $\pm$ 0.02	313.15	37.71 $\pm$ 0.01
323.15	33.14 $\pm$ 0.02	333.15	42.68 $\pm$ 0.02	313.15	32.26 $\pm$ 0.01	323.15	37.09 $\pm$ 0.01
333.15	32.67 $\pm$ 0.01	343.15	42.02 $\pm$ 0.02	323.15	31.67 $\pm$ 0.01	333.15	36.47 $\pm$ 0.01
343.15	31.98 $\pm$ 0.01	353.15	41.37 $\pm$ 0.02	333.15	30.87 $\pm$ 0.02	343.15	35.91 $\pm$ 0.04
				343.15	30.20 $\pm$ 0.02	353.15	35.15 $\pm$ 0.02

^a Expanded uncertainty with an approximately 95% level of confidence.

In addition to surface tension, contact angle is another parameter that reveals interfacial interactions between liquid and solid surfaces. It is known that contact angle is highly correlated with surface tension. The Young-Laplace equation involves the surface tension of solid-liquid interface (γ_{SL}), the surface tension of liquid (γ_L), the surface tension of solid (γ_S) and the contact angle θ expressed as follows.

$$\gamma_{SL} = \gamma_S - \gamma_L \cos \theta \quad (1.2)$$

As mentioned previously, ILs usually possess higher surface tension as compared to organic solvents, whereas water has the highest surface tension. Thus we can expect smaller contact angles for ILs as compared to water on equivalent substrates. **Figure 1.8** shows the contact angles of four ILs on different substrates including hydrophilic substrate (glass) and hydrophobic substrates (PTFE and UHMWPE).^[53] We observe that all five ILs exhibit smaller contact angles compared to contact angles of water on PTFE and UHMWPE ($\theta_{\text{water}} = 118^\circ$ on PTFE and 87° on UHMWPE), which agrees with the Young-Laplace equation.

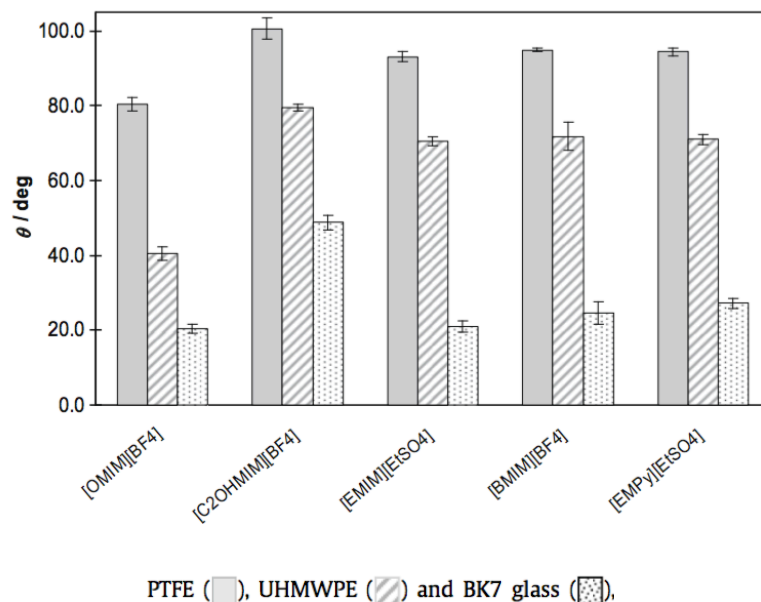


Figure 1.8. Contact angles for five ILs on PTFE, UHMWPE and BK7 glass at room temperature. Reproduced from ref. 53.

1.4 Literature Review for Advanced Polymer Electrolytes

In this section, I briefly summarize recently reported polymer electrolytes in order to provide new insights toward creating more advanced polymer electrolytes. The concepts introduced in these studies are closely associated with ILs, block copolymers and liquid crystal polymers. Meanwhile, we can gain deeper understanding of various methods that can be employed to characterize various properties of polymer electrolytes, such as morphology, anisotropy, conductivity, mechanical strength and thermal stability.

1.4.1 Ion Gels with Ionic Liquids Dispersed in Block Copolymers

Ionic liquids (ILs) are molten salts with broad range of unique properties, and these have been introduced in Section 1.3.^[12,13] Block copolymers are macromolecules with

two or more different repeat units connected in contiguous blocks. The immiscibility of different blocks drives nanophase separation in block copolymers and gives rise to various morphologies such as spherical, cylindrical and lamellar.^[54] The unique platform afforded by combining ILs and block copolymers offers opportunities to provide not only the high ionic conductivity and thermal stability attributed to ionic liquids, but also various self-assembled structures attributed to the phase separation of block copolymers.^[11] In recent years, Lodge, Balsara, Segalman and coworkers have studied gelation behavior, morphology, ionic conductivity, viscoelasticity, and capacitance of ion gels with ionic liquids dispersed inside block copolymers.^[18-20,55-58] Lodge *et al.* mainly employed the triblock copolymer poly (styrene)-b-(ethylene oxide)-b-(styrene) (SOS) as the supporting matrix.^[18,19,55] The terminal PS block aggregates into a micelle structure and serves as a physical crosslinker, whereas, the middle PEO sequence absorbs mobile ionic liquids and forms ion conducting pathways, as shown in **Figure 1.9**.^[18,19] Watanabe *et al.* have also successfully produced pyridinium and imidazolium salt-based ion gels by *in situ* polymerization of vinyl monomers in ILs.^[2,28,54,59-61] Some ion gels generated from low molar mass gelators and crystalline homopolymers were also reported.^[57,58] These researchers concluded that ionic conductivity is mainly determined by the volume fraction of IL in these ion gels. The observed ionic conductivity of ion gels is thus $\sim 1 \text{ mS cm}^{-1}$ at room temperature, while the observed modulus is usually $< 1 \text{ MPa}$.^[20,55] Thus, the challenge for current ion gels is to increase the modulus while maintaining high ionic conductivity. These ion gels are thermally stable up to at least 100°C . To effectively prevent or retard macroscopic dendritic formation in Li batteries, Lodge and coworkers have developed biocontinuous nanophase-separated polymer electrolyte membranes with

an elastic modulus approaching 300 MPa and ionic conductivity ~ 1 mS/cm at room temperature.^[16] **Figure 1.10** displays the formation of the Li dendrite growth on the Li metal anode surface. With repeated charge-discharge cycles, the Li dendrites continuously grow and finally bridge the cathode and anode, thus contributing to the short-circuit of the battery. The short-circuit can increase the risk of fire and even explosion. Thus one main goal of this project is to overcome this issue by improving the modulus of the ion gel electrolyte meanwhile maintaining the high ionic conductivity. The elevated modulus of the ion gel can significantly suppress or even block the Li dendrite growth, which is essential for developing next-generation Li batteries. By elaborate design of multi-block copolymers, we can optimize mechanical properties, thermal stability, and ionic conductivity of the ion gels so as to fit specific applications.

[11]

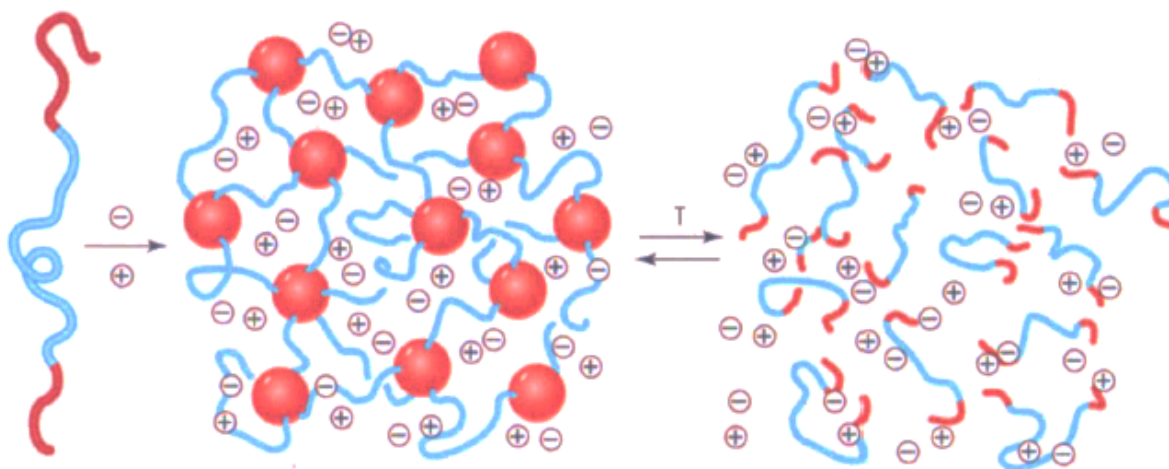


Figure 1.9. An ion gel formed by the combination of PS-PEO-PS triblock copolymer and ionic liquid. The red domains represent hard PS aggregations. The blue domains refer to the soft PEO sequence absorbed with the ionic liquid. The formed ion gel is thermally reversible. Reproduced from ref. 11.

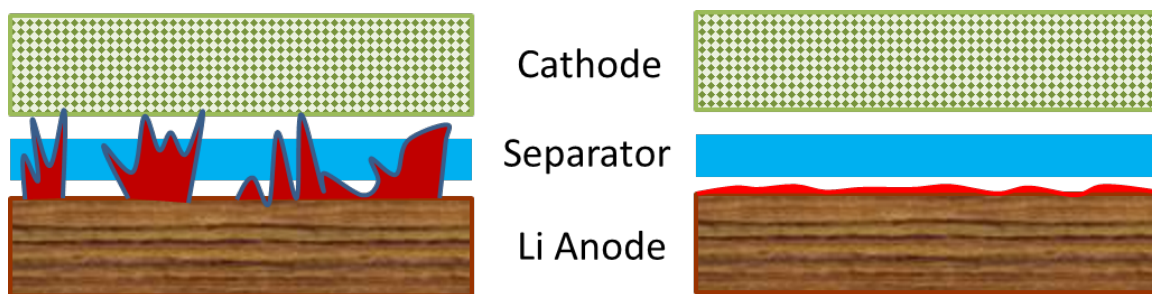


Figure 1.10. The phenomenon of Li dendrite growth on a Li metal anode surface. The elevated modulus of the ion gel electrolyte separator can significantly suppress or even block the Li dendrite growth, which is essential for developing next-generation Li batteries.

1.4.2 Polymerized Ionic Liquids

Polymerized ionic liquids (PILs) are a new class of solid-state polymer electrolytes that carry cationic and/or anionic characteristic of ionic liquids within the monomer units.^[12,62-66] PILs allow various applications, including catalysis, nanomaterials synthesis, gas separation, fuel cell membranes and battery separators.^[12,62-64] PILs usually contain bulky asymmetric organic cations, including imidazolium, pyridinium or ammonium, together with various organic or inorganic anions. For example, Chen and Elabd have synthesized the PILs shown in **Figure 1.11**.^[63] PILs share some favorable properties with ILs, for example excellent thermal stability and wide electrochemical stability.^[12,62-64] Additionally, solid-state PILs show potential to resolve the common problem for both liquid electrolytes and ion gel electrolytes, which is the leakage of the liquid phase. However, the challenge for next-generation PILs is to increase the ionic conductivity (currently $\sim 10^{-5}$ S/cm at room temperature), while maintaining the mechanical modulus of the membranes.

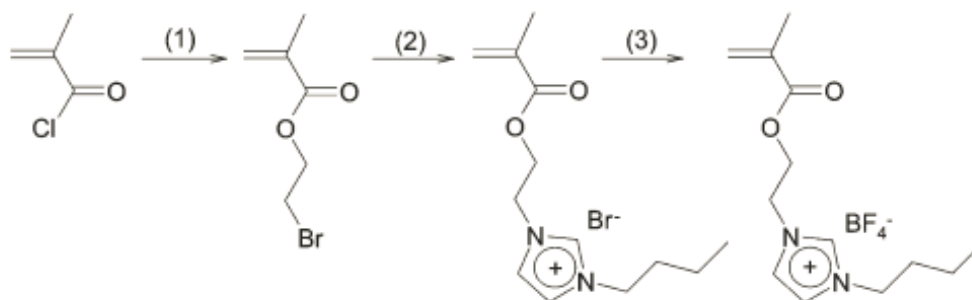


Figure 1.11. Synthesis process of imidazolium-containing Monomer, IMI- BF_4 . Figure reproduced from ref. 63.

Furthermore, Ohno and coworkers have studied the effect of the spacer length, which refers to the distance between the polymer backbone and the pendant ionogenic groups. They also described the effect of different anions on the conductivity in imidazolium-containing POILs.^[62] They have synthesized a mesogenic (LC-forming) PIL containing tris(alkoxy)phenyl groups attached to acryloyl groups. Recent studies have shown that lowering the T_g of POILs is critical to obtain high ionic conductivity. However, the low T_g minimizes the mechanical strength of the materials. Thus, it is challenging to fabricate ion containing polymers with mechanically robust as well as contiguous pathways for high ionic conductivity.^[62] Weber *et al.* (Elabd and Mahanthappa groups) have demonstrated that microphase-separated morphologies of POILs are important in controlling the ionic conductivity. For example, POILs with well-ordered lamellar morphology contribute to 10-fold increase in ionic conductivity ($\sim 0.1 \text{ mS cm}^{-1}$ at 150°C) compared to the copolymers with poorly organized hexagonal morphologies ($\sim 0.01 \text{ mS cm}^{-1}$ at 150°C).^[64]

1.4.3 Anisotropic Polymer Electrolyte Membranes based on Liquid Crystals

For recently developed polymer electrolytes, highly oriented morphology with faster diffusion rate along a predetermined axis is still a challenge. Osuji *et al.* successfully applied a magnetic field (**B**-field) to achieve higher through-plane conductivity in membranes by introducing a smectic LC sequence to a poly(ethylene oxide)-based polymer.^[23,24,67] The resulting hot pressed membrane shows conductivity anisotropy of up to 450, whereas the ionic conductivity ($10^{-10} - 10^{-7} \text{ S cm}^{-1}$ over 20 – 100°C) along the alignment axis is severely limited by the solid hydrophilic phase of PEO at room temperature. The features of this characteristic morphology is shown in **Figure 1.12**.^[23] The smectic poly(MA/CB) blocks align with the external magnetic field because of the positive magnetic susceptibility anisotropy of the rodlike cyanobiphenyl (CB) mesogens. The PEO blocks aggregate into a hexagonal phase, serving as the continuous Li^+ conducting pathway. The ionic conductivity of this system is highly associated with the PEO domains.^[23] By carefully designing the construction of block copolymers, researchers hope to achieve oriented morphology, thus contributing to higher ionic mobility along a predetermined axis. The challenge is to develop advanced polymer electrolyte membranes with controlled morphology while also retaining high ionic conductivity and thermal stability.

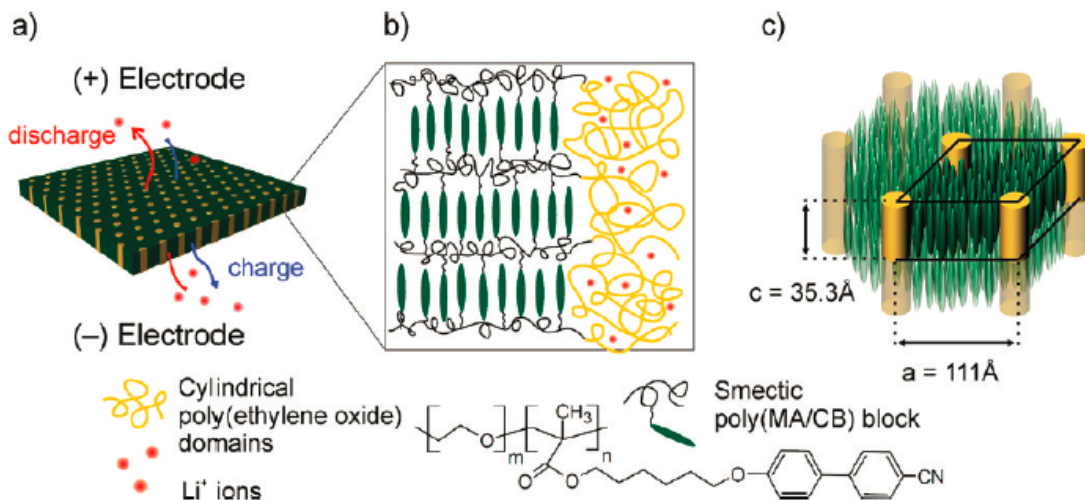


Figure 1.12. Fabrication of a block copolymer membrane in a magnetic field to produce a highly oriented structure. (a) Structure of the PEO-b-PMA/CB block copolymer membrane with lithium-conducting poly (ethylene oxide) cylindrical domains aligned uniformly in the flow direction of the Li^+ . (b) The zoomed-in views show the details of the structure of the polymer. (c) The liquid-crystalline unit cell with mesogenic backbone residues anchored in the layers transverse to the long axes of PEO cylinders. Reproduced from ref. 23.

In addition, Kato *et al.*^[25,68,69] also developed a class of one-dimensional ion-conducting polymer membranes with oriented ion nanochannels that are perpendicular to or parallel to the membrane surface, respectively. The resulting membranes were obtained based on photo-polymerization of aligned columnar liquid crystals as shown in **Figure 1.13**. The membrane with alignment in the perpendicular direction was achieved by modifying the surfaces of glass and indium tin oxide with 3-(aminopropyl)triethoxysilane. In contrast, alignment in the parallel direction was achieved by mechanical shearing. The membrane shows a hexagonal LC phase based on

X-ray diffraction results. However, the ionic conductivities of the films range from 10^{-8} to 10^{-3} S/cm over temperatures from 40 - 120 °C. Additionally, Gin *et al.*^[26] developed a new nanoporous Li ion conductor by photo crosslinking a lyotropic liquid crystal filled with liquid electrolyte.

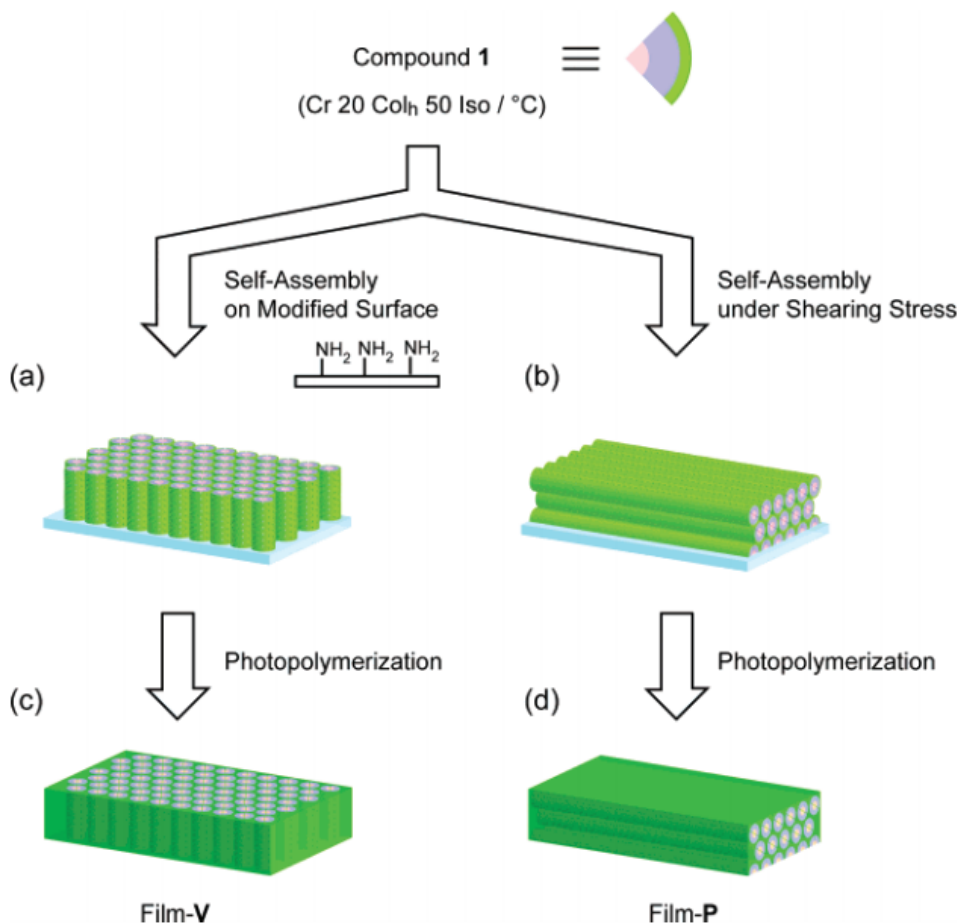


Figure 1.13. The fabrication of one-dimensional ion-conducting polymer membranes. (a) Vertical assembly of unpolymerized columns. (b) Parallel orientation of unpolymerized columns. (c) and (d) Polymer film with vertical and in-plane alignment, respectively, after photopolymerization. Reproduced from ref. 25.

In summary, it is significant to utilize properties of LCs to develop polymer electrolytes with ordered morphologies. As introduced previously, PBDT forms a lyotropic liquid crystal, which can be used as the assembly template to develop functionalized polymer electrolytes with long-range ordered structures.

1.4.4 Fabrication of Anisotropic Hydrogels from Polyelectrolytes

In addition to the ion gel concept mentioned previously, I would like to introduce some fabrication methods and formation mechanisms for anisotropic hydrogels based on natural polyelectrolytes. PBDT aqueous solution shares some similarities with many natural polyelectrolyte solutions. Thus, I highlight some anisotropic hydrogels formed from natural polyelectrolytes and salt solution. For example, curdlan is a natural polyelectrolyte. Dobashi *et al.* have studied gelation processes and diffusion mechanisms of the resulting liquid crystalline gel by ion exchange of salt solution into curdlan solutions.^[70,71] These authors concluded that the gelation and liquid crystalline formation occurred simultaneously to form a liquid crystalline gel (LCG). The sodium hydroxide solution of curdlan permeates into an aqueous solution of calcium chloride. The out fluxing of the hydroxide anions changes the conformation of curdlan molecules from random coils into a triple helix, and the influx of the calcium cations can crosslink these helical curdlan molecules. The resulting LCG exhibits an amorphous phase in alternating layers. The dynamics and mechanisms of the gel formation process have been reported by Dobashi.^[70,71] The hydrogel formation parameters, such as calcium concentration and pH of the inner curdlan solution were traced to understand the dynamics and mechanisms of the forming process. The ion exchange process could be explained by kinetic theories

based on Fick's law with an assumption that the gelation is induced by diffusion of calcium cations in a matrix with cylindrical symmetry.^[70,71] Similarly, Gong *et al.* reported the formation of hydrogels based on PBDT polyelectrolyte solutions.^[29,72,73] The dialysis of PBDT in the multivalent ion solutions will also generate birefringent optical hydrogels, as shown in **Figure 1.14**. The highly aligned PBDT system, serving as the ordering template, thus offers opportunities to achieve highly oriented gel systems for various applications.

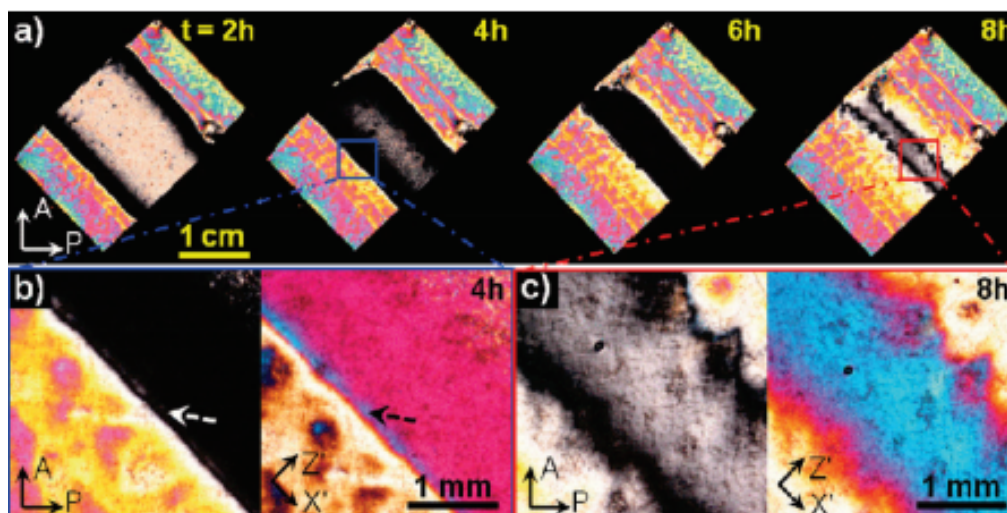


Figure 1.14. The formation of PBDT-derived birefringent optical hydrogels observed by POM. (a) POM images of 2wt% LC gel with increasing dialysis time. (b) Enlarged image of the diffusion front. (c) Image with tint plate. Reproduced from ref. 73.

In summary, these advanced polymeric and IL electrolyte materials have provided a foundation of ideas, mechanisms, and characterization methods for my work. Based on this framework, we have developed a highly conductive and thermally stable ion gel with tunable anisotropy and modulus by absorbing ionic liquids (ILs) into magnetically aligned liquid crystalline (LC) polyelectrolyte solutions of poly 2,2'-disulfonyl-4,4'-

benzidine terephthalamide (PBDT).^[17,30] In the following chapters, we will describe measurement techniques for characterizing the wide array of properties in our systems (Chapter 2), water solutions and dimer configurations of PBDT polymer (Chapters 3 and 4), the fundamentals of PBDT-IL ion gels (Chapter 5), and gel properties and tests working toward advanced lithium batteries (Chapter 6). This ion gel alignment reveals itself in macroscopic optical anisotropy and enhanced ion transport along the gel alignment axis compared to perpendicular directions. Ionic conductivity at ambient temperature along the gel alignment axis is a factor $10^2 - 10^4$ higher than known solid-state polymer electrolytes, and the gel modulus is a factor $10^1 - 10^3$ higher than previous IL-polymer electrolytes and with comparable conductivity.^[11,16,20,56] Moreover, using the concepts developed here, we are exploring the concepts and parameter space of ion gel electrolyte formation using a wide array of ionic liquids, non-aqueous co-solvents for gel formation, metal-ion salts, and other rigid-rod polyelectrolytes, in order to produce enhanced combinations of properties.

References

- [1] Li, J.; Park, J. K.; Moore, R. B.; Madsen, L. A., Linear coupling of alignment with transport in a polymer electrolyte membrane, *Nature Materials*, **2011**, *10*, 507.
- [2] Miyatake, K.; Chikashige, Y.; Higuchi, E.; Watanabe, M., Tuned polymer electrolyte membranes based on aromatic polyethers for fuel cell applications, *Journal of the American Chemical Society*, **2007**, *129*, 3879.
- [3] Peckham, T. J.; Holdcroft, S., Structure-Morphology-Property Relationships of Non-Perfluorinated Proton-Conducting Membranes, *Advanced Materials*, **2010**, *22*, 4667.
- [4] Kong, L. R.; Chen, W., Carbon Nanotube and Graphene-based Bioinspired Electrochemical Actuators, *Advanced Materials*, **2014**, *26*, 1025.
- [5] Liu, X.; Wu, D.; Wang, H.; Wang, Q., Self-Recovering Tough Gel Electrolyte with Adjustable Supercapacitor Performance, *Advanced Materials*, **2014**, *26*, 4370.
- [6] Gin, D. L.; Noble, R. D., Designing the Next Generation of Chemical Separation Membranes, *Science*, **2011**, *332*, 674.

- [7] Chen, C.-L.; Teng, H.; Lee, Y.-L., In Situ Gelation of Electrolytes for Highly Efficient Gel-State Dye-Sensitized Solar Cells, *Advanced Materials*, **2011**, *23*, 4199.
- [8] Mauritz, K. A.; Moore, R. B., State of understanding of Nafion, *Chemical Reviews*, **2004**, *104*, 4535.
- [9] Elabd, Y. A.; Hickner, M. A., Block Copolymers for Fuel Cells, *Macromolecules*, **2011**, *44*, 1.
- [10] Mauritz, K. A.; Moore, R. B., State of Understanding of Nafion, *Chemical Reviews*, **2004**, *104*, 4535.
- [11] Lodge, T. P., Materials science - A unique platform for materials design, *Science*, **2008**, *321*, 50.
- [12] Armand, M.; Endres, F.; MacFarlane, D. R.; Ohno, H.; Scrosati, B., Ionic-liquid materials for the electrochemical challenges of the future, *Nature Materials*, **2009**, *8*, 621.
- [13] Hallett, J. P.; Welton, T., Room-Temperature Ionic Liquids: Solvents for Synthesis and Catalysis. 2, *Chemical Reviews*, **2011**, *111*, 3508.
- [14] Hou, J. B.; Zhang, Z. Y.; Madsen, L. A., Cation/Anion Associations in Ionic Liquids Modulated by Hydration and Ionic Medium, *Journal of Physical Chemistry B*, **2011**, *115*, 4576.
- [15] Kim, O.; Shin, T. J.; Park, M. J., Fast low-voltage electroactive actuators using nanostructured polymer electrolytes, *Nature Communications*, **2013**, *4*.
- [16] Schulze, M. W.; McIntosh, L. D.; Hillmyer, M. A.; Lodge, T. P., High-Modulus, High-Conductivity Nanostructured Polymer Electrolyte Membranes via Polymerization-Induced Phase Separation, *Nano Letters*, **2014**, *14*, 122.
- [17] Wang, Y.; Chen, Y.; Gao, J. W.; Yoon, H. G.; Jin, L. Y.; Forsyth, M.; Dingemans, T. J.; Madsen, L. A., Highly Conductive and Thermally Stable Ion Gels with Tunable Anisotropy and Modulus, *Advanced Materials*, **2016**, *28*, 2571.
- [18] Zhang, S. P.; Lee, K. H.; Sun, J. R.; Frisbie, C. D.; Lodge, T. P., Viscoelastic Properties, Ionic Conductivity, and Materials Design Considerations for Poly(styrene-*b*-ethylene oxide-*b*-styrene)-Based Ion Gel Electrolytes, *Macromolecules*, **2011**, *44*, 8981.
- [19] Zhang, S. P.; Lee, K. H.; Frisbie, C. D.; Lodge, T. P., Ionic Conductivity, Capacitance, and Viscoelastic Properties of Block Copolymer-Based Ion Gels, *Macromolecules*, **2011**, *44*, 940.
- [20] He, Y.; Boswell, P. G.; Bühlmann, P.; Lodge, T. P., Ion Gels by Self-Assembly of a Triblock Copolymer in an Ionic Liquid†, *Journal of Physical Chemistry B*, **2006**, *111*, 4645.
- [21] Wu, Z. L.; Sawada, D.; Kurokawa, T.; Kakugo, A.; Yang, W.; Furukawa, H.; Gong, J. P., Strain-Induced Molecular Reorientation and Birefringence Reversion of a Robust, Anisotropic Double-Network Hydrogel, *Macromolecules*, **2011**, *44*, 3542.
- [22] Lee, M.; Park, J. K.; Lee, H. S.; Lane, O.; Moore, R. B.; McGrath, J. E.; Baird, D. G., Effects of block length and solution-casting conditions on the final morphology and properties of disulfonated poly(arylene ether sulfone) multiblock copolymer films for proton exchange membranes, *Polymer*, **2009**, *50*, 6129.
- [23] Majewski, P. W.; Gopinadhan, M.; Jang, W. S.; Lutkenhaus, J. L.; Osuji, C. O., Anisotropic Ionic Conductivity in Block Copolymer Membranes by Magnetic Field Alignment, *Journal of the American Chemical Society*, **2010**, *132*, 17516.

- [24] Gopinadhan, M.; Majewski, P. W.; Choo, Y.; Osuji, C. O., Order-Disorder Transition and Alignment Dynamics of a Block Copolymer Under High Magnetic Fields by In Situ X-Ray Scattering, ***Physical Review Letters***, **2013**, *110*.
- [25] Yoshio, M.; Kagata, T.; Hoshino, K.; Mukai, T.; Ohno, H.; Kato, T., One-Dimensional Ion-Conductive Polymer Films: Alignment and Fixation of Ionic Channels Formed by Self-Organization of Polymerizable Columnar Liquid Crystals, ***Journal of the American Chemical Society***, **2006**, *128*, 5570.
- [26] Kerr, R. L.; Miller, S. A.; Shoemaker, R. K.; Elliott, B. J.; Gin, D. L., New Type of Li Ion Conductor with 3D Interconnected Nanopores via Polymerization of a Liquid Organic Electrolyte-Filled Lyotropic Liquid-Crystal Assembly, ***Journal of the American Chemical Society***, **2009**, *131*, 15972.
- [27] Marincola, F. C.; Casu, M.; Saba, G.; Lai, A., Na-23 NMR relaxation studies of the Na-DNA/drug interaction, ***Chemphyschem***, **2001**, *2*, 569.
- [28] Okoshi, K.; Kamee, H.; Suzaki, G.; Tokita, M.; Fujiki, M.; Watanabe, J., Well-defined phase sequence including cholesteric, smectic A, and columnar phases observed in a thermotropic LC system of simple rigid-rod helical polysilane, ***Macromolecules***, **2002**, *35*, 4556.
- [29] Wu, Z. L.; Arifuzzaman, M.; Kurokawa, T.; Le, K.; Hu, J.; Sun, T. L.; Furukawa, H.; Masunaga, H.; Gong, J. P., Supramolecular Assemblies of a Semirigid Polyanion in Aqueous Solutions, ***Macromolecules***, **2013**, *46*, 3581.
- [30] Wang, Y.; Gao, J.; Dingemans, T. J.; Madsen, L. A., Molecular Alignment and Ion Transport in Rigid Rod Polyelectrolyte Solutions, ***Macromolecules***, **2014**, *47*, 2984.
- [31] Farinato Raymond, S. In *Polyelectrolytes and Polyzwitterions*; American Chemical Society: 2006; Vol. 937, p 153.
- [32] Burnell, E. E.; de Lange, C. A. *NMR of Ordered Liquids*; 1st, Ed.; Springer: The Netherlands, 2003.
- [33] Coates, D.; Rapra Technology Ltd.: 2000; Vol. Shawbury Shrewsbury.
- [34] Ciferri, A. *Liquid crystallinity in polymers: principles and fundamental properties*; 1st ed.; VCH Publishers: New York, 1991.
- [35] Cai, R.; Preston, J.; Samulski, E. T., New Liquid-Crystalline Aromatic Polyesters Derived from Thiophenes, ***Abstracts of Papers of the American Chemical Society***, **1989**, *198*, 82.
- [36] Cai, R.; Samulski, E. T., Liquid-Crystalline Aromatic Polyesters Containing Isophthalic Acid, ***Abstracts of Papers of the American Chemical Society***, **1992**, *203*, 188.
- [37] Polk, M. B.; Banks, H. D.; Onwumere, F.; Venkatasubramanian, N.; Nandu, M.; Phingbodhipakkiya, M.; Samulski, E. T., Thermotropic Copolyesters .3. Synthesis and Characterization of Liquid-Crystal Copolyesters Containing the Bicyclo[2.2.2]Octane Ring-System, ***Journal of Polymer Science Part a-Polymer Chemistry***, **1988**, *26*, 2405.
- [38] Cai, R. B.; Preston, J.; Samulski, E. T., Liquid-Crystalline Aromatic Polyesters Derived from 2,5-Thiophene, ***Macromolecules***, **1992**, *25*, 563.
- [39] Cai, R. B.; Samulski, E. T., Liquid-Crystalline Aromatic Polyesters Containing Isophthalic Acid, ***Macromolecules***, **1994**, *27*, 135.
- [40] Samulski, E. T.; Dupre, D. B., Lyotropic Polymeric Liquid-Crystals, ***Journal De Chimie Physique Et De Physico-Chimie Biologique***, **1983**, *80*, 25.
- [41] Charvolin, J.; Levelut, A. M.; Samulski, E. T., Lyotropic Nematics - Molecular Aggregation and Susceptibilities, ***Journal De Physique Lettres***, **1979**, *40*, L587.

- [42] Tang, J. X.; Janmey, P. A., The polyelectrolyte nature of F-actin and the mechanism of actin bundle formation, *Journal of Biological Chemistry*, **1996**, *271*, 8556.
- [43] Schwarz, G.; Bodenthin, Y.; Tomkowicz, Z.; Haase, W.; Geue, T.; Kohlbrecher, J.; Pietsch, U.; Kurth, D. G., Tuning the Structure and the Magnetic Properties of Metallo-supramolecular Polyelectrolyte-Amphiphile Complexes, *Journal of the American Chemical Society*, **2011**, *133*, 547.
- [44] Rapakousiou, A.; Jimenez, L. H.; Wang, Y. L.; Mouche, C.; Astruc, D., Rhodicenium Salts: From Basic Chemistry to Polyelectrolyte and Dendritic Macromolecules, *Organometallics*, **2014**, *33*, 1259.
- [45] Manning, G.; Joy, A.; Mathias, C. J.; McDonald, C. J.; MillarCraig, M. W., Double-blind, parallel, comparative multicentre study of a new combination of diltiazem and hydrochlorothiazide with individual components in patients with mild or moderate hypertension, *Journal of Human Hypertension*, **1996**, *10*, 443.
- [46] Manning, G. S., The critical onset of counterion condensation: A survey of its experimental and theoretical basis, *Berichte Der Bunsen-Gesellschaft-Physical Chemistry Chemical Physics*, **1996**, *100*, 909.
- [47] Manning, G. S., The counterion distribution in solutions of rod-shaped polyelectrolytes - Comments, *Journal of Polymer Science Part B-Polymer Physics*, **1996**, *34*, 393.
- [48] Manning, G. S., Counterion condensation theory constructed from different models, *Physica A*, **1996**, *231*, 236.
- [49] Fogolari, F.; Brigo, A.; Molinari, H., The Poisson-Boltzmann equation for biomolecular electrostatics: a tool for structural biology, *Journal of Molecular Recognition*, **2002**, *15*, 377.
- [50] Welton, T., Room-temperature ionic liquids. Solvents for synthesis and catalysis, *Chemical Reviews*, **1999**, *99*, 2071.
- [51] Cremer, T., Ionic Liquid Bulk and Interface Properties Electronic Interaction, Molecular Orientation and Growth Characteristics, **2013**.
- [52] Freire, M. G.; Carvalho, P. J.; Fernandes, A. M.; Marrucho, I. M.; Queimada, A. J.; Coutinho, J. A. P., Surface tensions of imidazolium based ionic liquids: Anion, cation, temperature and water effect, *Journal of Colloid and Interface Science*, **2007**, *314*, 621.
- [53] Restolho, J.; Mata, J. L.; Saramago, B., On the interfacial behavior of ionic liquids: Surface tensions and contact angles, *Journal of Colloid and Interface Science*, **2009**, *340*, 82.
- [54] Ueki, T.; Watanabe, M., Macromolecules in ionic liquids: Progress, challenges, and opportunities, *Macromolecules*, **2008**, *41*, 3739.
- [55] Zhang, S.; Lee, K. H.; Sun, J.; Frisbie, C. D.; Lodge, T. P., Viscoelastic Properties, Ionic Conductivity, and Materials Design Considerations for Poly(styrene-*b*-ethylene oxide-*b*-styrene)-Based Ion Gel Electrolytes, *Macromolecules*, **2011**, *44*, 8981.
- [56] Cho, J. H.; Lee, J.; He, Y.; Kim, B.; Lodge, T. P.; Frisbie, C. D., High-capacitance ion gel gate dielectrics with faster polarization response times for organic thin film transistors, *Advanced Materials*, **2008**, *20*, 686.
- [57] Virgili, J. M.; Nedoma, A. J.; Segalman, R. A.; Balsara, N. P., Ionic Liquid Distribution in Ordered Block Copolymer Solutions, *Macromolecules*, **2010**, *43*, 3750.
- [58] Hoarfrost, M. L.; Segalman, R. A., Ionic Conductivity of Nanostructured Block Copolymer/Ionic Liquid Membranes, *Macromolecules*, **2011**, *44*, 5281.

- [59] Susan, M. A. B. H.; Kaneko, T.; Noda, A.; Watanabe, M., Ion Gels Prepared by in Situ Radical Polymerization of Vinyl Monomers in an Ionic Liquid and Their Characterization as Polymer Electrolytes, *Journal of the American Chemical Society*, **2005**, *127*, 4976.
- [60] Schauser, N. S.; Harry, K. J.; Parkinson, D. Y.; Watanabe, H.; Balsara, N. P., Lithium Dendrite Growth in Glassy and Rubbery Nanostructured Block Copolymer Electrolytes, *Journal of the Electrochemical Society*, **2014**, *162*, A398.
- [61] Ueno, K.; Hata, K.; Katakabe, T.; Kondoh, M.; Watanabe, M., Nanocomposite ion gels based on silica nanoparticles and an ionic liquid: Ionic transport, viscoelastic properties, and microstructure, *Journal of Physical Chemistry B*, **2008**, *112*, 9013.
- [62] Ohno, H.; Yoshizawa, M. In *Ionic Liquids IIIB: Fundamentals, Progress, Challenges, and Opportunities*; American Chemical Society: 2005; Vol. 902, p 159.
- [63] Chen, H.; Elabd, Y. A., Polymerized Ionic Liquids: Solution Properties and Electrospinning, *Macromolecules*, **2009**, *42*, 3368.
- [64] Weber, R. L.; Ye, Y.; Schmitt, A. L.; Banik, S. M.; Elabd, Y. A.; Mahanthappa, M. K., Effect of Nanoscale Morphology on the Conductivity of Polymerized Ionic Liquid Block Copolymers, *Macromolecules*, **2011**, *44*, 5727.
- [65] Jangu, C.; Savage, A. M.; Zhang, Z. Y.; Schultz, A. R.; Madsen, L. A.; Beyer, F. L.; Long, T. E., Sulfonimide-Containing Triblock Copolymers for Improved Conductivity and Mechanical Performance, *Macromolecules*, **2015**, *48*, 4520.
- [66] Jangu, C.; Wang, J. H. H.; Wang, D.; Fahs, G.; Heflin, J. R.; Moore, R. B.; Colby, R. H.; Long, T. E., Imidazole-containing triblock copolymers with a synergy of ether and imidazolium sites, *Journal of Materials Chemistry C*, **2015**, *3*, 3891.
- [67] Tran, H.; Gopinadhan, M.; Majewski, P. W.; Shade, R.; Steffes, V.; Osuji, C.; Campos, L. M., Monoliths of Semiconducting Block Copolymers by Magnetic Alignment, *Acs Nano*, **2013**, *7*, 5514.
- [68] Ichikawa, T.; Yoshio, M.; Hamasaki, A.; Kagimoto, J.; Ohno, H.; Kato, T., 3D Interconnected Ionic Nano-Channels Formed in Polymer Films: Self-Organization and Polymerization of Thermotropic Bicontinuous Cubic Liquid Crystals, *Journal of the American Chemical Society*, **2011**, *133*, 2163.
- [69] Shimura, H.; Yoshio, M.; Hoshino, K.; Mukai, T.; Ohno, H.; Kato, T., Noncovalent Approach to One-Dimensional Ion Conductors: Enhancement of Ionic Conductivities in Nanostructured Columnar Liquid Crystals, *Journal of the American Chemical Society*, **2008**, *130*, 1759.
- [70] Dobashi, T.; Nobe, M.; Yoshihara, H.; Yamamoto, T.; Konno, A., Liquid crystalline gel with refractive index gradient of curdlan, *Langmuir*, **2004**, *20*, 6530.
- [71] Nobe, M.; Dobashi, T.; Yamamoto, T., Dynamics in dialysis process for liquid crystalline gel formation, *Langmuir*, **2005**, *21*, 8155.
- [72] Wu, Z. L.; Kurokawa, T.; Sawada, D.; Hu, J.; Furukawa, H.; Gong, J. P., Anisotropic Hydrogel from Complexation-Driven Reorientation of Semirigid Polyanion at Ca²⁺ Diffusion Flux Front, *Macromolecules*, **2011**, *44*, 3535.
- [73] Wu, Z. L.; Takahashi, R.; Sawada, D.; Arifuzzaman, M.; Nakajima, T.; Kurokawa, T.; Hu, J.; Gong, J. P., In Situ Observation of Ca²⁺ Diffusion-Induced Superstructure Formation of a Rigid Polyanion, *Macromolecules*, **2014**, *47*, 7208.

Chapter 2

Characterization of Multi-scale Properties in Anisotropic Polymeric Systems

Based on a combination of analysis techniques, we can investigate the diverse and multi-scale properties of materials derived from anisotropic polymers such as PBDT. These properties include: self-assembled nanoscale morphology, thermal stability, mechanical modulus, optical anisotropy, ionic conductivity, diffusion anisotropy, and electrochemical properties. Here, I will summarize commonly used methods for characterizing anisotropic liquid crystal polymers. In addition, I will also briefly introduce basic techniques to study electrochemical, thermal and mechanical properties of ion conducting polymers. Thus, we can obtain a systematic understanding of the characterization methods that can be employed to study the polymer solutions and ion gels developed in my project.

2.1 Polarized Optical Microscopy (POM)

As illustrated in Chapter 1, PBDT aqueous solutions exhibit a lyotropic nematic LC phase above the critical concentration (≈ 1.5 wt%). Thus we can employ POM to easily and directly observe this LC phase due to its *birefringence* Δn , in which a material possesses distinct refractive index n along different directions. As a type of optical microscopy involving polarized light, POM is used for studying absorption color and optical path boundaries for various systems, including phase-separated materials, liquid crystals and other oriented materials.^[1,2] The two polarizing filters in POM are called polarizer and analyzer. With the configuration of polarizer crossed with analyzer, a dark

view is observed for isotropic materials. The detailed components of POM are shown in the **Figure 2.1a**.^[3] The POM images for various LC phases, including nematic, smectic, and cholesteric, are shown in **Figure 2.1b-d**. A nematic phase usually shows the Schlieren texture, a smectic phase displays the focal-conic fan texture, and a cholesteric phase shows the fingerprint texture.^[2] In addition, POM is also a useful technique to study the behaviors of spherulites, phase separation and phase transitions in polymeric materials.^[4] The spherulite is the most common crystalline morphology for polymers, such as polypropylene and some polyesters.^[4] Gong *et al.* have studied phase separation behavior of rigid-rod PBDT aqueous solutions.^[5] The observed upper and lower phases show different POM textures, with nematic colloid droplets in the upper phase and a Schlieren texture in the lower phase, respectively.^[5] In our project, we are using a combination of POM and ^2H NMR spectroscopy to study the phase transition and phase separation behaviors of PBDT aqueous solutions in more detail.^[6]

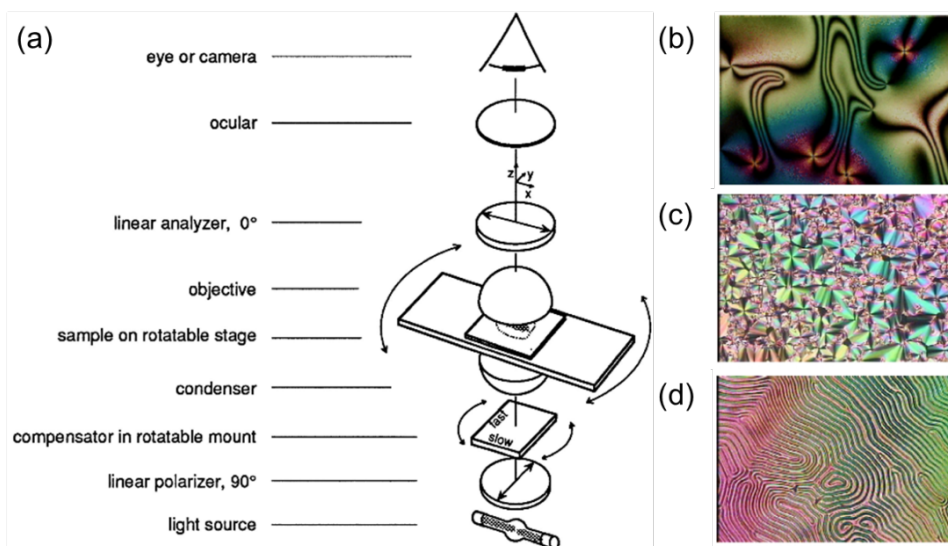


Figure 2.1. POM instrument components and POM images in various LCs. (a) The detailed components of a POM. (b) Schlieren texture for nematic LC with surface point

defects. (c) Focal-conic fan texture for a chiral smectic LC. (d) Fingerprint texture for a cholesteric LC . Reproduced from ref. 3.

Here, I would like to introduce some basic rules for us to understand POM analysis.^[2]

1. The main source of birefringence (Δn) in liquid crystals is the orientational order of the system (S). Thus, Δn is proportional to the order parameter S .

$$\Delta n \propto S \quad (2.1)$$

2. The orientational order parameter S is defined as the statistical (ensemble) average of the angle θ between each molecule and the LC director. The expression is shown as follows.

$$S = \frac{1}{2} \langle 3\cos^2 \theta - 1 \rangle \quad (2.2)$$

3. The observed POM intensity I depends on various parameters, such as 1) birefringence Δn of the liquid crystal, 2) orientational angle $\emptyset$ between sample and the polarizer of POM, 3) thickness d of the sample and 4) wavelength λ of the incident light. The equation is shown as follows.

$$I = I_0 \sin^2 [2\emptyset(x, y)] \sin^2 \left[\frac{\pi}{\lambda} d \Delta n(x, y) \right] \quad (2.3)$$

4. A bright domain in the image represents large I , while a dark domain represents small I . I is related to a square of the sinusoidal function in Equation 1.3. Thus, we can see the crossed dark and light domains in the polarized images.
5. By using white light rather than monochromatic light, the results are able to show both intensity differences and color differences. The local defects (disclinations) and the layer thickness contribute to shifts in observed wavelength. Defect structures in LCs can be conveniently monitored by POM. Usually the defect zone shows uniform

color, which can be demonstrated by rotating the sample between the crossed polarizers. In this case, the product of d and Δn is constant in the equation of I . The core of the defect is a very small object, with diameter of 30 – 50 nm, and surrounded by a high refractive index gradient that spans hundreds of nm up to μm in length scale.

6. POM probes changes that appear on a scale larger than the light wavelength of $\sim 0.5 \mu\text{m}$. The layer thickness d influences the pattern because of the accumulation of light polarization angle as the light passes through the sample.

Here, I will introduce POM textures for nematic and smectic phases, respectively. The nematic phase has one-dimensional ordering along the long axis of the rigid-rod molecules. Nematics exhibit a Schlieren texture. The point defect patterns formed are called disclinations in the LC domain structure. The form of an observed disclination depends on the winding strength. In Nematic textures, disclinations with winding strength (denoted +/-) equals to 1 or 0.5 are observed. As shown in **Figure 2.2**, when the strength equals 1, we can observe four sided crosses (four bright and four dark regions surrounding the point). When the strength equals 0.5, we observe defects with only 2 sides.

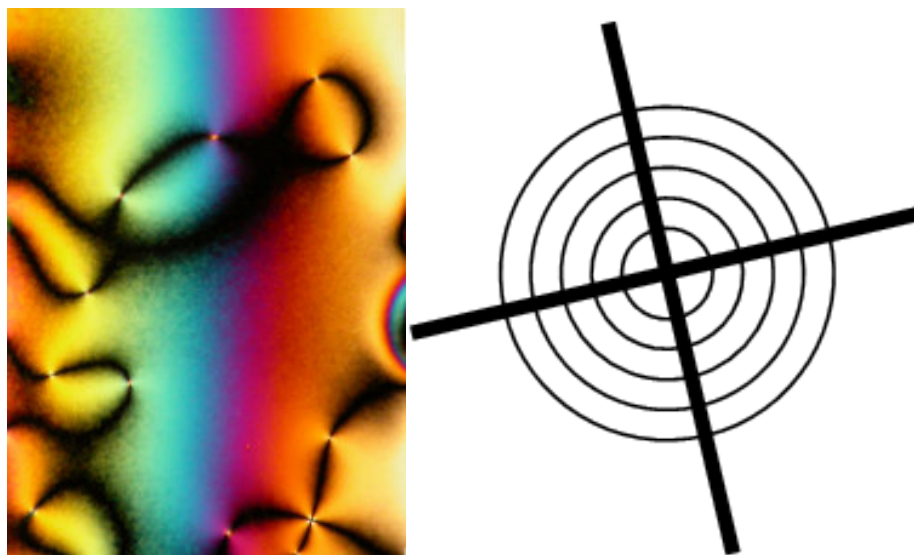


Figure 2.2. The Schlieren pattern of a nematic phase. A nematic disclination creates a cross-shaped pattern. Depending on the winding strength ($\pm = 1$ or $\pm = 1/2$), we can observe the cross with 4 or 2 sides, respectively. Here, a disclination is shown for winding strength = 1. Figure reproduced from ref. 3

The smectic phase shown in **Figure 2.3** possesses two-dimensional ordering. The interaction among rigid-rod molecular chains contributes to the alignment in both the direction along the polymer chain and in the lamellar direction. The formed layers can slide over one another. Furthermore, smectic phases can be classified into different types, such as smectic-A and smectic-C. For example, a smectic-A phase possesses the optic axis parallel with the layer normal. This smectic phase produces characteristic patterns as shown in **Figure 2.3** when observed in POM. These patterns contain long and hyperbolic lines with smaller secondary lines crossing them around the circular focal-conic domain, which can be seen as the center of the hyperbolas. Smectic-C is one of the higher order smectic phases. In this phase, the molecules are tilted away from the layer-normal

direction. Although displaying similarities with Smectic-A layers, this higher order smectic structure gives less ‘clean’ polarization micrographs.

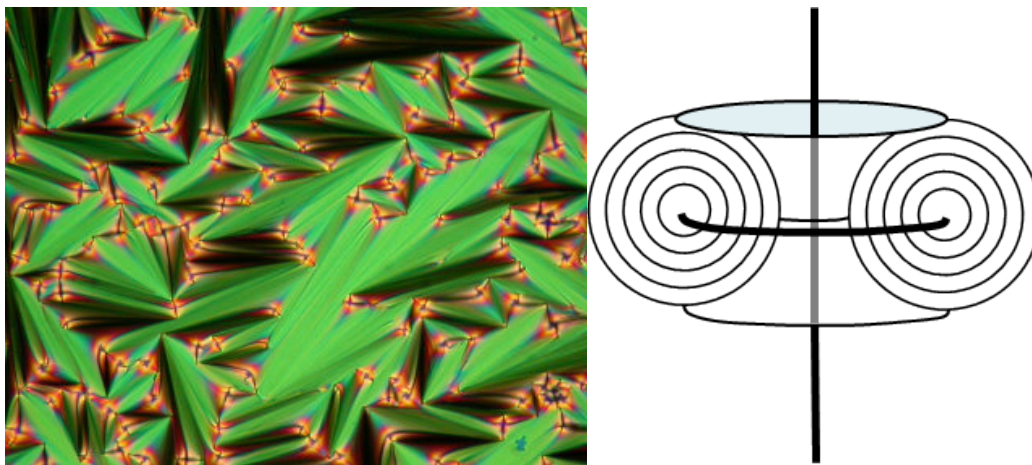


Figure 2.3. The focal-conic texture of a smectic-A phase. Disclinations in a smectic-A phase create focal-conic textures shown at left. These textures are seen as crosses with one long side (the vertical line) and a short side (the horizontal line) that crosses the vertical line at the center. Figure reproduced from ref. 3.

2.2 ^2H and ^{23}Na Quadrupolar NMR Spectroscopy

Quadrupolar NMR spectroscopy is a useful technique to study both molecular and phase orientation in materials. Our studies employ ^2H and ^{23}Na quadrupolar NMR to quantify the molecular alignment of PBDT and PBDT-derived materials. Specific splitting patterns of quadrupolar nuclei provide information regarding anisotropic interactions and alignment degree in solution and solid materials. Nuclei with spin $I > \frac{1}{2}$ are called quadrupolar nuclei, which are special because of the intrinsic nuclear quadrupole moment.^[7,8] Deuterium (^2H) is a spin $I = 1$ nucleus with very low natural

abundance (0.012%).^[7] Sodium (^{23}Na) is a spin $I = 3/2$ nucleus with natural abundance of 100%.^[7] NMR of quadrupolar nuclei provides many theoretical and practical challenges in understanding orientational order in the anisotropic systems due to the interactions between the nuclear electric quadrupole moments Q and the local electric field gradients (efg).^[7]

In the presence of a strong magnetic field B_0 , the energy level diagram for a spin-1 nucleus is shown in **Figure 2.4a**. For a spin-1 nucleus, there are three eigenstates of angular momentum along the z-axis, denoted +1, 0, and -1, that exhibit Zeeman splitting.^[7] By considering Zeeman splitting (with strength ω_0) and Zeeman first-order quadrupole interaction $\omega_Q(1)$, we can observe the quadrupolar splitting $\Delta\nu_Q$ with the expression

$$\Delta\nu_Q = \omega_Q(1) = \frac{3\pi C_Q}{2I(2I-1)} \times (3\cos^2\theta_Q - 1), \quad (2.4)$$

where $\omega_Q(1)$ is the first order quadrupolar coupling, C_Q is the quadrupolar coupling constant, and θ_Q is the angle between the principle axis of the efg tensor V_{zz} and the magnetic field B_0 .^[7] For deuterium, the quadrupolar coupling constant $C_Q = e^2qQ/h$, where e is the elementary charge, approximately equals 1.606×10^{-19} C, where eq is the largest magnitude of the electric field gradient tensor, and eQ is the electric quadrupolar moment.^[7] Spin-1 spectra for isotropic liquid, nematic liquid crystal and solid powder are shown in **Figure 2.5a**.^[7] The isotropic liquid in **Figure 2.5a(1)** shows a singlet with zero quadrupolar splitting since the first-order quadrupole coupling $\omega_Q(1)$ vanishes due to rapid molecular tumbling.^[7] However, the quadrupolar splitting is observable for liquid

crystals in **Figure 2.5a(2)** with doublet splitting of $\Delta\nu_Q$.^[7] In solids, the splitting between “parallel” outermost shoulders is $3C_Q/2$, and the splitting between the “perpendicular” strong inner shoulders is $3C_Q/4$ as shown in **Figure 2.5a(3)**.^[7] The molecules possess all orientations with respect to the magnetic field B_0 , which contributes to a distribution of first-order splittings $\omega_Q(1)$.^[7] Thus, the observed broad “powder” spectrum has a characteristic shape, called a *Pake doublet*, in the common case of a uniaxial *efg* tensor ($\eta_Q = 0$).^[7]

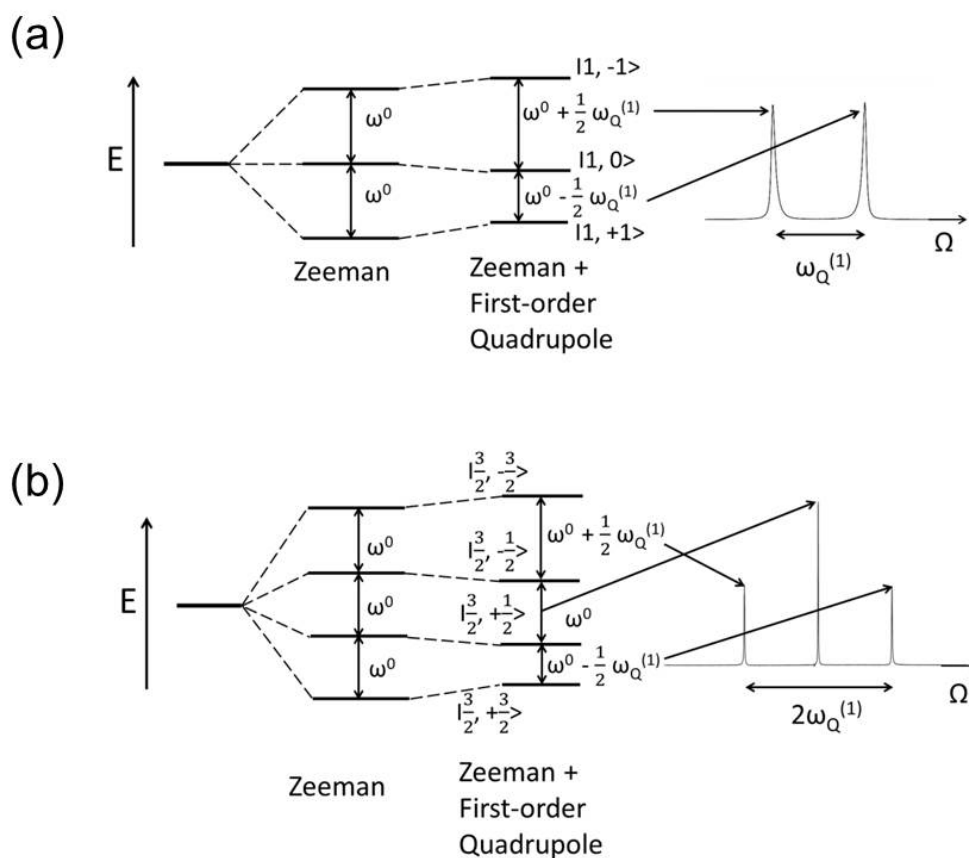


Figure 2.4. Energy level diagrams and resulting NMR spectra for a nuclei with spin quantum number $I = 1$ or $3/2$. (a) a spin-1 nucleus and (b) a spin-3/2 nucleus. The ratio of integration peak area should be 3:4:3.

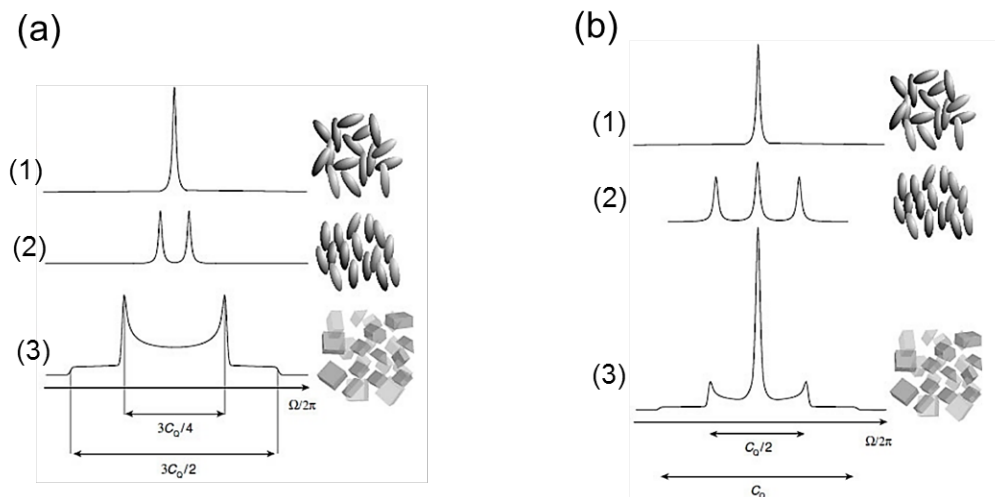


Figure 2.5. Quadrupolar NMR spectra for different phases, including isotropic liquid, liquid crystal and powder (polycrystalline) solid. (a) Appearance of spin-1 spectra for (1) Isotropic liquid; (2) Nematic liquid crystal; (3) Solid powder. (b) Appearance of spin-3/2 spectra for (1) Isotropic liquid; (2) Nematic liquid crystal; (3) Solid powder. Figure reproduced from ref. 7.

Alkali metals often possess spin-3/2 nuclei. For example, the nuclear spin energy states of ^{23}Na are shown in **Figure 2.4b**. For a spin-3/2 nucleus, there are four eigenstates of angular momentum along the z-axis, denoted with $+3/2$, $+1/2$, $-1/2$ or $-3/2$.^[7] The first-order quadrupolar coupling $\omega_Q(1)$ contributes to the energy shift of the four eigenstates observed in the Zeeman splitting. If $\omega_Q(1)$ is positive, the states $|\frac{3}{2}, \pm\frac{3}{2}\rangle$ are shifted upwards by $\omega_Q(1)/2$, while the $|\frac{3}{2}, \pm\frac{1}{2}\rangle$ are shifted down by $\omega_Q(1)/2$. Similar to the spin-1 case, and as depicted in **Figure 2.5b**, there is no quadrupolar splitting for a spin-3/2 in an isotropic liquid. For an anisotropic (LC) liquid, a triplet with peak integration of

3:4:3 can be observed for spin-3/2. For solid powders, the broad powder pattern is generated by assuming the uniaxial electric field gradient tensor $\eta_Q = 0$. The splitting between the “parallel” shoulders is C_Q , and the splitting between the sharp shoulders is $C_Q/2$. The central transition is not affected by the first-order quadrupolar coupling and appears as a central peak of the powder pattern.^[7]

^2H NMR spectroscopy on labeled probe molecules in anisotropic matrices has been widely used to determine orientational ordering in a diverse array of aligned materials including liquid crystals, wormlike micelles, intact wood cell walls, stretched polymers, and fuel-cell polymer electrolyte membranes.^[7,9-12] Li *et al.* studied the ^2H NMR of D_2O molecules in Nafion with different draw ratios.^[9,13] As shown in **Figure 2.6**, the quadrupole splitting $\Delta\nu_Q$ shows alignment of the water molecules inside the hydrophilic channels of Nafion® membrane.^[9] The quadrupole splitting ($\Delta\nu_Q$) for a uniaxially symmetric phase, defined as the distance between the doublet peaks, is expressed as

$$\Delta\nu_Q = Q_P S_{\text{O-D}} \left(\frac{3\cos^2\theta - 1}{2} \right) = Q_P \rho S_{\text{matrix}} \left(\frac{3\cos^2\theta - 1}{2} \right), \quad (2.5)$$

where Q_P is the quadrupole splitting (≈ 255 kHz) for D_2O molecules corresponding to the situation where all O-D bonds are perfectly aligned with B_0 .^[6,11] $S_{\text{O-D}}$ is the ensemble average orientational order parameter for the O-D bond with respect to the aligned hydrophilic polymer domain or matrix.^[6] θ is the angle between the director of polymer hydrophilic domains and the B_0 direction.^[6] S_{matrix} refers to the orientational order parameter for the hydrophilic channel matrix.^[6] The scaling factor ρ represents the coupling interaction between the deuterium probe molecules and the polymer matrix.^[6] ρ is often relatively insensitive to temperature in oriented systems, whereas, it is highly

sensitive to the water uptake of the system.^[6] With increasing draw ratio L of the Nafion membranes from 1 to 4, the quadrupole splitting increases from ~ 50 to ~ 1000 Hz as shown in **Figure 2.6**, which indicates the increasing S_{matrix} of the polymer matrix.^[9,13] ^2H NMR is efficient to study the mobile species in the aligned polymeric materials. In my project, PBDT forms a water-miscible system with D_2O , thus ^2H NMR can conveniently detect the molecular alignment of PBDT polymer chains based on the probe molecule D_2O .

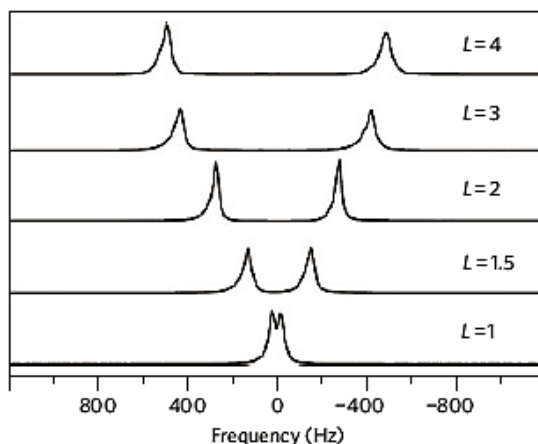


Figure 2.6. ^2H NMR spectra of D_2O inside Nafion Membranes with increasing draw ratio L , ranging from 1 to 4. Figure reproduced from ref. 9.

Furthermore, ^{23}Na is another useful quadrupolar nucleus for detecting orientational order in polymeric materials. ^{23}Na NMR spectroscopy has been employed to study the LC phase of DNA aqueous solutions with Na as the counterion.^[14] As shown in **Figure 2.7**, triplet spectra of ^{23}Na will be observed for DNA aqueous solutions above the critical concentration for forming the lyotropic nematic LC phase.^[14] The value of the

quadrupole splitting indicates the degree of orientation of DNA in aqueous solutions. At 20°C, the quadrupole splitting decreases with increasing DNA concentration. However, at 60°C, the quadrupole splitting is proportional to the DNA concentration.^[14] The unique relationships between the quadrupole splitting and the DNA concentration are strongly correlated with the temperature of the environment. Thus, we can conclude that the interaction between the quadrupole moment of Na and the *efg* of the Na environment is closely associated with the polymer concentration as well as the temperature. Similarly, we are combining ^{23}Na NMR and NMR diffusometry to investigate the association and transport of Na^+ counterions in PBDT solutions. We observe many similarities between DNA and PBDT solutions, which we discuss in detail in Chapter 4.

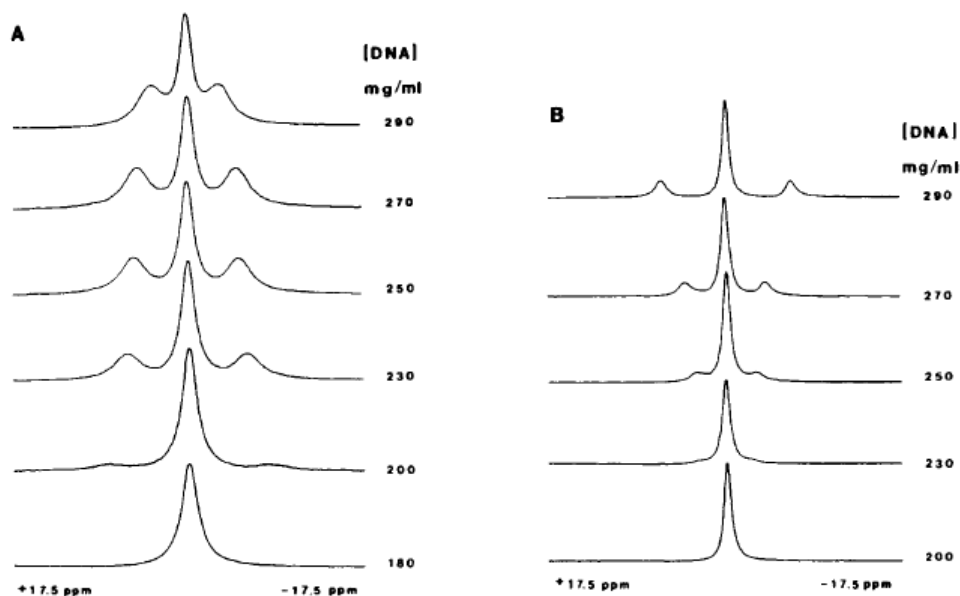


Figure 2.7. The quadrupole splitting of ^{23}Na DNA aqueous solutions as a function of concentration and temperature. (A) at 20 °C and (B) at 60 °C. Note that the quadrupole splitting decreases with increasing concentration at 20 °C, whereas it increases with

concentration at 60 °C. These different dependencies show similarities with our observations of Na splittings in PBDT, as described in Chapter 4 (Figure 4.2). Figure reproduced from ref. 14.

2.3 Direct Dipole-dipole Coupling by ^1H NMR

Direct intramolecular dipole-dipole coupling gives additional information about the anisotropic properties of LCs and LC ion gel materials, especially for absorbed mobile species such as cations and anions. Based on a comprehensive understanding of the nuclear quadrupole and *internuclear* dipole-dipole interactions, we can get a clearer image of the investigated system. The direct dipole-dipole coupling refers the direct *intramolecular* or *intermolecular* interaction between two nuclei, shown in **Figure 2.8a**.^[7] The magnetic field generated by one spin will interact through space with the second spin. If the spins are of the same isotopic species, the secular dipole-dipole coupling is expressed as

$$d_{ij} = b_{ij} \frac{1}{2} (3\cos^2\theta_{ij} - 1), \quad (2.6)$$

where θ_{ij} is the angle between the internuclear vector and the external magnetic field.^[7] b_{ij} is the dipole-dipole coupling constant with expression $b_{ij} = -\frac{\mu_0}{4\pi} \frac{\gamma_i \gamma_j \hbar}{r_{ij}^3}$.^[7] γ_i is the gyromagnetic ratio of the specific nucleus. The equation 2.6 is the simplified expression of dipole-dipole coupling based on the “secular approximation”, which is valid in high magnetic fields and simplifies the Hamiltonian by only retaining the components parallel to the z axis. First, in terms of isotropic liquids, the *intramolecular* dipole-dipole coupling

is averaged out due to the extremely fast tumbling rate of the molecules relative to b_{ij} .^[7] The short-range *intermolecular* dipole-dipole coupling is also averaged to zero, while the long-range dipole-dipole coupling is very small and it can be ignored as well.^[7] Second, in an anisotropic liquid, the short range *intermolecular* dipole-dipole coupling is averaged out by the rapid diffusional motion. The long-range *intermolecular* dipole-dipole coupling survives, but is very small and can be usually ignored.^[7] However, the *intramolecular* dipole-dipole coupling does not average out. Dipole-dipole coupling in a liquid crystal is described in **Figure 2.8b**.^[7]

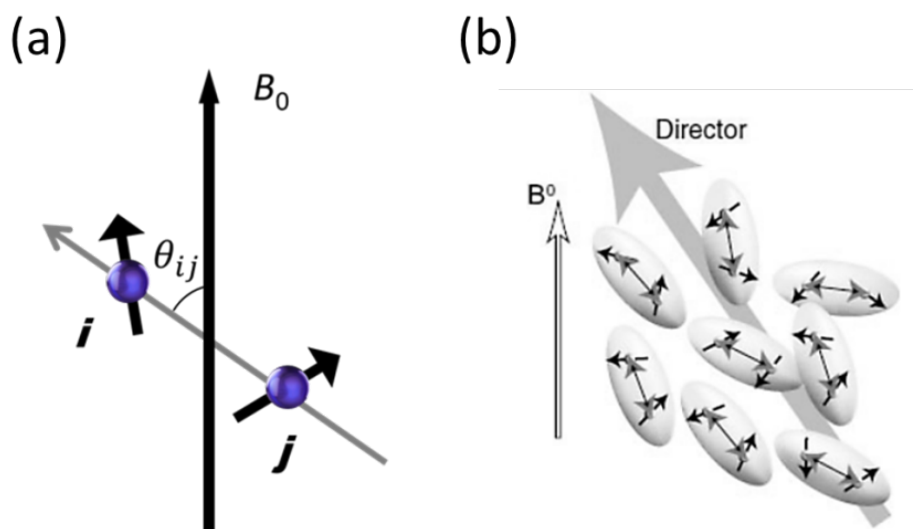


Figure 2.8. Dipole-dipole coupling in liquid crystals. (a) Secular dipole-dipole coupling. “Secular approximation” is considered here and used to simplify the expression of equation 2.6. (b) Dipole-dipole coupling in a liquid crystal. Part b reproduced from ref. 7.

In 1971, Samulski *et al.* utilized nematic polypeptide liquid crystals to study the alignment status of the probe solvent molecule - dimethylformamide.^[15] The

intramolecular direct dipole-dipole coupling was observed as shown in **Figure 2.9**.^[15] The protons of DMF are labelled as A, B, and C. The interactions between the aligned polymer chains and the solvent molecules contribute to observable intramolecular direct dipole-dipole couplings including $\Delta\nu_{AA}$, $\Delta\nu_{AX}$, $\Delta\nu_{BB}$, and $\Delta\nu_{BX}$.^[16] According to these coupling results, the orientational tensor of the solvent inside the polymer solution can be further resolved. Also, by using this technique, we can get detailed geometric information of the probe molecules inside the nematic LC phase. According to Equation 2.6, the splittings are only dependent on the internuclear distance r_{ij} and the θ_{ij} . From the absolute value of the splittings, we can also infer the orientational order of the aligning matrix.

In our PBDT-IL ion gels (Chapter 5), we expect elucidate the alignment of ionic liquid molecules in the PBDT supporting matrix based on the intramolecular dipole-dipole coupling. Chapter 5 describes these studies in detail.

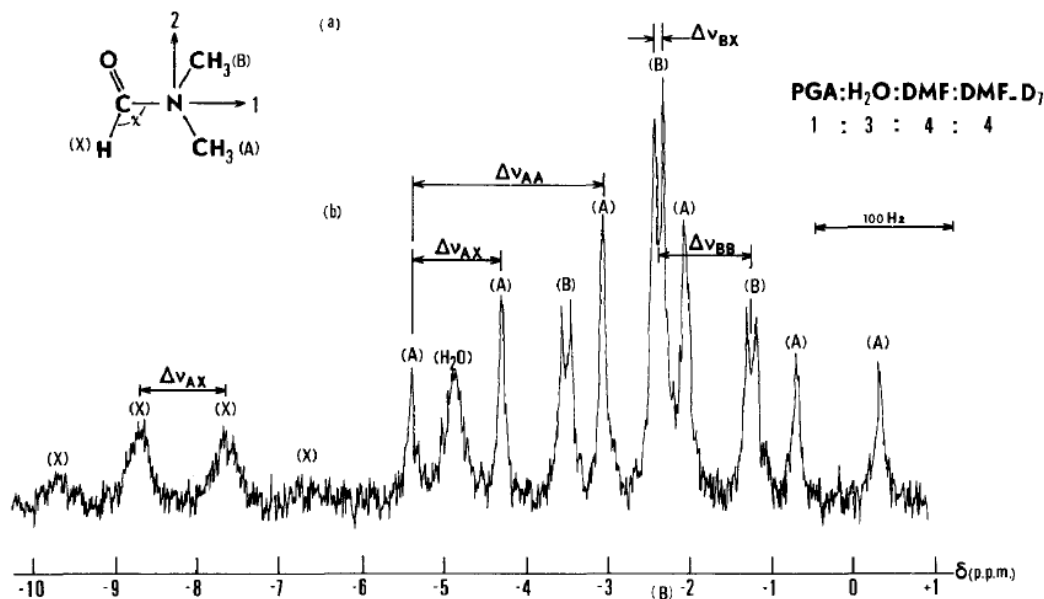


Figure 2.9. The direct dipole-dipole coupling of DMF inside the highly aligned polypeptide nematic LC phase. Figure reproduced from ref. 16.

2.4 Multi-nuclear and Multi-axis NMR Diffusometry

NMR diffusometry is an accurate and convenient technique to quantify diffusion coefficients of separate mobile species including anions, cations, and water molecules absorbed in hydrophilic aggregations of bulk polymer, generally with accuracy and precision errors in the range of 2 to 10%.^[6,9,10,12,13,17] We can obtain diffusion coefficients of absorbed species inside the PBDT bulk matrix along multiple axes. To avoid artifacts and maintain sufficient signal strength, we generally apply simple and robust diffusometry pulse sequences, such as the pulsed-gradient spin echo (PGSE) and the pulsed-gradient stimulated-echo (PGSTE).^[18] These pulse sequences are shown in the **Figure 2.10**. The observed signal strength in PGSE is T_2 (transverse spin relaxation)

limited, whereas PGSTE is mostly T_1 (longitudinal spin relaxation) limited. The PGSE and PGSTE give similar results for small molecule systems, which usually have similar magnitudes of T_1 and T_2 .^[18] However, most polymeric, liquid crystalline, or nanostructured systems exhibit $T_1 > T_2$. Therefore, we tend to use PGSTE, which yields higher signal noise ratio (SNR) compared to PGSE since PGSTE stores magnetization along the Z direction during the diffusion encoding time Δ . For both of these experiments, the NMR signal attenuation due to diffusion follows the Stejskal-Tanner equation^[18]

$$I = I_0 e^{-D\gamma^2 g^2 \delta^2 (\Delta - \frac{\delta}{3})}, \quad (2.7)$$

where I and I_0 refer to the spin-echo signal intensity and spin-echo signal intensity at zero gradient, respectively. γ is the gyromagnetic ratio of the nucleus, g is the gradient strength, δ is the pulse duration time and Δ is the diffusion time. Thus, diffusion coefficients (D) of a desired nucleus can be obtained by fitting the experimental I vs. g data using Equation 2.7.^[18] The T_1 (by inversion-recovery) and T_2 (by CPMG spin echo) values for the samples under study are obtained first, and then all diffusion parameters are properly selected ($\Delta < 1.5T_1$, $\delta < T_2$) to ensure sufficient SNR.^[17]

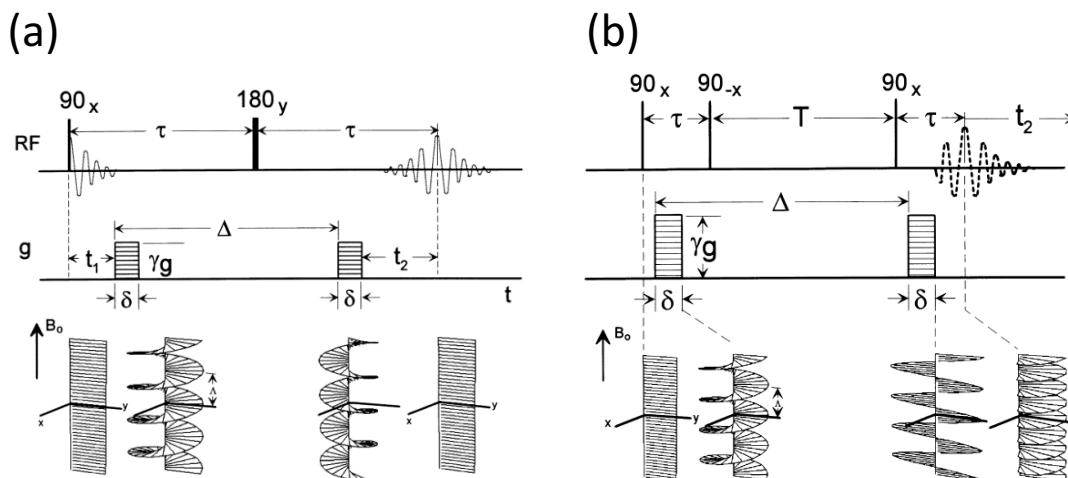


Figure 2.10. PGSE and PGSTE NMR diffusometry pulse sequences. (a) The simple spin echo (SE, also called the “Hahn echo”). (b) The stimulated echo (STE). The upper lines labeled with “RF” represent radiofrequency NMR pulses. The lower lines labeled with “ g ” represent the pulsed magnetic field gradients. Figure reproduced from ref. 18.

Multi-nuclear NMR diffusometry can be used to selectively detect diffusion coefficient of different species inside the system. Madsen *et al.* have studied the diffusion coefficients of water, cation, and anion in Nafion® membranes.^[9,10,12,17,19] The sealed Teflon cell shown in **Figure 2.11a**, can be utilized to control the water uptake of the samples.^[19] Figure **2.11b** and **c** show the diffusion coefficients of two ionic liquids inside Nafion® membranes with varying mole ratio of IL to water molecules.^[19] Also, by using a multi-axis PFG NMR probe and this specific sample cell, we can obtain information on diffusion anisotropy in polymer matrices by measuring the diffusion rates along different directions. The diffusion anisotropy can be expressed in some cases as $R = (D_{\parallel} - D_{\perp}) / (2D_{\parallel} + D_{\perp})$,^[9] or in many cases as simply $D_{\parallel} / D_{\perp}$. Based on the diffusion anisotropy, we can resolve more information about the alignment and morphology of the hydrophilic

aggregation. Li *et al.* reported the diffusion anisotropy of water molecules inside Nafion® membranes with increasing draw (stretch) ratios. The results are displayed in **Figure 2.12**.^[9] By using a combination of quadrupolar NMR and multi-axis PFG NMR, these researchers found a specific relationship between the draw ratio of the Nafion® and the orientational order of the polymer matrix. The diffusion anisotropy R of Nafion® is linearly proportional to the orientational order of the polymer matrix (S_{matrix}).^[9] By carefully employing the combination of quadrupolar NMR and NMR diffusometry, we can obtain a more comprehensive understanding of morphology, alignment, diffusion coefficient and ion association in many other polymeric systems.

In this project, by using NMR diffusometry, we are obtaining information about diffusion rate and diffusion anisotropy in PBDT solutions and PBDT-derived ion gels. We can measure diffusion coefficients of Na^+ counterions and water in PBDT aqueous solutions. We can also detect the aligned morphology in PBDT ion gels based on the diffusion anisotropy of absorbed ions. In summary, we have a wealth of freedom to investigate a wide array of properties in anisotropic polymeric systems containing mobile molecules.

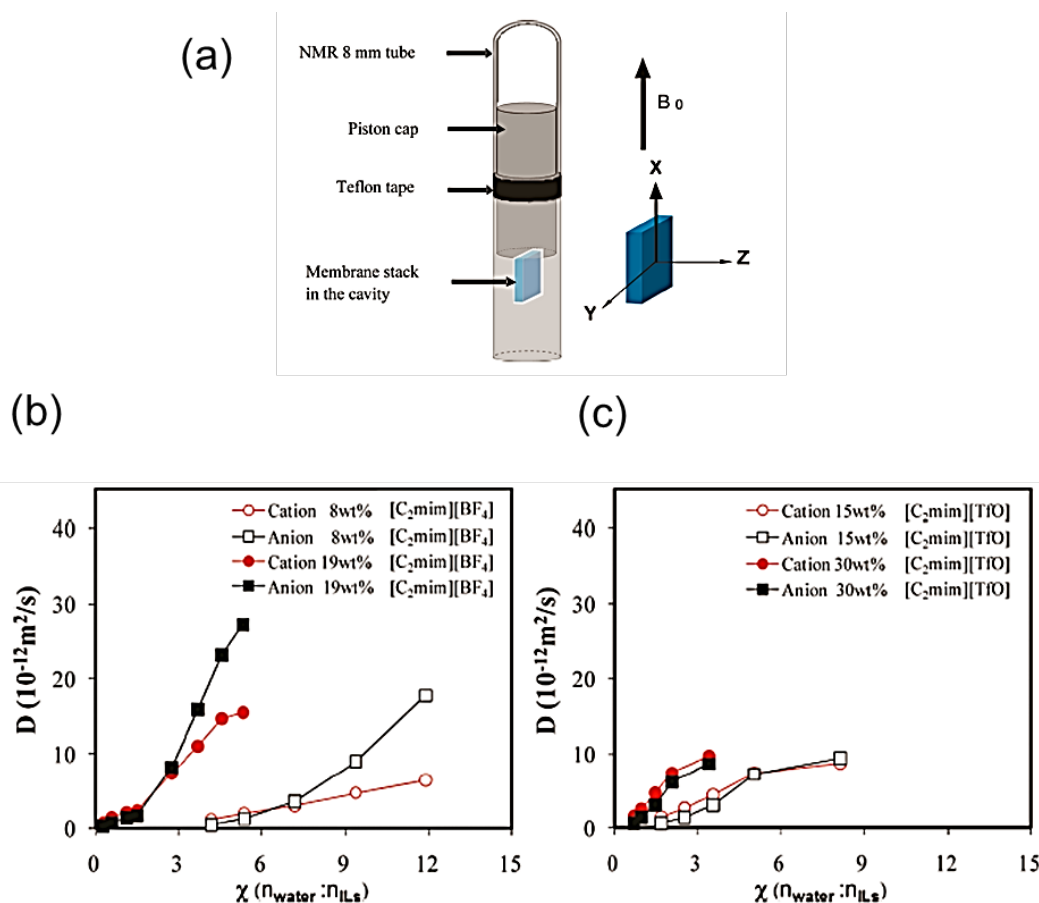


Figure 2.11. Sample cell and ionic liquid diffusion coefficients obtained from NMR diffusometry.^[19] (a) Configuration of sealed Teflon cell. (b) Cation and anion diffusion inside Nafion membrane vs. water content and with different uptakes of C_2mimBF_4 and C_2mimTfO . Figure reproduced from ref. 19.

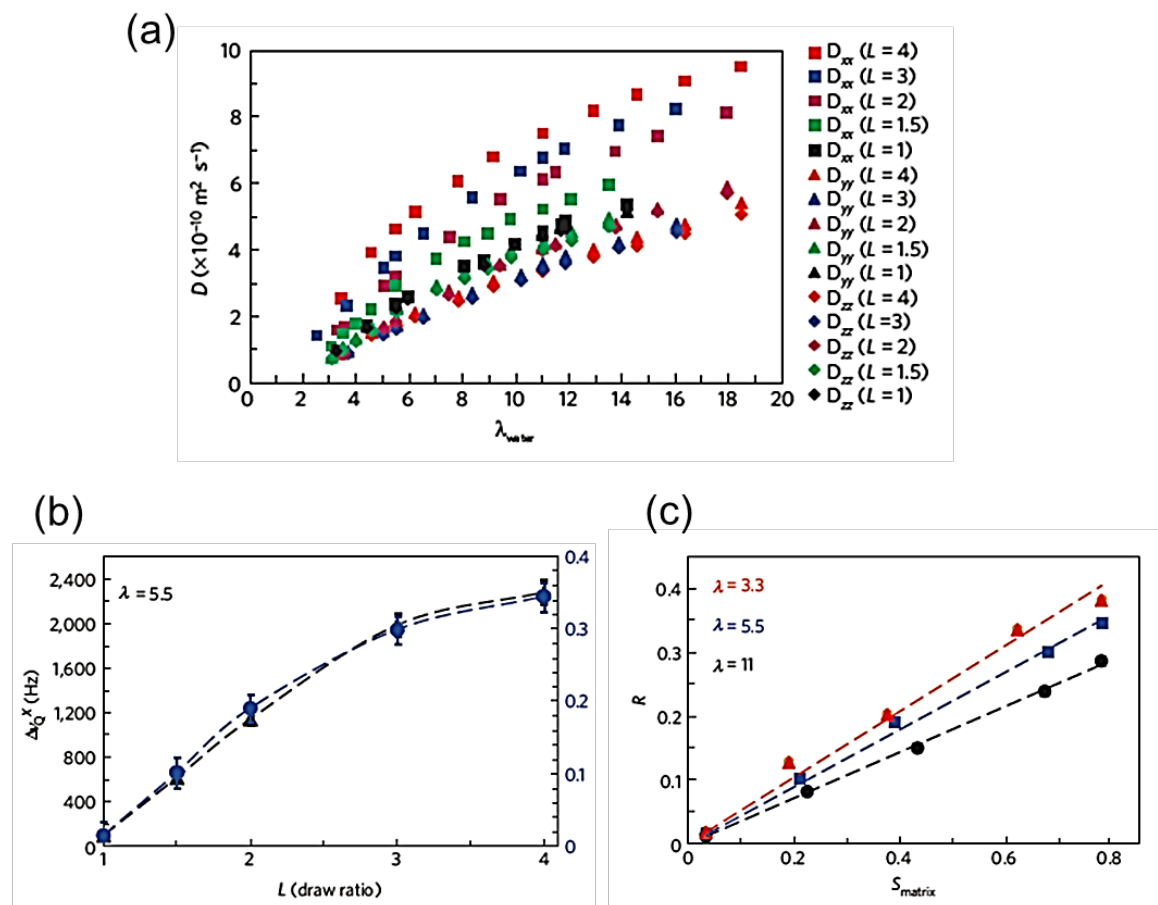


Figure 2.12. The diffusion coefficient, quadrupole splitting and diffusion anisotropy in Nafion membranes with varying draw ratio.^[9] (a) H₂O diffusion in three orthogonal directions vs H₂O uptake at different draw ratio L . (b) D₂O splitting values $\Delta\nu_Q$ and diffusion anisotropy R vs draw ratio L for Nafion® membrane at water uptake $\lambda = 5.5$ (water molecules per SO_3^- group). (c) Linear relation of S_{matrix} vs R at different water uptake. Figure reproduced from ref. 9.

2.5 X-ray Scattering and Diffraction Techniques

X-ray techniques, for example, wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS), are widely used to study the morphology of polymeric materials.^[12] X-ray fiber diffraction can be effectively employed to study the crystalline or liquid crystalline packing structure of PBDT molecular chains, as well as materials with similar aligned morphologies, such as DNA molecules. Single-crystal X-ray diffraction can easily provide precise crystalline structure of bulk crystalline materials. The main difference between SAXS and WAXD is the sample to detector distance l . WAXD tends to detect angstrom to nanometer length scales with shorter l , whereas, SAXS is usually employed to study nanometer micrometer scale domains with longer l . Single-crystal X-ray diffraction is the oldest and most precise technique compared to SAXS and WAXD. However, it requires bulk pieces of single crystalline materials, which limits its applications. The mechanism of these techniques is based on Bragg's law. Bragg's law was proposed by William L. Bragg in 1912, the expression of which is shown in **Figure 2.13**.^[20] By modeling the crystal as a set of parallel planes with a constant separation l , the incident X-ray produces a Bragg peak if the reflections from different planes constructively interfere, whereas the diffraction is cancelled if the reflections are destructive. The interference is constructive when the net phase shift of the light is a multiple of 2π . Bragg's law is then expressed as

$$m\lambda = 2l\sin\theta_{\text{Bragg}}, \quad (2.8)$$

where m is an integer, λ is the wavelength of the incident beam, l is the spacing between two crystalline planes, and θ_{Bragg} is the angle between the crystalline plane and the incident beams.^[20] Thus the angle between the incident and reflected beam is $2\theta_{\text{Bragg}}$.

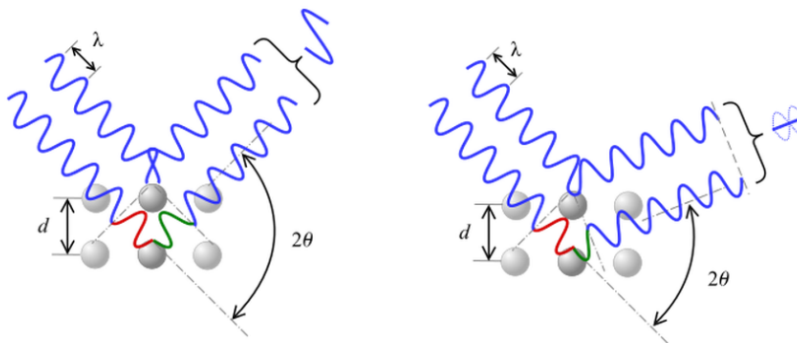


Figure 2.13. Bragg's Law. The left illustration corresponds to Bragg's law with reflections (from scattering/diffraction of the two waves off of particles on a lattice) that constructively interfere. The right illustration corresponds to destructive interference. Figure reproduced from https://en.wikipedia.org/wiki/Bragg%27s_law.

Over the past few decades, X-ray crystallography has been successfully utilized to study the self-assembled morphology of DNA molecules.^[21] The double helix assembly can be clearly illustrated by the diffraction patterns observed from DNA fibers. **Figure 2.14** shows the classical diffraction pattern of DNA molecules in aligned fibers.^[21] In this project, we also use X-ray diffraction techniques to study the self-assembled conformation and crystalline packing of PBDT polymer chains in magnetically oriented aqueous solutions and ion gels with varying polymer concentration.

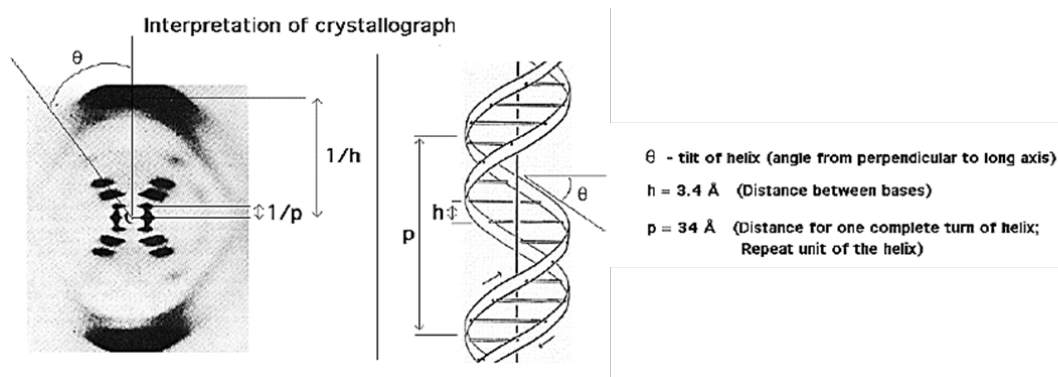


Figure 2.14. X-ray crystallography of DNA molecules in aligned fibers. The “cross” pattern and X-ray pattern dimensions are assigned to different structural features of the DNA double helix. Figure reproduced from ref. 21.

In addition to the wide angle X-ray diffraction, SAXS is also an important technique that can be used to study the ~ 10 nm scale morphology and orientation in polymeric materials, for example, the lyotropic nematic LC phase of PBDT aqueous solutions. Two-dimensional SAXS has also been successfully utilized to study the morphology and alignment in Nafion membrane as a function of draw ratio by Park *et al.*^[13] The SAXS patterns are shown in **Figure 2.15**.^[13] For **Figure 2.15a**, the outer diffuse ring at $q = 0.2 \text{ \AA}^{-1}$ is attributed to the scattering from the ionic aggregates dispersed in the PTFE matrix. The intense scattering near the beam stop is associated with heterogeneous ionic aggregate and PTFE crystalline domains. With increasing draw ratio, equatorial streaking is observed, which is consistent with the formation of a fibrillar morphology.^[13] Thus, we can infer that the fibrillary ionic aggregate domains in Nafion® membranes are aligned preferentially along the stretching direction. The scattering intensity of the ionomer peak increases along the equatorial direction as a function of the draw ratio L . To quantify the

orientational order of the ionomers, the Herman's orientation function f , also known as the polymer orientational order parameter (S_{matrix}) can be obtained through the azimuthal SAXS profiles.^[6,13] Here, $f = \frac{3\langle \cos^2 \chi \rangle - 1}{2}$, where χ is the azimuthal angle from $\chi_1 = 0^\circ$ to $\chi_2 = 180^\circ$, and the average of $\cos^2 \chi$ is

$$\langle \cos^2 \chi \rangle = \frac{\int_{\chi_1}^{\chi_2} I(\chi) \cos^2 \chi \sin \chi d\chi}{\int_{\chi_1}^{\chi_2} I(\chi) \sin \chi d\chi}, \quad (2.9)$$

where $I(\chi)$ is the intensity of the azimuthal SAXS plot (**Figure 2.16**) at specific angle χ . According to this calculation, the Herman's orientation function increases from 0.08 to 0.76 with draw ratio varied from 1.0 to 4.0 for dried Nafion membrane.^[13] Similarly, we can also conduct SAXS on PBDT aqueous solutions with increasing concentration in order to detect the lyotropic nematic LC phase and corresponding self-assembled chain alignment.

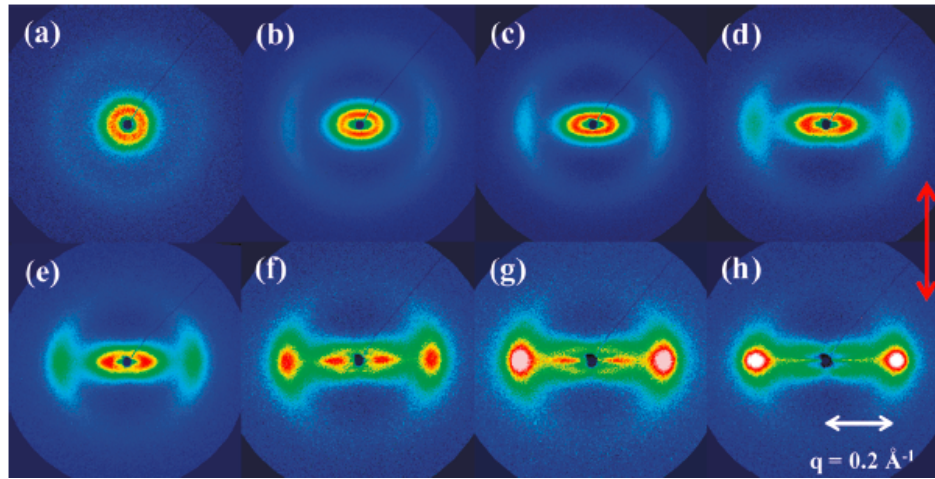


Figure 2.15. Two-dimensional SAXS patterns for acid form Nafion versus draw ratio L , where $L = (\text{final membrane length})/(\text{initial membrane length})$. (a) $L = 1.0$, (b) $L = 1.25$, (c) $L = 1.5$, (d) $L = 1.75$, (e) $L = 2.0$, (f) $L = 2.5$, (g) $L = 3.0$, (h) $L = 4.0$. The red arrow is the stretching direction. Figure reproduced from ref. 13.

SAXS can give us information about the positional and orientational order of morphological structures or molecules in LC phases and in polymeric systems. In addition, SAXS can be used to distinguish between different LC phases. The SAXS will give a graph with distinct peaks, $2\pi m/d_1$ (with integer m and rod-rod distance d_1) in one direction and $2\pi m/d_2$ (with molecular length d_2) in a normal direction. ^[5] The characteristic scattering plots for different LC phases are shown in **Figure 2.17**. SAXS can generally deliver structural information of macromolecules between 5 and 25 nm and repeat distances in partially ordered systems of up to ~ 100 nm. If the system possesses smaller or larger scale structure, we need to employ WAXD or other microscopy or imaging methods.

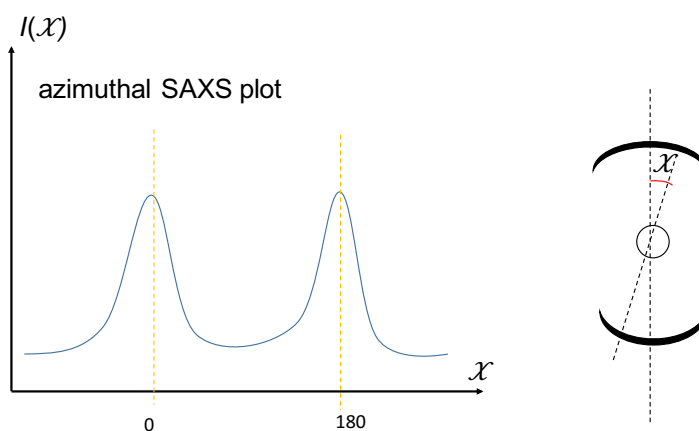


Figure 2.16. Azimuthal plot from SAXS. The y axes of the graph at left shows the intensity of the scattering pattern at azimuthal angle of χ , which is indicated in the scattering image shown at right.

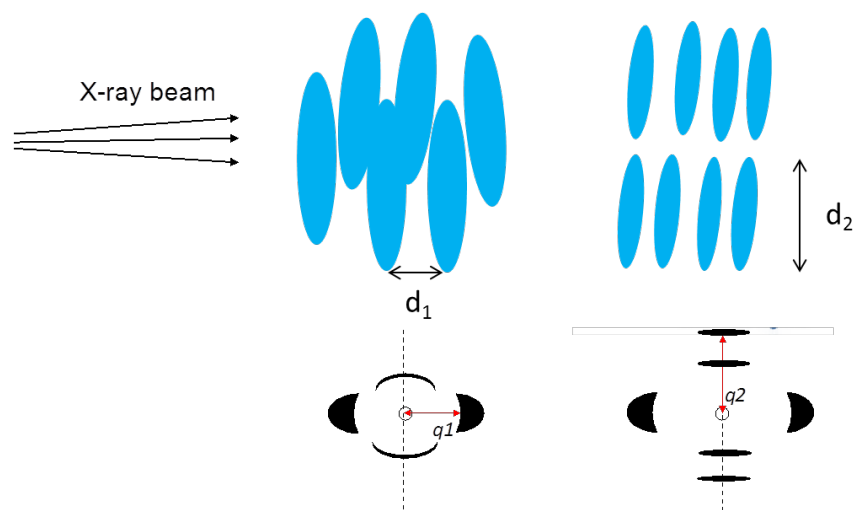


Figure 2.17. Expected SAXS results for nematic and smectic phases, respectively. The nematic phase shows simply single ordered dimension along the aligning *director* and perpendicular direction. However, the smectic phase exhibits multiple ordered dimensions along both directions.

2.6 Ionic Conductivity from Impedance Spectroscopy

In order to apply polymer electrolytes as component materials in batteries or fuel cells, the ionic conductivity should be one of the most important properties. Impedance spectroscopy (also called dielectric spectroscopy) is usually utilized to study the ionic conductivity of fuel cell membranes and battery electrolytes.^[13] Here, I will introduce impedance spectroscopy and its capability to study ionic conductivity of polymer electrolyte materials, such as fuel cell membranes and ion gels. Ionic conductivity refers to the movement of ions in an applied electric field from one position to another through defects in crystal lattice of a solid or around the liquid molecules aqueous solution.^[22] The ionic conductivity σ is calculated using the definition of the resistance shown in

equation 2.10 and 2.11, where R is the resistance of the sample (Ω), ρ is the resistivity ($\Omega \cdot \text{cm}$), A is the cross-section area perpendicular to the current flow, and h is the thickness of the membrane sample.^[13]

$$\sigma = \frac{1}{\rho} = \frac{h}{RA} \quad (2.10)$$

$$R = \frac{\rho h}{A} \quad (2.11)$$

Figure 2.18 displays the functions of electric potential E (Voltage) and I (Current) versus time, the Randles equivalent circuit, the Nyquist plot and the Bode plot, which are all analytical results that can be generated by impedance spectroscopy.^[23] The membrane resistance is determined by the real Z -axis intercept of the complex impedance plot, or more specifically the real Z value when the phase angle ϕ equals 0, which is denoted as R_{ct} . By varying the orientation of the sample between the electrodes, we can get the conductivities of polymer electrolytes along different directions. The anisotropy can be denoted as the ratio of $\sigma_{\parallel}$ to $\sigma_{\perp}$. Meanwhile, the conductivity anisotropy can also provide evidence for and show correlations with aligned morphologies in ion conductive materials as measured by other techniques, such as X-ray diffraction, NMR diffusometry, quadrupolar NMR and POM.

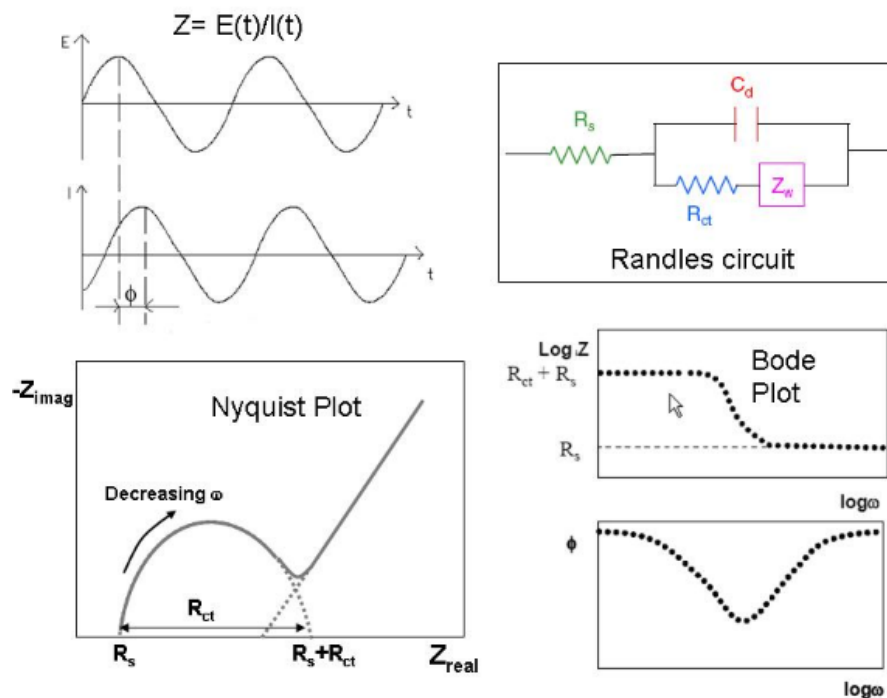


Figure 2.18. Impedance functions and typical equivalent circuit at the electrochemical interface, as shown by a Nyquist plot, Bode plot, and Randles circuit. Figure reproduced from ref. 23.

2.7 Thermal and Mechanical Properties from DSC, TGA and DMTA

In addition to ionic conductivity, we can evaluate phase transitions, decomposition temperature and weight loss percentage of PBDT and PBDT-derived materials by some traditional polymer characterization methods. The most common techniques include differential scanning calorimetry (DSC)^[24] and thermogravimetric analysis (TGA)^[25]. DSC is a thermal analysis technique, which detects the difference in amount of enthalpy (ΔH) required to compensate the sample in order to maintain the same temperature as compared to the control reference. DSC can efficiently provide information such as

phase transition and glass transition temperatures of polymeric materials. TGA is another thermal evaluation technique to study physical and chemical properties of materials as a function of increasing temperature. TGA can provide information about various phase transitions, including vaporization, sublimation, absorption, and desorption. Thus, TGA is usually employed to estimate the thermal stability of a material. If the sample is thermally stable over a certain temperature range, there will be no observed mass loss. Little or no slope will be shown in the TGA trace. In short, TGA can usually indicate the maximum useable temperature of a material in a real application. However, note that TGA is a dynamic method, and thus it cannot necessarily show the long-term useable temperatures for polymeric materials. Static measurements at a certain T over enough long time are also required to verify the thermal stabilities of materials.

In order to test the mechanical properties of PBDT-derived polymer electrolytes, dynamic mechanical thermal analysis (DMTA) can be employed to study the elastic modulus of these materials. As we mentioned previously, strong mechanical strength is required to counteract Li dendrite growth on the anode of Li-metal batteries. DMTA is a useful technique to study viscoelastic properties, glass transitions, and complex modulus of a material. Viscoelastic properties can be studied by applying an oscillating stress to a sample, and a corresponding strain will be detected.^[26,27] For a perfectly elastic solid, the induced strain is perfectly in phase with the input strain. For a viscous fluid, the strain will have a 90 degree lag with respect to the stress. To understand the mechanism of the DMTA technique, I will introduce the Equation 2.12 and 2.13 as follows, which represent the relationship between the applied stress and the induced strain of a material.

$$\sigma = \sigma_0 \sin (t\omega + \delta) \quad (2.12)$$

$$\epsilon = \epsilon_0 \sin (tw) \quad (2.13)$$

Here, σ is the stress applied to the sample, ϵ is the induced strain of the sample, t is the time over which the stress is applied to the sample, w is the oscillation frequency of the strain, and δ is the phase lag between stress and strain.

The complex modulus including storage modulus, loss modulus and the phase angle are expressed as

$$\text{Storage Modulus: } E' = \frac{\sigma_0}{\epsilon_0} \cos \delta \quad (2.14)$$

$$\text{Loss Modulus: } E'' = \frac{\sigma_0}{\epsilon_0} \sin \delta \quad (2.15)$$

$$\text{Phase Angle: } \delta = \arctan \frac{E''}{E'} \quad (2.16)$$

The storage modulus indicates the elastic property of the (isotropic) material, whereas, the loss modulus indicates the viscosity of the material. All of these properties are temperature (T) and frequency (w) dependent. Note that an anisotropic material can have more than one complex modulus.

Based on the literature reviews introduced in Chapter 1 and characterization methods illustrated in Chapter 2, we have gained a systematic understanding of the fabrication and characterization of aligned systems with various ion species present. I will introduce my research plan in the remaining Chapters. Chapter 3 introduces the self-assembled morphology and ion transport of PBDT aqueous solutions. Chapter 4 investigates the crystalline packing structure of PBDT polymer chains by molecular dynamic simulation,

SAXS and NMR techniques. Chapter 5 illustrates development and characterization of ion gel polymer electrolytes based on PBDT solutions and ionic liquids. Chapter 6 describes the successful application of the gel electrolytes in Li battery devices.

2.8 Combination of Techniques to Understand the Relaxation of Polymeric Materials

2.8.1 Glass Transition Temperature

Glass transition temperatures (T_g) of polymeric materials can be revealed by NMR, DSC and DMTA, or combinations of these techniques.

DSC and DMA are traditional techniques to study T_g in polymeric materials. However, the obtained value of T_g is highly dependent on the experimental conditions, such as sample preparation, heating rate and tensile modulation frequency.

Temperature-dependent NMR can be used to study the T_g of polymeric materials. T_1 (spin-lattice relaxation) and T_2 (spin-spin relaxation) relaxation of proton NMR can be measured to indicate the motions of polymer chain segments. The example shown in **Figure 2.19a** displays the T_1 and T_2 relaxation times as a function of temperature for amorphous maltodextrin in varying moisture.^[28] The turning points on the plots for T_1 and T_2 as a function of temperature indicate the value of T_g . It is concluded that the temperature dependence of proton T_2 relaxation is insignificant when the temperature is lower than T_g , but will show significant increase with temperature above T_g . T_1 relaxation time will decrease with temperature below T_g , whereas it will increase with temperature above T_g . **Figure 2.19b** shows the corresponding T_g values obtained from NMR relaxation methods (T_1 and T_2) along with DSC.

We can observe that T_g obtained from DSC is higher than that obtained from NMR relaxation experiments. This can be explained by using different heating rate for the two techniques. The heating rate of DSC is 5°C/min, which is higher than the “quasi static” NMR relaxation methods where temperature is held constant before and during the measurement for at least many seconds if not minutes or hours. In other words, in NMR techniques the samples are allowed to equilibrate under a specified temperature for a long time. Based on the concept of “internal consistency”, the T_g from NMR relaxation techniques should in general be lower than results obtained from traditional DSC and DMTA techniques.

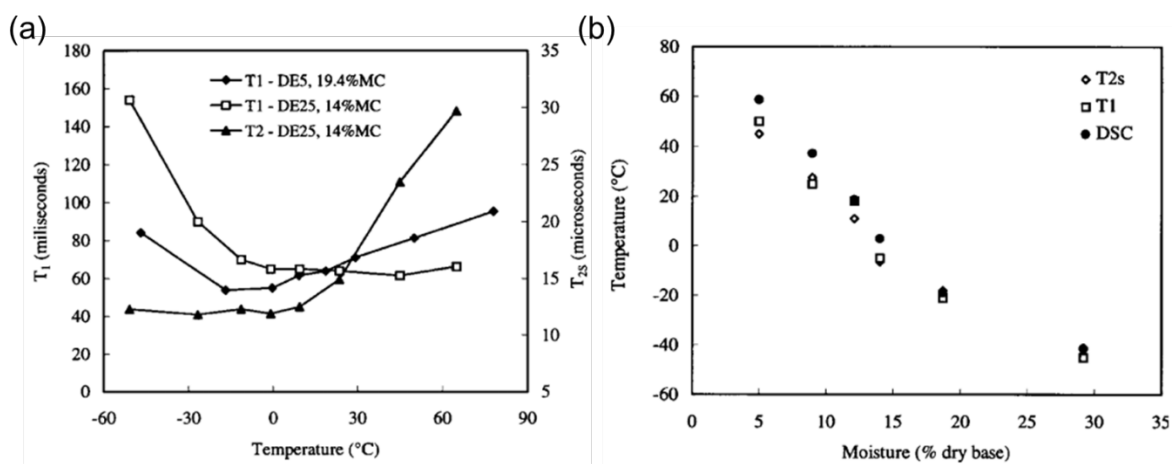


Figure 2.19. T_g of hydrated maltodextrin obtained by NMR and DSC. (a) T_1 and T_2 of hydrated maltodextrin as a function of temperature. The turning point of T_1 and T_2 values vs. T indicate the glass transition temperature. (b) Glass transition temperatures obtained from T_1 , T_2 and DSC. Figure reproduced from ref. 28.

2.8.2 Phase Transition Behavior

Phase transition behavior of liquid crystal polymers can be verified by information obtained from different characterization techniques, for example, the splittings and chemical shifts of NMR spectroscopy, the diffraction of XRD and heat flow of DSC.

XRD and DSC are common techniques to detect the phase transitions of LC polymers. LC polymers can display different LC phases over different temperature ranges. For example, **Figure 2.20** shows typical XRD patterns for a nematic LC phase and an isotropic phase, respectively. The DSC curve shown in **Figure 2.21** corresponds to various transitions of the LC, such as glassy, smectic and isotropic states, as a function of temperature.

In addition, quadrupole NMR is very useful technique to investigate LC phases of polymeric materials. For example, we usually observe doublet splittings in ^2H NMR spectra for an anisotropic LC phase. With increasing temperature, the LC phase will transition into an isotropic phase, which manifests as a singlet peak in the ^2H NMR spectrum, as shown in **Figure 2.20**. Meanwhile, proton NMR for LC phase is also highly dependent on the temperature, showing chemical shift jumps at specific transitions.

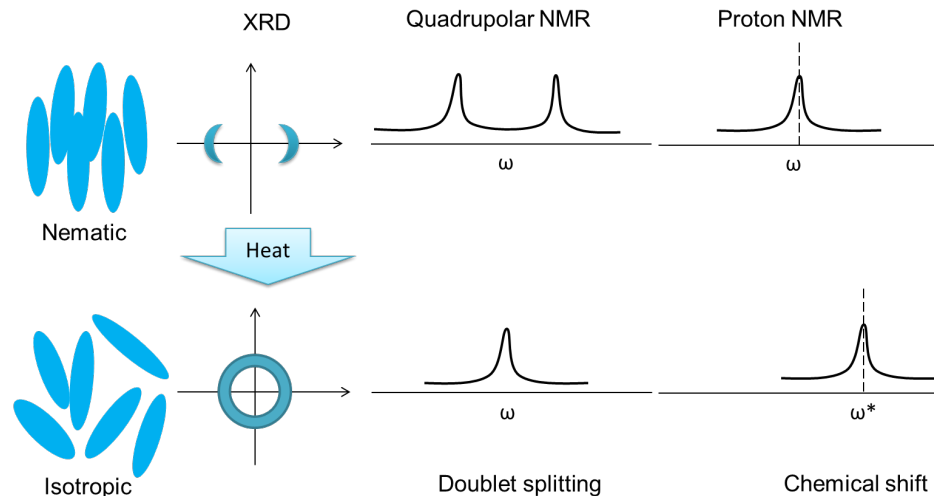


Figure 2.20. The corresponding spectra of X-ray diffraction, ^2H NMR and proton NMR for isotropic and nematic phases. Nematic phase can transition into isotropic phase by increasing temperature of the system. The transition can be demonstrated by various methods, including XRD (Scattering arcs to amorphous halo), ^2H NMR (Doublet splittings to singlet splitting) and proton NMR (Jump of chemical shift).

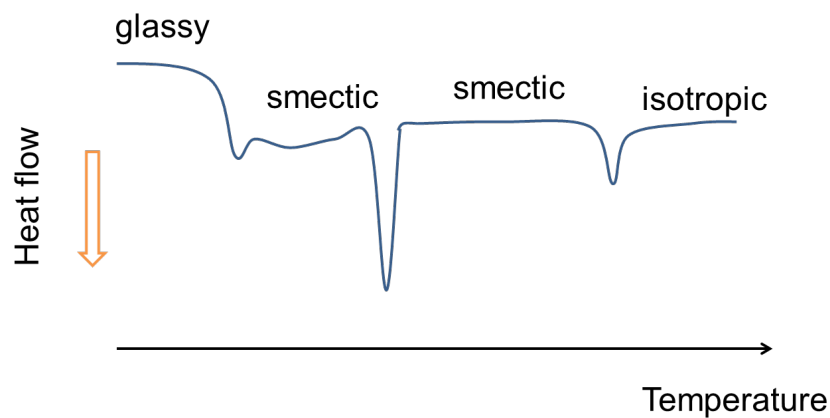


Figure 2.21. The DSC curve of phase transitions in liquid crystals.

Madsen *et al.* reported substantial difference in Tg of PEO obtained from NMR(T₁ relaxation) as compared to DSC.^[29] The information obtained from NMR, such as T₁, T₂, quadrupole splitting, indicates “static” properties of materials. Similarly, XRD indicates morphology and structure at near zero cooling rates. However, DSC can only provide temperature or frequency dependent properties of the LC phases, which is the main limitation for the thermal dynamic methods.

2.8.3 Particle Dimension and Transport in Polymer Solutions

We can use NMR diffusometry and/or dynamic light scattering (DLS) to study the particle or molecule dimension (size) and transport of mobile species in polymer solutions. First, I will briefly introduce these two techniques. DLS can be used to study the dimension and distribution of particles based on the light fluctuation obtained from scattering of particles in polymer solutions. The obtained dimension is the hydrodynamic diameter of the particles. The swelling property of particles can also be studied by varying the temperature or solution quality in DLS experiments.

NMR diffusometry can also be used to study the diffusion coefficient, dimension, and distribution of polymer chains in solutions. The diameter of the polymer particle can be obtained from the Stokes-Einstein equation as

$$D = kT/6\pi\eta, \quad (2.17)$$

where D is the diffusion coefficient of the particle, k is Boltzmann’s constant, T is the temperature, η is the viscosity of the solvent medium, and r is the hydrodynamic radius of the diffusing particle. The hydrodynamic radius of a particle refers to the solvated radius of the particle in specific solvent, which cannot directly represent the real dimension of

the particles. The radius obtained from NMR diffusometry should be approximately equal to the radius obtained from DLS technique. NMR diffusometry with varying temperature and/or solvent quality also allows us to detect the morphological variation of particles in polymer solutions.

2.9 Summary

Understanding both molecular alignment and ion dynamics can increase the freedom to design ion-conducting polymeric materials, and thus enhance sustainable energy supplies such as battery electrolytes, fuel cells, artificial muscles, and reverse osmosis membranes. This chapter has introduced a wide variety of characterization methods and associated concepts to study anisotropic polymeric materials. These methods include POM, SEM, WAXD, SAXS and quadrupolar NMR to study orientational order of molecules and morphology, DSC, TGA and DMTA to study bulk thermal, stability, and mechanical properties, NMR diffusometry to study molecular (including ionic) transport, and IS to study the ionic conductivity.

References

- [1] Gresham, K. D.; Mchugh, C. M.; Bunning, T. J.; Crane, R. L.; Klei, H. E.; Samulski, E. T., Phase-Behavior of Cyclic Siloxane-Based Liquid-Crystalline Compounds, ***Journal of Polymer Science Part a-Polymer Chemistry***, **1994**, 32, 2039.
- [2] Nishikawa, E.; Samulski, E. T., New mesogens with cubic phases: hydrogen-bonded bipyridines and siloxane-containing benzoic acids - I. Preparation and phase behaviour, ***Liquid Crystals***, **2000**, 27, 1457.
- [3] Inoue, S.; Oldenbourg, R., Microtubule dynamics in mitotic spindle displayed by polarized light microscopy, ***Molecular Biology of the Cell***, **1998**, 9, 1603.
- [4] Carraher, C. E. *Seymour/Carraher's Polymer Chemistry: Sixth Edition*; Taylor & Francis: 2003.

- [5] Wu, Z. L.; Arifuzzaman, M.; Kurokawa, T.; Le, K.; Hu, J.; Sun, T. L.; Furukawa, H.; Masunaga, H.; Gong, J. P., Supramolecular Assemblies of a Semirigid Polyanion in Aqueous Solutions, *Macromolecules*, **2013**, *46*, 3581.
- [6] Wang, Y.; Gao, J.; Dingemans, T. J.; Madsen, L. A., Molecular Alignment and Ion Transport in Rigid Rod Polyelectrolyte Solutions, *Macromolecules*, **2014**, *47*, 2984.
- [7] Levitt, M. H. *Spin Dynamics: Basics of Nuclear Magnetic Resonance*; Wiley: 2001.
- [8] Levitt, M. H.; Suter, D.; Ernst, R. R., Spin Dynamics and Thermodynamics in Solid-State Nmr Cross Polarization, *Journal of Chemical Physics*, **1986**, *84*, 4243.
- [9] Li, J.; Park, J. K.; Moore, R. B.; Madsen, L. A., Linear coupling of alignment with transport in a polymer electrolyte membrane, *Nature Materials*, **2011**, *10*, 507.
- [10] Li, J.; Wilmsmeyer, K. G.; Hou, J. B.; Madsen, L. A., The role of water in transport of ionic liquids in polymeric artificial muscle actuators, *Soft Matter*, **2009**, *5*, 2596.
- [11] Li, J.; Wilmsmeyer, K. G.; Madsen, L. A., Hydrophilic channel alignment modes in perfluorosulfonate ionomers: Implications for proton transport, *Macromolecules*, **2008**, *41*, 4555.
- [12] Li, J.; Wilmsmeyer, K. G.; Madsen, L. A., Anisotropic Diffusion and Morphology in Perfluorosulfonate Ionomers Investigated by NMR, *Macromolecules*, **2009**, *42*, 255.
- [13] Park, J. K.; Li, J.; Divoux, G. M.; Madsen, L. A.; Moore, R. B., Oriented Morphology and Anisotropic Transport in Uniaxially Stretched Perfluorosulfonate Ionomer Membranes, *Macromolecules*, **2011**, *44*, 5701.
- [14] Strzelecka, T. E.; Rill, R. L., A Na-23-Nmr Study of Sodium DNA Interactions in Concentrated DNA Solutions at Low-Supporting Electrolyte Concentration, *Biopolymers*, **1990**, *30*, 803.
- [15] Samulski, E. T.; Berendsen, H. J. C., Proton, Deuteron, and Nitrogen Resonance of Dimethylformamide in Nematic Polypeptide Liquid Crystals, *The Journal of Chemical Physics*, **1972**, *56*, 3920.
- [16] Nelson, E. J.; Samulski, E. T., Preparation of Cds Nanoparticles within an Ordered Polypeptide Matrix, *Materials Science & Engineering C-Biomimetic Materials Sensors and Systems*, **1995**, *2*, 133.
- [17] Hou, J. B.; Zhang, Z. Y.; Madsen, L. A., Cation/Anion Associations in Ionic Liquids Modulated by Hydration and Ionic Medium, *Journal of Physical Chemistry B*, **2011**, *115*, 4576.
- [18] Price, W. S., Pulsed-field gradient nuclear magnetic resonance as a tool for studying translational diffusion .1. Basic theory, *Concepts in Magnetic Resonance*, **1997**, *9*, 299.
- [19] Hou, J. B.; Li, J.; Madsen, L. A., Anisotropy and Transport in Poly(arylene ether sulfone) Hydrophilic-Hydrophobic Block Copolymers, *Macromolecules*, **2010**, *43*, 347.
- [20] Bragg, W. H. *Rayons X et structure cristalline*; Gauthier-Villars: Paris,, 1921, p 209 p.
- [21] Livolant, F.; Levelut, A. M.; Doucet, J.; Benoit, J. P., The Highly Concentrated Liquid-Crystalline Phase of DNA Is Columnar Hexagonal, *Nature*, **1989**, *339*, 724.
- [22] Kreuer, K. D., Proton conductivity: Materials and applications, *Chemistry of Materials*, **1996**, *8*, 610.
- [23] Pacios, M.; Martín-Fernández, I.; Villa, R.; Godignon, P.; Valle, M. D.; Bartrolí, J.; Esplandiú, M. J. *Carbon Nanotubes as Suitable Electrochemical Platforms for Metalloprotein Sensors and Genosensors* 2011.

- [24] Franco-Marques, E.; Mendez, J. A.; Girones, J.; Pelach, M. A., Thermal and dynamic mechanical characterization of acrylic bone cements modified with biodegradable polymers, *Journal of Applied Polymer Science*, **2013**, *128*, 3455.
- [25] Coats, A. W.; Redfern, J. P., Thermogravimetric analysis. A review, *Analyst*, **1963**, *88*, 906.
- [26] Ferry, J. D., Some reflections on the early development of polymer dynamics: viscoelasticity, dielectric dispersion, and self-diffusion, *Macromolecules*, **1991**, *24*, 5237.
- [27] Hosford, W. F. *Mechanical Behavior of Materials*; Cambridge University Press: New York, 2005.
- [28] Ruan, R.; Long, Z.; Chen, P.; Huang, V.; Almaer, S.; Taub, I., Pulse NMR study of glass transition in maltodextrin, *Journal of Food Science*, **1999**, *64*, 6.
- [29] Madsen, L. A., Plasticization of poly(ethylene oxide) in fluid CO₂ measured by in-situ NMR, *Macromolecules*, **2006**, *39*, 1483.

Chapter 3

Molecular Alignment and Ion Transport in Rigid Rod Polyelectrolyte Solutions

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3.1 Abstract

Combining molecular alignment with selective ion transport can increase the freedom to design ion-conducting polymeric materials, and thus enhance applications such as battery electrolytes, fuel cells, and water purification. Here we employ pulsed-field-gradient (PFG) NMR diffusometry, ^2H NMR spectroscopy, polarized optical microscopy, and small-angle X-ray scattering to determine relations between counterion transport, dynamic coupling of water, and molecular alignment in aqueous solutions of a rigid-rod sulfonated-aramid polyelectrolyte -- poly (2,2'-disulfonyl-4,4'-benzidine terephthalamide) (PBDT). ^{23}Na PFG NMR on PBDT solutions and simple sodium salt solutions shows significantly slower Na^+ counterion diffusion in PBDT, providing agreement between counterion condensation theory and quantitative transport information. Strikingly, from ^2H NMR spectroscopy we observe that the orientational order parameter of partially aligned solvent D_2O molecules increases linearly with polymer weight percentage over a large concentration range (1.4 wt % to > 20 wt %), while the polymer chains possess essentially a large and fixed order parameter $S_{\text{matrix}} = 0.76$ as observed using both SAXS and ^2H NMR on labeled polymers. Finally, we apply a two state model of water dynamics and a physical lattice model to quantitatively relate D_2O spectral splittings and nematic rod-rod distance. These studies promise to open new pathways to understanding

a range of anisotropic polymer systems including aligned polymer electrolyte membranes, wood composites, aligned hydrogels, liquid crystals and stretched elastomers.

3.2 Introduction

Rigid rod polyelectrolytes possessing an anisotropic (liquid crystal) phase form the basis of a variety of natural biopolymers such as DNA^[1], polypeptides^[2], tobacco mosaic virus^[3] and cationic liposomes^[3], and also comprise a range of synthetic ion functionalized polymers.^[4] Here we explore a synthetic sulfonated aramid polyanion, poly (2,2'-disulfonyl-4,4'-benzidine terephthalamide) (PBDT),^[4,5] shown in **Figure 3.1**. Above a critical concentration $C^* = 1.2$ wt%, this water-miscible system forms a lyotropic nematic liquid crystal (LC) and has a high ion density along the polymer backbone. Using anisotropic aqueous solutions of PBDT, we investigate alignment of the rigid rod polymer chains as well as the dynamic transport and associations of the small mobile species present (water and Na^+ counterions). PBDT is a sulfonated polyamide with multicomponent intermolecular interactions, including π - π interactions between the rigid aromatic rings and electrostatic interactions from the ionogenic sulfonate groups, thus contributing to the anisotropic interactions underlying the aligned rigid rod structure in aqueous solutions.^[6] Additionally, hydrogen bonding and the biased rotation of benzene rings further influence the self-assembled conformation of PBDT molecular chains. In a magnetic field B_0 , this lyotropic nematic phase reorganizes from a randomly distributed polydomain nematic to a monodomain nematic with the alignment axis (director) parallel to B_0 .^[7] We seek to understand how such an anisotropic morphology

relates to mobile species transport in order to fundamentally design next-generation polymeric materials.^[8-10]

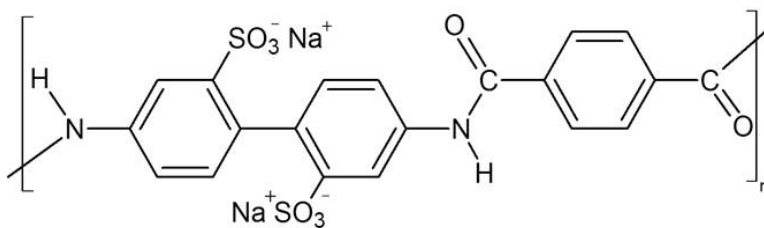


Figure 3.1. The chemical structure of poly (2,2'-disulfonyl-4,4'-benzidine terephthalamide) (PBDT). A rigid rod liquid crystalline polyelectrolyte.

Self-assembled LC polyelectrolyte solutions can be studied by various techniques including transmission electric microscopy (TEM), dynamic light scattering (DLS), small-angle X-ray scattering (SAXS) and polarized optical microscopy (POM).^[11-13] However, it is difficult to extract information about transport of mobile species (counterions, water), or coupling interactions between the aligned polymer matrices and mobile species using the above techniques. Molecular dynamics simulations and NMR spectroscopy have previously been utilized to illustrate orientational ordering and intermolecular coupling within nematic LC phases.^{[14],[15]} The molecular basis of ordering in nematics is commonly attributed to short-range repulsive interactions (excluded volume) as being the dominant interactions, but long-range electrostatic interactions, including dispersion and dipole-dipole effects, can also be important but have a lesser influence on ordering.^[14-17] Using a variety of NMR methods, we can detect the orientational order of polymer chains, anisotropic coupling of small molecules, oriented domain size, and anisotropic transport of various mobile species in polymer membranes and solutions.^[18-21] These methods represent complementary tools to understand structure,

chain conformation, and morphology in aligned polymeric materials, and the influence of these structural features on dynamics and transport.

^2H NMR spectroscopy on labeled probe molecules absorbed in anisotropic matrices has been widely used to determine ordering in a diverse array of aligned materials including liquid crystals,^[22] wormlike micelles,^[23] intact wood cell walls,^[24] stretched polymers,^[25] and fuel-cell polymer electrolyte membranes.^[18,26] Our group has used ^2H NMR and PFG NMR diffusometry to relate polymer alignment and morphology to transport properties and molecular associations on lengthscales ranging from sub-nanometer to micrometer.^[8,18,20,24-26] Here we investigate the diffusion of counterions (Na^+) in PBDT aqueous solutions via PFG NMR to elucidate counterion condensation behavior and relate this concept to ion transport in this system. Additionally, from concentration-dependent ^2H NMR spectroscopy, we observe a striking linear relationship between the degree of alignment (orientational order parameter) of water molecules (D_2O) and the PBDT polymer weight percentage C in solution. This linear dependence gives us insight into the mechanisms that dynamically couple small molecules to an aligned matrix, and provides an opportunity to expand our understanding of using ^2H -labeled probe molecules to quantitatively measure alignment of a surrounding matrix.^[10,27-29] Finally, we measure the concentration dependence of polymer ordering and water ordering using ^2H NMR as well as the characteristic rod-rod distance using SAXS. We then combine these observations with a physical model based on a simple lattice and dynamic exchange of water to comprehend water-polymer coupling and polymer morphology in PBDT solutions. This model promises significant new insights into the self-assembly of rigid rod LC polyelectrolytes, with implications for, *e.g.*, enhancing

anisotropic ion conductivity and mechanical properties in technologically important ionic polymer membranes and solutions.^[30-33]

3.3 Experimental

PBDT Materials: PBDT with Na⁺ counterions was synthesized by interfacial condensation using a synthetic process introduced elsewhere.^[6] Intrinsic Viscosity and Gel Permeation Chromatography (GPC) were employed to detect the molecular weight of the received PBDT samples. The intrinsic viscosity = 10 dL/g using a Ubbelohd Dilution Viscometer (Cannon Instrument Company). For GPC measurements, samples were dissolved in concentrated sulfuric acid (1 mg/ml) and diluted before column injection. The number-average molecular weight M_n , weight-average molecular weight M_w , and polydispersity index (M_w/M_n) were 7900, 17300, and 2.2, respectively.

Selectively deuterated (²H) PBDT polymer: Perdeuterated terephthalic acid monomer was employed to produce ²H PBDT bulk polymer, which was utilized to generate the ²H NMR spectra in Section 3.4. The molecular weight of ²H PBDT is unspecified. However, the intrinsic viscosity is 5 dL/g, which is half that of fully protonated PBDT sample.

PBDT solutions: PBDT bulk polymer was dried under vacuum at room temperature for two days. Aqueous solutions with PBDT weight percentage (wt %) ranging from 1% – 15% were prepared by loading the prescribed amount of PBDT and D₂O into 5 mm NMR tubes. D₂O was used as received from Cambridge Isotope Laboratories (~ 99.9%). All of the sample tubes were flame sealed immediately to prevent evaporation of water and were equilibrated at 80°C in a water bath for one week to ensure complete dissolution and homogenization.

PBDT membranes: 0.5 wt % PBDT aqueous solution was prepared by dissolving dried PBDT polymer in D₂O then holding at 40°C in an oven overnight. The homogenized polymer solution was spread onto plastic petri dishes. After putting the plates in a vacuum oven for 2 hours at room temperature, 5 μ m thick membranes were carefully peeled off from the substrate.

Isotropic salt solutions: Sodium chloride (NaCl, 99.5%) and sodium trifluoromethanesulfonate (NaTriflate, 98%) were purchased from Sigma-Aldrich Company and used without further purification. The aqueous solutions of NaCl and NaTriflate were prepared similarly with that of PBDT aqueous solutions.

Comparison rigid rod polyelectrolyte: Poly-L-glutamic acid (PLGA) was purchased from Pilot Chemical Co. with $M_w = 79000$. Aqueous solutions (in D₂O) of PLGA were neutralized into the Na⁺ salt form by adding the equal molar quantity of NaOH using 1 N solution. The chemical structure of PLGA is included in the supporting information.^[34]

Polarizing Optical Microscopy: A polarizing microscope (Meiji Technology MX9430 Japan) and digital camera (Infinity Canon) have been employed to observe the LC structure of PBDT solutions and membranes. The aqueous solution and membrane samples were sandwiched between glass slides and observed at room temperature. The space between two glass slides was maintained at 450 μ m using stack of glass coverslips as the spacer for the aqueous solution samples.

²H quadrupole NMR Spectroscopy and PFG NMR Diffusometry: All ²H NMR spectroscopy was performed at 25 $\pm$ 0.1°C using a Bruker Avance III 9.4 T widebore spectrometer equipped with a 5 mm axial saddle ¹H/²H rf coil corresponding to a ²H frequency of 61.42 MHz. For ¹H PBDT aqueous (D₂O) solutions, ²H NMR was carried

out using a single $\pi/2$ pulse time of $7.5 \mu\text{s}$, relaxation delay time of 1 s, and 4 scans per spectrum. However, with respect to the ^2H -labelled PBDT aqueous solutions, a single $\pi/2$ pulse time of $7.5 \mu\text{s}$, relaxation delay time of 0.25 s, and 2000 scans per spectrum were employed to generate the ^2H NMR spectra. Deuterium quadrupole splittings ($\Delta\nu_Q$) were quantified by fitting each spectrum with two Lorentzian peaks using MestReNova software.

PFG NMR is an accurate and convenient technique to quantify diffusion coefficients of separate mobile species including anions, cations, and water molecules in hydrophilic aggregations of bulk polymer, generally with accuracy and precision errors of $< 3\%$. The simple and robust pulsed-gradient stimulated-echo sequence (PGSTE) was applied for all diffusion measurements at 25°C (± 0.1). For Na^+ diffusion, the same Bruker Avance III WB 400 MHz (9.4 T) NMR was equipped with Diff 60 pulsed-field-gradient diffusion probe having a maximum gradient value of 2000 G/cm (at 34 A current) along the Z (B_0) axis and 5 mm axial saddle ^{23}Na rf coil. The PGSTE sequence used a $\pi/2$ pulse time of $4.5 \mu\text{s}$, gradient pulse duration δ of 1 ~ 2 ms, diffusion times Δ of 10 ~ 20 ms (δ and Δ depend on water uptake and thus ^{23}Na relaxation times), and the number of scans for each step was adjusted from 1 - 64 to ensure good signal-to-noise ratio (SNR). 16 gradient steps were applied for each diffusion experiment, and the maximum gradient strength was selected to achieve $\geq 90\%$ NMR signal attenuation. All parameters for the gradient have been calibrated and optimized as reported earlier.^{[26],[35]} The NMR signal attenuation due to diffusion follows the Stejskal-Tanner equation^[29]

$$I = I_0 e^{-D\gamma^2 g^2 \delta^2 (\Delta - \frac{\delta}{3})}, \quad (3.1)$$

where I and I_0 refer to the spin-echo signal intensity and spin-echo signal intensity at zero gradient, respectively. γ is the gyromagnetic ratio of the nucleus, g is the gradient strength, δ is the pulse duration time and Δ is the diffusion time. Thus, diffusion coefficients (D) of a desired nucleus can be obtained by fitting the experimental I vs. g data using Equation 1. The T_1 (*inversion*-recovery) and T_2 (CPMG) values of the solution samples are listed in the **Table 3.1** for reference, and all diffusion parameters are properly selected ($\Delta < 1.5T_1$, $\delta < T_2$) to ensure sufficient SNR.

Table 3.1. Sample properties and NMR relaxation times. All of the samples were dissolved in D₂O. Errors in concentrations are $\pm 0.5\% \times C$, and errors in T_1 and T_2 are $\pm 10\%$.

Sample Name	Concentration Range (wt %)	(D ₂ O+H ₂ O)/Na ⁺ (Mole ratio)	T_1 (ms) (Na ⁺)	T_2 (ms) (Na ⁺)
PBDT	1.0% ~ 15.4%	68 ~ 1234	13 ~ 30	12 ~ 24
PLGA	0.4% ~ 6.4%	44 ~ 1088	15 ~ 36	10 ~ 33
NaCl	1.3% ~ 28.6%	7 ~ 228	31 ~ 47	33 ~ 46
NaTriflate	2.3% ~ 14.2%	52 ~ 357	31 ~ 48	27 ~ 37

Small Angle X-ray Scattering (SAXS): All SAXS experiments were operated on a Rigaku S-Max 3000 pinhole SAXS system, equipped with a copper rotating anode emitting X-rays with a wavelength λ of 0.154 nm (Cu K α) and a sample-to-detector distance of 1600 mm. The relationship between pixel width and scattering vector q was determined by calibrating a silver behenate standard sample. PBDT aqueous solutions with concentrations from 0.94% to 5.0% were sealed in capillaries with 1.5 mm diameter and 0.01 mm wall thickness. Before the SAXS measurements, the capillaries with

polymer solutions inside were placed axially along in the field of a 7.1 T (300 MHz) NMR magnet to achieve uniaxial alignment. Then the capillaries were placed horizontally in the SAXS sample chamber with zero magnetic field. All 2D SAXS patterns were analyzed by SAXSGUI software package (Rigaku Innovative Technologies, Inc) to generate the integrated SAXS intensity $I(q)$ as a function of scattering vector q , where $q = \frac{4\pi \sin \theta}{\lambda}$. The angle θ refers to one half of the total scattering angle.

3.4 Results and Discussion

3.4.1 Nematic Phase Transitions and Phase Separation in PBDT Solutions

Here, POM and ^2H NMR spectroscopy are combined to explore the isotropic-nematic phase transition as well as the phase separation behavior of PBDT aqueous solutions. From POM images, the homogeneous dark blue view observed at 1.0 wt % (**Figure 3.2a**) indicates the isotropic phase of PBDT aqueous solution. The Schlieren texture in **Figure 3.2b** shows the induced nematic LC phase when concentration $C \geq 1.8\%$. When $1\% < C < 1.8\%$, a liquid-liquid phase separation occurs in the NMR sample tubes. The upper (nearly) isotropic phase in the NMR tube of 1.2% PBDT solution sample is pipetted out and observed under POM (**Figure 3.2c**), which shows $\sim 100\ \mu\text{m}$ birefringent LC droplets with Maltese crosses. Meanwhile, the lower LC phase (**Figure 3.2d**) displays the Schlieren texture of a nematic LC. This overlapping phase transition was studied by Gong et al. through POM.⁴⁰ They employed the solvent evaporation method and observed the isotropic-nematic transition at the air-liquid surface of the PBDT polymer solution. With increasing polymer concentration, the relative smaller LC droplets (**Figure 3.2c**) coarsen to form larger LC droplets, which are finally dragged and absorbed into the

nematic LC phase.⁴⁰ This specific phase separation is also observed by ^2H NMR spectroscopy. ^2H NMR spectra of adsorbed D_2O probe molecules with doublet splittings (two line spectra) are commonly seen in liquid crystal, stretched polymer membranes, polymer fibers and anisotropic phase separated membranes.^[8,18,26] The doublet splittings originate from anisotropic coupling interactions between solvent molecules and aligned polymer matrices. As shown in **Figure 3.2e**, the singlet peak in the D_2O spectrum for 1.0% PBDT solution corresponds to the pure isotropic phase. However, when the concentration increases to 1.2%, we observe three lines in the spectrum. In order to assign these three peaks, the upper phase was pipetted out and its ^2H NMR spectrum shows a singlet peak, whereas, the bottom phase shows a doublet. Thus, we conclude that the spectrum originates from the coexistence of the bottom pure nematic LC phase (doublet peak) and the upper pure isotropic phase (singlet). As the concentration increases to $\geq 1.8\%$, the nematic LC phase exists throughout the polymer solution, and only a doublet appears. The biphasic region including the upper isotropic phase and the bottom nematic LC phase in certain concentration ranges is commonly seen in many other liquid crystalline polymers.^[36] However, the concentration range is variable and closely relates to the molecular weight of polymer, which can be further verified by the ^2H NMR results on ^2H labeled PBDT with lower molecular weight (Section 3.4.4 below). Note that we expect this phase separation behavior to follow a “lever rule” as in the case of gas-liquid equilibria, but this will require further study for this system.

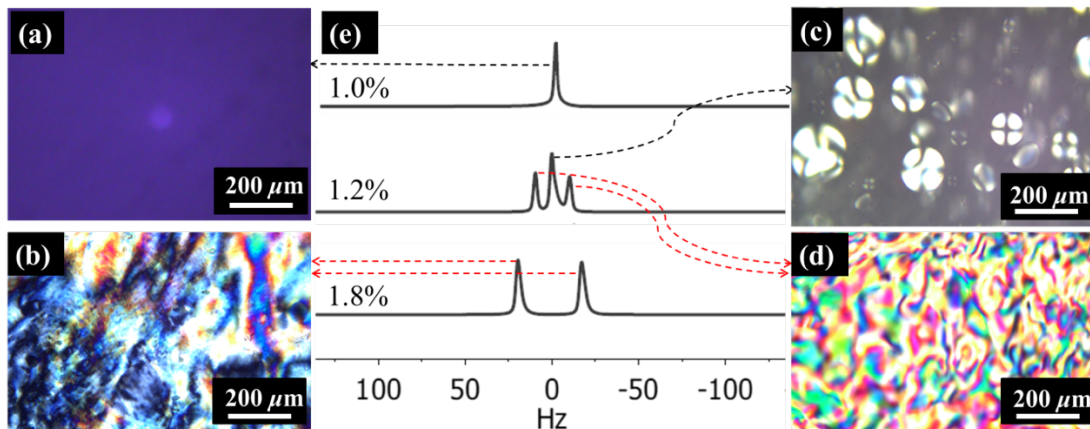


Figure 3.2. POM images for PBDT aqueous solutions. With concentration C of (a) 1.0% and (b) 1.8%. (c) Nematic LC droplets with Maltese cross observed in the upper transparent phase pipetted from 1.2% solution. (d) Nematic Schlieren texture for the bottom translucent LC phase of 1.2% solution. (e) ^2H NMR spectra for ^1H PBDT aqueous solutions with $C = 1.0\%$, 1.2% and 1.8% . Errors in polymer concentrations are $\pm 0.05\% \times C$.

In addition to PBDT aqueous solutions, the LC texture was also observed in PBDT membranes. **Figure 3.3** shows POM images of PBDT membrane formed on a petri dish. The observed Schlieren texture confirms that the nematic phase is preserved in the solid state.^[11] The conformation of the PBDT molecular chains can be easily influenced by the substrate and other environmental conditions. Studying the alignment and morphology of polymer chains and the coupling interactions between solvent probe molecules and polymer backbones promotes better control of conformational alignment in the polymer membrane, which is essential to develop novel functional polymer membranes with ordered pathways.

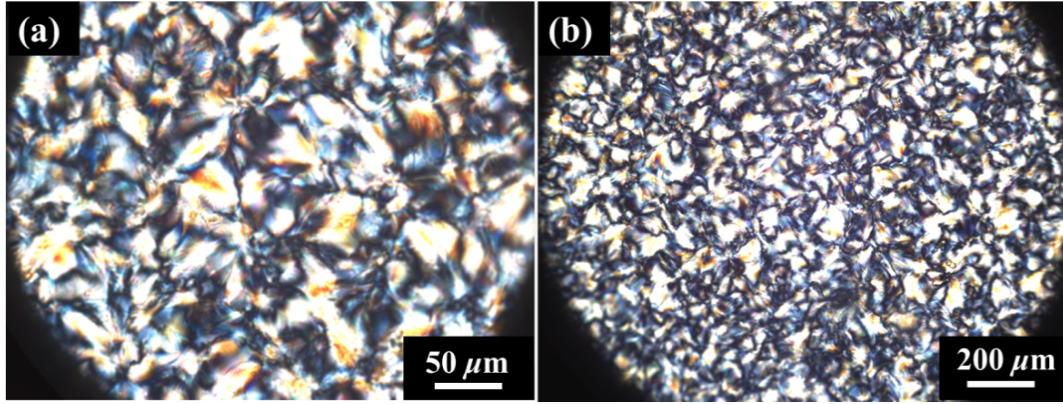


Figure 3.3. POM images for PBDT membrane formed on petri dishes. With magnifications of (a) 400 X and (b) 100 X (Crossed polars).

3.4.2 Counterion Condensation and Ion Transport in PBDT Solutions

Besides the lyotropic LC properties of PBDT aqueous solutions, the status of Na^+ counterions in PBDT aqueous solutions can also affect the polyelectrolyte conformation.^[37,38] According to the counterion condensation theory by Manning et al,^[37] the counterions tend to tightly associate with the ionogenic groups of the polymer when the charge parameter ξ of the polyelectrolyte molecular chain is larger than 1. The charge parameter can be expressed as

$$\xi = \frac{\sigma^2 \alpha}{4\pi\epsilon_0\epsilon_r k T l}, \quad (3.2)$$

where σ is the charge value and α the number of ionogenic sites per chemical repeat unit.^[31,37-39] ϵ_0 and ϵ_r are absolute and relative dielectric constants. l is the length of chemical repeat unit. k is the Boltzmann constant. This theory is based on a rigid rod polyelectrolyte with equally spaced charges that smear out continuously along the polymer chain. Here, we can generate two results of ξ based on the theory. (1) When the two sulfonated groups per chemical repeat unit of PBDT are considered as one unit, since

the distance between the two sulfonate groups is very close, then $\sigma = 2e$ (e is the unit charge value), $\alpha = 1$ (half the number of sulfonate groups per chemical repeat unit) and $l = 1.6$ nm. Substituting these parameters in Equation 3.2, we obtain $\xi = 1.78 > 1$. (2) When the two sulfonate groups are considered as equally distributed in one chemical repeat unit, thus $\sigma = e$, $\alpha = 2$, $l = 1.6$ nm, then $\xi = 0.89 < 1$. In light of these two calculations, it seems that the counterion condensation theory cannot unambiguously describe the condensation behavior of Na^+ ions in PBDT. However, according to the calculation from Section 3.5 below, we propose the possibility that two PBDT molecules tend to assemble together to form the nematic LC mesogens, so the calculated results become (1) $\xi = 3.56$ ($\sigma = 2e$, $\alpha = 2$) and (2) $\xi = 1.78$ ($\sigma = e$, $\alpha = 4$). Both results with $\xi > 1$ support the idea that the Na^+ ions tend to condense on the PBDT polymer chains. For comparison, the charge parameter for the rigid rod polyelectrolyte poly-L-glutamic acid (PLGA) is calculated to be $\xi = 2.4$.

In order to further explore counterion condensation and the proposed supramolecular dimerization, we also employed ^{23}Na PFG NMR to measure the diffusion coefficient of Na^+ ions (D_{Na^+}) directly in PBDT aqueous solution. We note that all of these diffusion results are along the Z direction that is parallel with the magnetic field and the director of the PBDT nematic phase. **Figure 3.4** (blue dots) shows that D_{Na^+} does not change much with respect to the wide range of PBDT polymer weight percent. The maximum D_{Na^+} occurs at $\sim 2\%$, where the nematic phase is fully formed. Apparently, the alignment of the polymer chains promotes diffusion of Na^+ ions along the rigid rod chains in the nematic LC phase. For comparison, we measured D_{Na^+} in PLGA, NaCl and NaTriflate aqueous solutions using the same PFG NMR experiments at 25°C . From Section 2.4.1

results, we know that the nematic LC phase starts to form when $C > 1\%$, so D_{Na^+} for PBDT concentration $\leq 1\%$ refers to the diffusion of Na^+ in the isotropic polymer solution. Also from Figure 4, D_{Na^+} in 1% PBDT ($\sim 6.5 \times 10^{-10} \text{ m}^2/\text{s}$) is 60% of D_{Na^+} in NaCl (red dots) and in NaCF_3SO_3 (black dots) ($\sim 1.1 \times 10^{-9} \text{ m}^2/\text{s}$) dilute aqueous solutions with water uptake > 300 , whereas, D_{Na^+} is similar to that of PLGA sodium salt aqueous solutions (yellow dots). “Water uptake” refers to the mole ratio of $(\text{D}_2\text{O} + \text{H}_2\text{O})$ and Na^+ . Above all, the results from PFG NMR display that Na^+ ions tend to condense on the PBDT polymer chain because of the comparably smaller D_{Na^+} , which is consistent with the counterion condensation theory described above. The chemical structure of poly-L-glutamic acid (PLGA) is shown in **Figure 3.5**. **Figure 3.6** shows the ^{23}Na spectra for PBDT, NaCl, NaTriflate, and PLGA aqueous solutions. **Figure 3.7** shows the Normalized signal amplitudes (I/I_0) of stimulated echo decays vs Stejskal-Tanner parameter b (Equation 3) for aqueous solutions of PBDT, PLGA, NaCl, and NaTriflate with different water uptake λ . Solid symbols indicate the experimental signal decay. The solid lines are linear least squares one-component fits for the experimental data with detailed results summarized in **Table 3.2**.

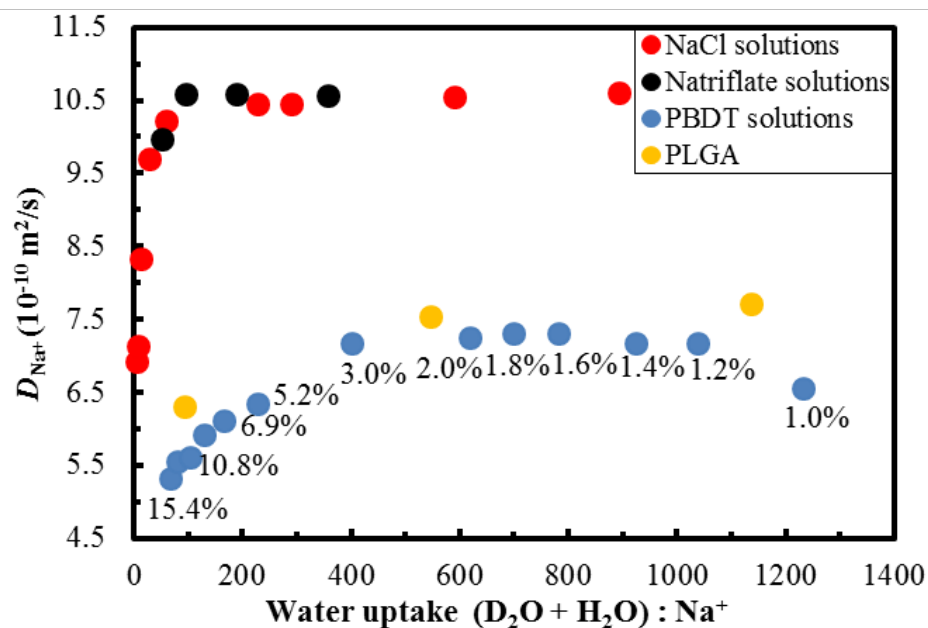


Figure 3.4. Na⁺ diffusion coefficients (D_{Na^+}) in various aqueous solutions. D_{Na^+} of PBDT, PLGA, NaCl and NaTriflate aqueous solutions in D₂O as a function of mole ratios of (D₂O + H₂O) : Na⁺ (also D₂O : SO₃⁻). The labels on the blue dots represent the polymer concentrations (wt %). Polymer concentration errors in solution samples are $\pm 0.5\% \times C$, and in D values are $\pm 3\%$.

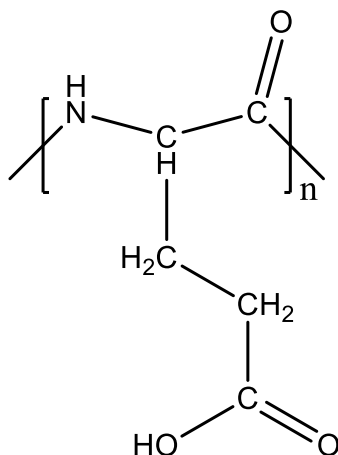


Figure 3.5. The chemical structure of PLGA. 1M NaOH aqueous solution was used to transform H⁺ form PLGA into Na⁺ form PLGA.

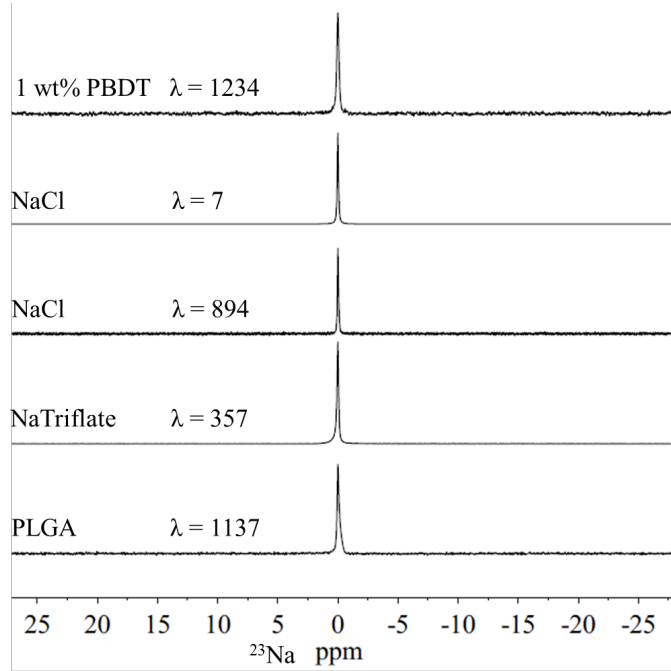


Figure 3.6. ^{23}Na spectra for aqueous solutions of PBDT, NaCl, NaTriflate, and PLGA with different water uptake λ . λ is defined as the mole ratio $(\text{D}_2\text{O} + \text{H}_2\text{O}):\text{Na}^+$ (same as $\text{D}_2\text{O}:\text{SO}_3^-$).

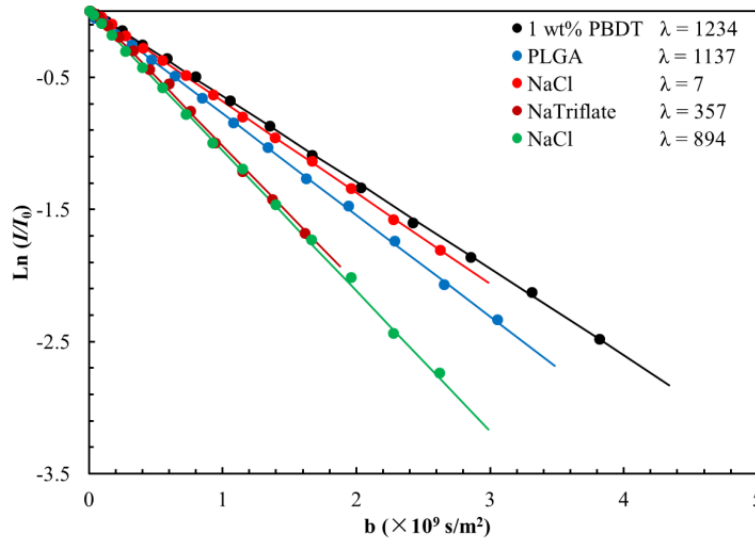


Figure 3.7. Normalized signal amplitudes (I/I_0) of stimulated echo decays vs Stejskal-Tanner parameter b for aqueous solutions of PBDT, PLGA, NaCl, and NaTriflate with different water uptake λ . The expression of b is shown as follows in Equation 3.3.

$$b = \gamma^2 g^2 \delta^2 \left(\Delta - \frac{\delta}{3} \right), \quad (3.3)$$

Table 3.2. The fitting results of Na^+ diffusion coefficients are listed in the table. The maximum diffusion rate for Na^+ in simple salt solutions is around 10.60×10^{-10} , which is only 30% faster than Na^+ ions diffuse in aqueous solutions of PBDT and PLGA with similar water uptake λ . Errors in D are $\pm 3\%$.

Solutions	λ	$D \cdot 10^{-10} \text{ (m}^2/\text{s)}$
1 wt% PBDT	1234	6.55
PLGA	1137	7.70
NaCl	7	6.92
NaTriflate	357	10.56
NaCl	894	10.60

3.4.3 Coupling and Alignment of Probe Molecules in PBDT Solutions

We further quantify the orientational order of solvent D_2O in PBDT aqueous solution as a function of the polymer concentration using ^2H NMR spectroscopy. The interaction between the deuterium electric quadrupole moment and the electric field gradient of the O-D bond contribute to the doublet splitting (two lines) in the deuterium spectrum.^[27] The quadrupole splitting for a uniaxially symmetric phase ($\Delta\nu_Q$), defined as the distance between the doublet peaks, is expressed as

$$\Delta\nu_Q = Q_P S_{\text{O-D}} \left(\frac{3\cos^2\theta - 1}{2} \right) = Q_P \rho S_{\text{matrix}} \left(\frac{3\cos^2\theta - 1}{2} \right), \quad (3.4)$$

where Q_P is the quadrupole splitting ($\approx 255 \text{ kHz}$) for D_2O molecules for the situation where all O-D bonds are perfectly aligned with B_0 . $S_{\text{O-D}}$ is the ensemble average orientational order of the O-D bond with respect to the aligned hydrophilic polymer domain or matrix. θ is the angle between the director of polymer hydrophilic domains

and the spectrometer field B_0 . S_{matrix} refers to the orientational order of the polymeric LC matrix. The scaling factor ρ represents the coupling interaction between deuterium probe molecules and the hydrophilic region in polymer aqueous solutions. ρ is often relatively insensitive to temperature in oriented systems, whereas, it is highly sensitive to the water uptake of the system.^[24-26,40]

In general, rigid rod PBDT and similar nematic LC molecules have positive magnetic susceptibility anisotropy $\Delta\chi = \chi_{\perp} - \chi_{\parallel} > 0$, indicating that the PBDT molecules align parallel with an applied magnetic field ($\cos\theta = 1$).^[22] In this case, the hydrophilic domains of PBDT aqueous solutions refer to the integration of the sulfonate (hydrophilic) groups on polymer chains and the water solvent present between the polymer chains. Here we explore water-polymer coupling interactions based on concentration-dependent ^2H NMR on PBDT solutions. **Figure 3.8a** shows the D_2O quadrupole splittings $\Delta\nu_Q$ for PBDT aqueous solutions as a function of C . Clearly $\Delta\nu_Q$ increases with C . By fitting the doublet spectra and plotting $\Delta\nu_Q$ vs. C (**Figure 3.8b**), we observe a remarkably linear dependence of $\Delta\nu_Q$ on C over a wide concentration range from 2.0% to 15.4%. Using Equation 3, we can simply derive the proportionalities $\Delta\nu_Q \propto S_{\text{O-D}} \propto C$, which can give useful physical insights into this anisotropic polyelectrolyte system.

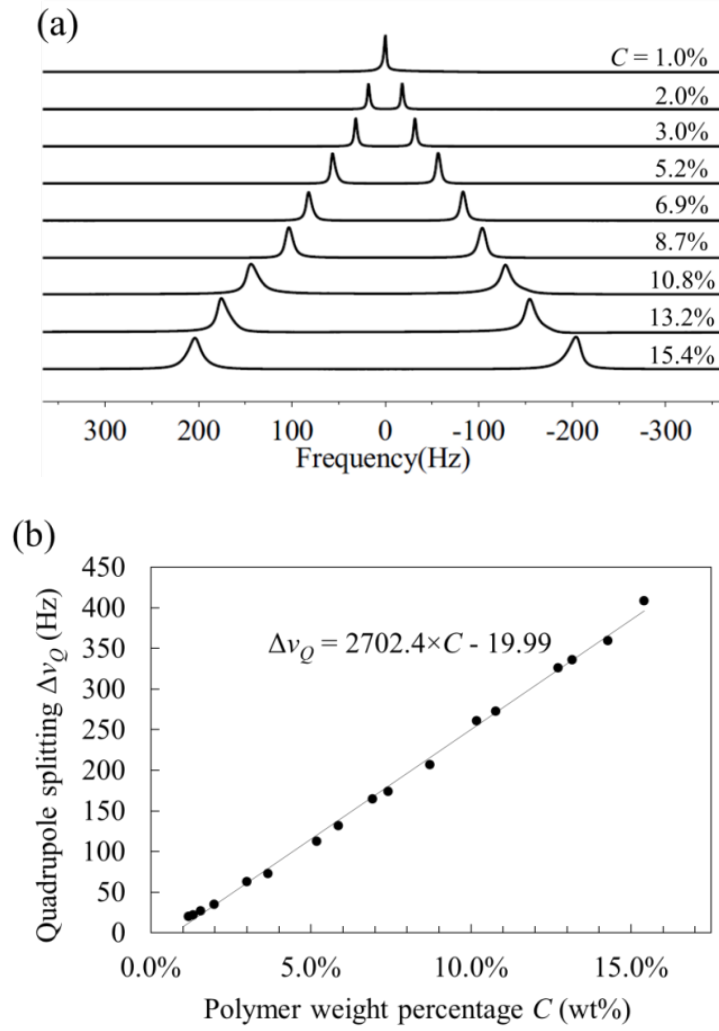


Figure 3.8. Doublet splitting as a function of PBDT polymer weight percent. (a) ^2H NMR spectra for PBDT in D_2O with concentration C from 1.0% to 15.4%. When $C \leq 1\%$, the ^2H spectrum shows a singlet peak, but when $C > 1\%$, the spectra show a doublet indicating uniform alignment of the liquid crystalline solution. (b) Quadrupole splitting as a function of polymer weight percent. Errors in $\Delta\nu_Q$ are $\pm 2\%$

What are the critical factors hidden behind this simple linear relationship? We draw key conclusions as follows: (1) The observed quadrupole splittings arise from anisotropic

coupling of D₂O molecules to hydrophilic sites on the PBDT chains, including sulfonate groups and amide groups. This anisotropic coupling refers to specific O-D bond orientations that must fit into the anisotropic cavity or shape formed by the hydrophilic aggregations of the polymer matrix. Equivalently, we can say that the O-D bonds form particular coordinations with the polymer chain moieties. These “associated” water molecules exchange with freely rotating water on sub- μ s timescales. (2) S_{O-D} is increasing linearly with C , which indicates that the water molecules probabilistically couple with the polymer chain sites, while the number of freely rotating water molecules is varying linearly with water content. (3) We can propose the following quantitative model in Equation 3.5. Considering the molecular repeat unit of PBDT, we specify the number of hydrophilic groups per chemical repeat unit (N). The total collision frequency (p) between water molecules and hydrophilic sites within the rigid rod repeat unit volume (V_e) is constant and independent of C for a given experimental time period and for this range of C . V_e is the total volume (in solution) of the rigid rod repeat unit, including the D₂O molecules surrounding the rodlike nematic repeat unit. From the ²H NMR splitting dependence we can introduce E_C , the overall anisotropic coupling of D₂O per V_e , which is proportional to C .

$$E_C = \frac{\Sigma(N*p*\kappa)}{V_e} = a C \quad (3.5)$$

κ is the average individual coupling interaction factor between one water molecule and the hydrophilic groups. We usually assume that this temperature dependent (kT) intermolecular orientational coupling factor (κ) is independent of polymer concentration.^[41] Thus, the volume of the chemical repeat unit (V_e) decreases with increasing C ($V_e \propto C^{-1}$) based on the invariants N , p , and κ . We will compare this picture

with the physical model of PBDT aqueous solutions derived in Section 3.5 below. Significantly, this highly ordered LC polymer system provides an opportunity to further study the general phenomena of dynamic coupling between water molecules and hydrophilic groups in oriented systems.^[27,28] Furthermore, we can begin to understand physically how ^2H NMR “probe molecule” measurements of order (here, $S_{\text{O-D}}$) quantitatively relate, through the coupling parameter ρ , to the order parameters of the host oriented matrix (S_{matrix}).^[24,25,27,28,40]

3.4.4 Polymer Chain Alignment Investigated by SAXS and ^2H NMR

We have also characterized the alignment of PBDT chains directly by two-dimensional (2D) SAXS and ^2H NMR of selectively ^2H -labeled PBDT. **Figure 3.9a** shows the SAXS patterns as a function of PBDT concentration C after being aligned in a 7 T magnetic field. The isotropic SAXS pattern for 0.94% shows a diffuse outer ring of maximum intensity at the scattering vector $q = 0.054$, which we attribute to the scattering due to the average chain-chain distance. With increasing C , the induced two-spot pattern indicates formation of the nematic LC phase and strong uniaxial alignment. q shifts from 0.054 to 0.12 as the concentration increases from 0.94% to 5.0%. The characteristic length (ζ) of the polymer solutions (interchain distance) can be estimated through the relationship $\zeta = 2\pi/q$. The diminishing of ζ with respect to C (**Table 3.3**) will be revisited in Section 3.4.5, in relation to the key ^2H NMR result on water ($V_e \propto C^{-1}$). To quantify the alignment degree of the polymer chains, we extracted the Herman’s orientation function f , also known as the polymer orientational order parameter (S_{matrix}), through fitting the azimuthal SAXS profiles. Here, $f = \frac{3\langle \cos^2\chi \rangle - 1}{2}$, where χ is the azimuthal angle from $\chi_1 = 0^\circ$ to $\chi_2 = 180^\circ$, and the average of $\cos^2\chi$ is^[40]

$$\langle \cos^2 \chi \rangle = \frac{\int_{\chi_1}^{\chi_2} I(\chi) \cos^2 \chi \sin \chi d\chi}{\int_{\chi_1}^{\chi_2} I(\chi) \sin \chi d\chi}. \quad (3.6)$$

As shown in **Table 3.3**, f increases with C from 0.94% to 5.0%, and plateaus when $C \geq 2.9\%$.

^2H NMR spectroscopy provides a complementary measurement of S_{matrix} . **Figure 3.9c** shows ^2H NMR spectra for labeled ^2H PBDT aqueous solutions from $C = 1.9\%$ to 5.2% . The biphasic region (coexistence of doublet peak and singlet peak) for ^2H PBDT solutions is broader for these samples (C from 3.0% to $> 5.2\%$). The critical concentration C^* for pure nematic formation in the labeled PBDT compared to the ^1H PBDT likely originates from the lower molecular weight of ^2H PBDT, as observed in the 50% lower intrinsic viscosity compared to ^1H PBDT. We calculate S_{matrix} from $\Delta\nu_Q = Q_P S_{\text{matrix}} \frac{3 \cos \beta^2 - 1}{2}$, where β is the average angle between the C-D bond on terephthalic acid and B_0 . We assume $\beta = 60^\circ$ with the PBDT molecular chains aligned with B_0 and $Q_P = 255 \text{ kHz}$.^[42,43] Table 2 shows the NMR splittings and S_{matrix} results. The NMR order parameters match those from SAXS to well within errors, and similarly S_{matrix} from NMR also plateaus when $C \geq 3.0\%$. Thus we conclude that S_{matrix} is invariant above the critical concentration C^* .

Table 3.3. Sample parameters, observed quantities, and S_{matrix} from both SAXS and ^2H NMR. (Errors in polymer concentrations are $\pm 0.5\% \times C$, scattering vectors are $\pm 3\%$, Herman's orientation function f are $\pm 5\%$, and NMR splittings are $\pm 5\%$.)

SAXS				^2H NMR		
Polymer Concentration (wt %)	Scattering Vector $q(\text{\AA}^{-1})$	Characteristic Length (nm)	S_{matrix} (Hermans's Orientation function f)	S_{matrix}	Polymer Concentration (wt %)	$\Delta\nu_Q$ (Hz)

0.94%	0.054	12	N/A	N/A	N/A	N/A
2.0%	0.078	8.1	0.61	N/A	1.9%	N/A
2.9%	0.093	6.8	0.76	0.74	3.0%	23437
4.0%	0.10	6.0	0.79	0.76	4.1%	24315
5.0%	0.12	5.4	0.79	0.77	5.2%	24505

Additionally, SAXS reveals the strong and persistent alignment properties of PBDT solutions, including the influence of a magnetic (B_0) field. **Figure 3.9b** shows SAXS results for 3.0% PBDT solution in a 1.5 mm OD capillary before (right) and after (left) alignment in $B = 7$ T. Surprisingly, the sample acquires bulk alignment ($S_{\text{matrix}} \sim 0.58$) simply due to interaction with the anisotropic (cylindrical) sample container (Figure 6b, left). Furthermore, the strong monodomain orientational order induced by the B field is maintained for > 24 hrs after removal from the field (**Figure 3.9b**, right). This long term stability of orientational order must originate from the high effective aspect ratio of the (rigid rod) polymer chain, which has a long persistence length that prohibits flexibility of PBDT polymer chains. This rigid rod nature propagates into the LC phase in the form of very large natural aligned LC domain sizes (~ 1 mm), requiring only tiny external interactions to produce monodomain alignment.

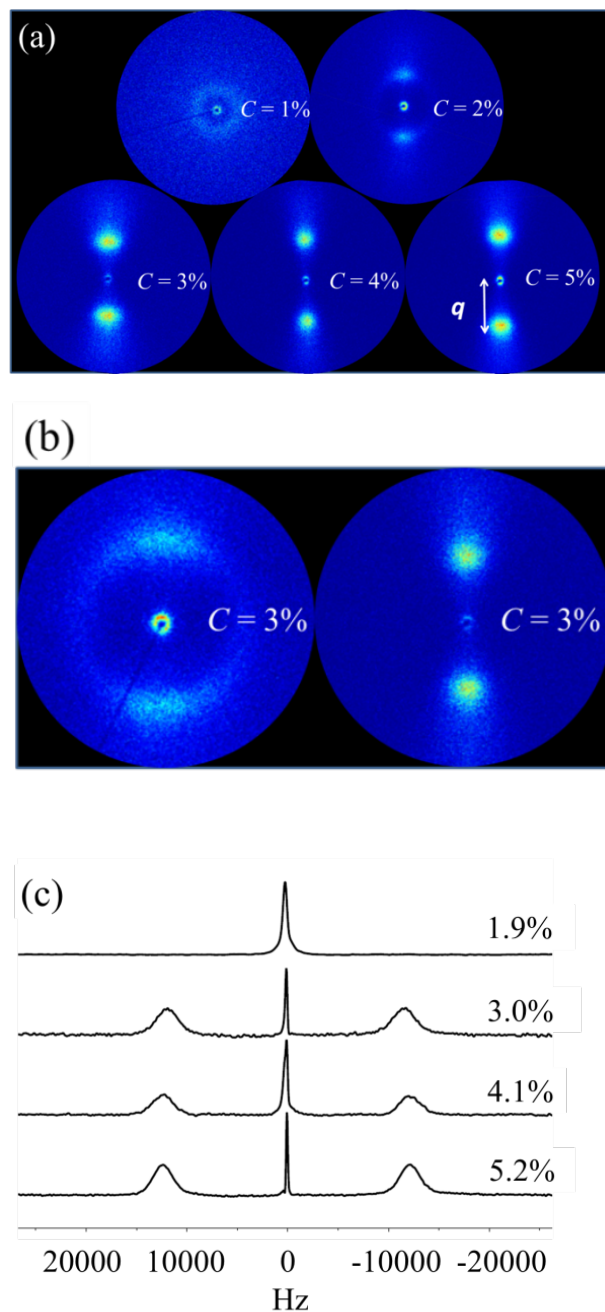


Figure 3.9. SAXS for magnetically aligned PBDT aqueous solution and ^2H NMR spectra for ^2H PBDT. (a) SAXS patterns for PBDT aqueous solutions aligned remotely in NMR spectrometer 7 T magnetic field from $C = 0.94\%$ to 5.0% . (b) SAXS results for 2.9% solution before (left) and after (right) alignment in the B_0 field. (c) ^2H NMR spectra for ^2H PBDT aqueous solutions from 1.9% to 5.2% .

3.4.5 Physical Lattice Model for PBDT Aqueous Solutions

Here we present a physical lattice model to aid in understanding the morphology of PBDT aqueous solution in the nematic phase, shown in **Figure 3.10a**. Blue lines represent the rigid rod PBDT chains, building up the nematic LC phase. Green Na^+ counterions, tend to condense around the PBDT sulfonate groups. D_2O molecules are dispersed in the solution, including orange freely rotating molecules and purple hindered water molecules. Water molecules interchange rapidly between freely rotating molecules and hindered water molecules. Each water molecule experiences collisions with PBDT molecules on ps – ns timescales and samples essentially all possible configurations during the experimental timescale ($1/\Delta\nu_Q \sim 1$ ms). In other words, all of the water molecules are “partially hindered” (in a time average) on the experimental timescale of the ^2H NMR spectral splitting.^[18,25,27] By assuming that the rigid rods form a hexagonal phase (**Figure 3.10b**) and using a simple lattice model calculation, we can estimate the rod-rod distance (r) using

$$V(\text{PBDT} + \text{D}_2\text{O}) = \frac{m(\text{PBDT})}{d(\text{PBDT})} + \frac{m(\text{D}_2\text{O})}{d(\text{D}_2\text{O})} = N * V_e, \quad (3.7)$$

$$V_e = V_{\text{shaded}} = 2 \times \frac{1}{2} \times r \times \frac{\sqrt{3}}{2} r \times l(\text{repeat unit}) \sim r^2, \quad (3.8)$$

where the density of PBDT bulk polymer $d(\text{PBDT}) = 1.565 \text{ g/cm}^3$, and $d(\text{D}_2\text{O}) = 1.11 \text{ g/cm}^3$ and the chemical repeat unit length $l(\text{repeat unit}) = 1.6 \text{ nm}$. $V(\text{PBDT} + \text{D}_2\text{O})$ is the total volume of the polymer solution. $m(\text{PBDT})$ and $m(\text{D}_2\text{O})$ are the mass of polymer and solvent in solution, respectively. $N = \frac{m(\text{PBDT})}{M(\text{PBDT})} \times \frac{1}{n}$ refers to the number of nematic rigid rod repeat units with a length of l , $M(\text{PBDT})$ is the molar mass of the PBDT repeat unit, and n is the number of PBDT molecule chains per nematic rigid rod. n allows for the

idea that multiple chains may aggregate to form one rod, which we discuss further below. V_e is the total volume of the nematic rigid rod repeat unit including its surrounding water molecules with the cross section shown in the shaded region in Figure 7b. Note that each nematic rigid rod occupies two triangle areas.

By assuming $n = 1, 2$ or 3 , we calculate three curves in **Figure 3.11a** based on the model in **Figure 3.10** along with Equations 3.7 and 3.8. From comparison of the three calculated curves, the model that assumes two PBDT molecules assemble to form the nematic rigid rod bundles (blue line) fits well with the SAXS data, with a difference $\leq 10\%$. The observed underestimate of r by this model sensibly originates from the assumed perfect hexagonal physical lattice, which will have approximately 10% smaller rod-rod distance than the nematic system,^[44] which is less ordered and thus the chains will be further separated. Based on our SAXS measurements and lattice model, we propose that a double helix structure for PBDT in solution, formed by two PBDT molecules, may serve as the rigid rod building block (mesogenic unit) in the nematic LC phase. PBDT chains associate into supramolecular bundles in solution has been implied by TEM and cryo-TEM measurements on samples dried or frozen from nematic.^[3,45] We are further investigating this indication of double helix formation, which has implications for control of supramolecular ordering in a range of synthetic polymers.

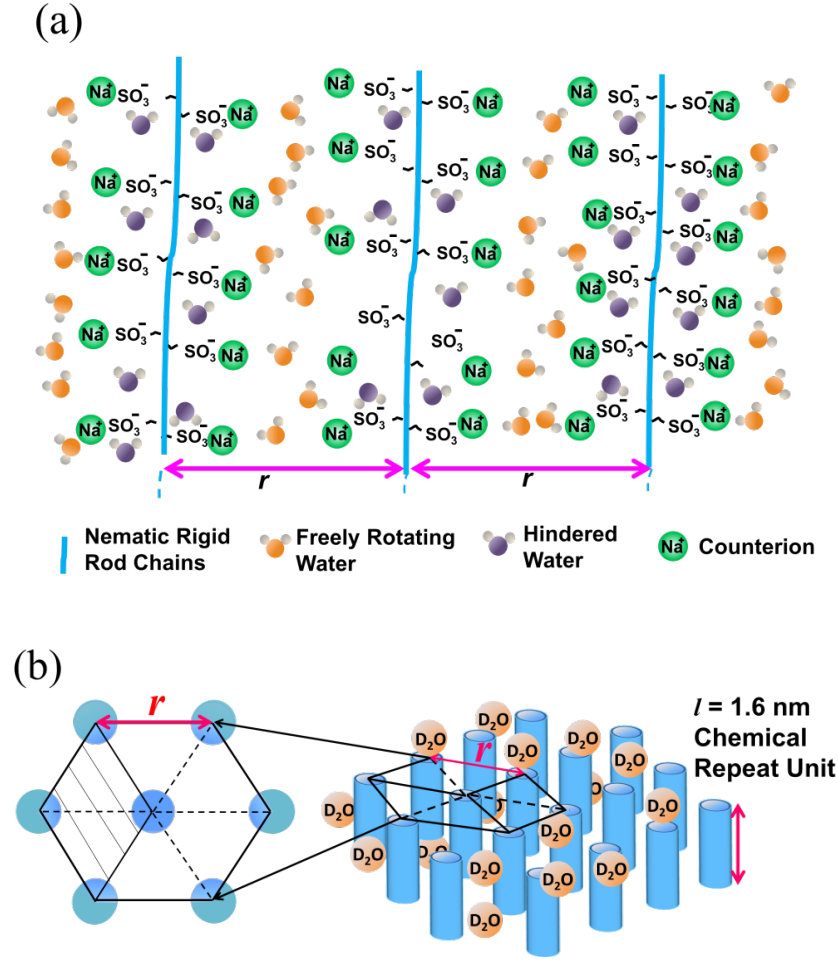


Figure 3.10. Physical lattice model for PBDT aqueous solutions. (a) Water molecules and PBDT chains forming an aligned hydrophilic phase. Blue lines represent aligned nematic rigid rod polymer chains, orange molecules are freely rotating water molecules, and purple molecules are momentarily hindered water molecules (coordinated on nanosecond timescales). (b) Hexagonal lattice model for nematic phase. The left picture shows the top view of the lattice model. The line-shaded region represents the excluded volume V_e per rigid rod chain repeat unit. The right picture shows an oblique view of the lattice model. $l = 1.6$ nm is the chemical repeat unit length and r is the average distance

between two rods. Orange D₂O molecules are dispersed within the aligned PBDT polymer matrix.

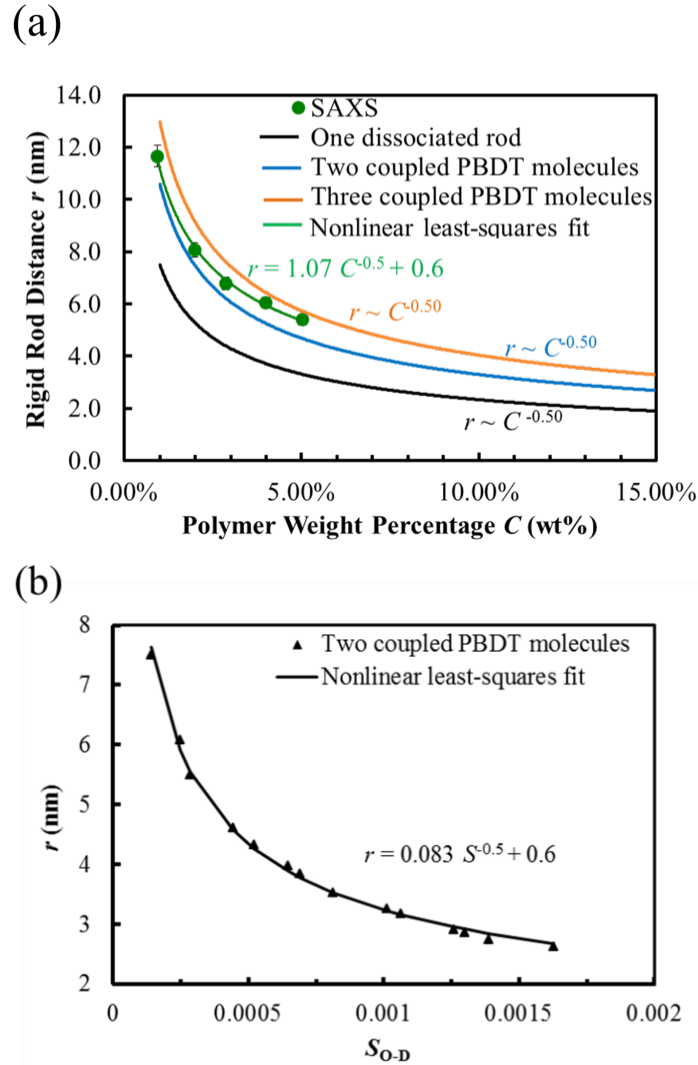


Figure 3.11. The calculated results of rod-rod distance in the proposed model as compared to the experimental results from SAXS. (a) Rigid rod distance as a function of polymer weight percent. The solid curves are calculations corresponding to the number of PBDT chains representing the nematic phase building block, encompassing: one dissociated chain (black line), two coupled PBDT molecules (blue lines), or three coupled

PBDT molecules (orange line). SAXS results are shown as green points and the green line is a two-parameter fit using $C^{0.5}$ dependence plus an intercept representing the rod distance at zero hydration. (b) Rigid rod distance vs. water alignment S_{O-D} (black triangle). The black line shows the nonlinear least-squares fit using the $r \propto S_{O-D}^{-0.5}$ dependence.

Figure 3.11a shows that the rod-rod distance observed using SAXS decreases with increasing polymer concentration, and this experimental curve fits well using the relation $r \propto C^{0.5}$. Since D_2O molecules are also increasingly confined and ordered as rod-rod distance decreases, we can combine the results from ^2H NMR spectroscopy (Section 2.4.3), where we observe $V_e \propto C^{-1}$, with the scaling relation $V_e \propto r^2$ from Equation 3.8 to understand the origin of the scaling $r \propto C^{-0.5}$. In other words, the volume of the hydrated oriented (cylindrical) repeat unit is inversely proportional to the polymer concentration.

In Figure 11b, we can also fit the rod-rod distance as a function of D_2O NMR splittings using the proportionalities $\Delta\nu_Q \propto S_{O-D} \propto C$ to derive the following equation that relates r to the O-D bond order parameter S_{O-D} .

$$r = c (S_{O-D})^{-0.5} + d \quad (3.9)$$

We briefly discuss the physical meanings of the parameters c and d as follows. When $S_{O-D} = 1$ (all O-D bonds are perfectly aligned with B_0), the rod-rod distance $r = c + d = 0.68$ nm, which may be considered as the minimum average hard-sphere distance between two rigid rods. We note again here that each rod may consist of a double helix dimer. The constant $c = 0.083$ nm relates to the interaction between the polymer matrix and water molecules, and can be considered as the proportion of the rod-rod distance on average occupied by the water molecules at the physically relevant value $S_{O-D} = 1$ (perfect ordering). Using these experimentally supported dependencies, we expect to extend such

domain distance vs. orientational order relationships ($r \propto S_{O-D}^{-0.5}$) to investigations of other polymer systems containing nanostructured assemblies and labeled probe molecules.

3.5 Conclusions

We have investigated the ion transport and molecular alignment properties of rigid rod polyelectrolyte solutions using an array of multi-modal NMR, POM, and SAXS analyses. From concentration-dependent ^2H NMR spectroscopy, we observe a proportional relationship between the orientational order of D_2O solvent S_{O-D} and the polymer weight percentage C . We also apply a two state model of water dynamics and a lattice model to expose a relation between the D_2O spectra and nematic rod-rod distance ($r \propto S_{O-D}^{-0.5}$). This result extends our fundamental understanding of how probe molecule (*e.g.*, water) ordering relates quantitatively to polymer matrix ordering. Through PFG NMR diffusometry and counterion condensation theory, we see significantly smaller diffusion coefficients of Na^+ counterions in PBDT solutions compared to other (isotropic, small ion) Na^+ salt solutions, indicating that Na^+ ions tend to condense on PBDT polymer chains. From analysis and comparison of SAXS results, ^2H -labeled PBDT NMR, and the lattice model, we further suggest that two PBDT molecules self-assemble into a double helix to serve as the mesogenic unit of the nematic LC phase. This proposal requires further investigation, but could have significant implications for understanding and controlling supramolecular ordering in synthetic polymer.

Studying the alignment properties and ion transport in these ionomers will help to generate functional materials with ordered hydrophilic aggregations for use in various fields including, polymer electrolyte membranes (PEMs),^[32,46] reverse osmosis membranes,^[47] and anisotropic hydrogels.^[45] Aligned hydrophilic domains in

macromolecular systems can be achieved by selectively applying mechanical stretching,^[18,40] casting schemes (using substrate surface effects and/or capillary/evaporation forces),^[20,25,26] magnetic^[48-50] or electric fields^[51]. However, in most cases relevant to applications, the degree of alignment achieved is small or in the wrong direction for ion conduction. At present, we are producing uniformly aligned PBDT aqueous solutions up to 50 wt % by evaporating solutions in a magnetic field. In the future, we expect to achieve PBDT and PBDT-inspired membranes with conductive pathways strongly oriented through the membrane plane for enhanced ion and water transport in a range of applications.

References

- [1] Marincola, F. C.; Casu, M.; Saba, G.; Lai, A., Na-23 NMR relaxation studies of the Na-DNA/drug interaction, *Chemphyschem*, **2001**, 2, 569.
- [2] Okoshi, K.; Kamee, H.; Suzaki, G.; Tokita, M.; Fujiki, M.; Watanabe, J., Well-defined phase sequence including cholesteric, smectic A, and columnar phases observed in a thermotropic LC system of simple rigid-rod helical polysilane, *Macromolecules*, **2002**, 35, 4556.
- [3] Wu, Z. L.; Arifuzzaman, M.; Kurokawa, T.; Le, K.; Hu, J.; Sun, T. L.; Furukawa, H.; Masunaga, H.; Gong, J. P., Supramolecular Assemblies of a Semirigid Polyanion in Aqueous Solutions, *Macromolecules*, **2013**, 46, 3581.
- [4] Wang, Y.; Gao, J.; Dingemans, T. J.; Madsen, L. A., Molecular Alignment and Ion Transport in Rigid Rod Polyelectrolyte Solutions, *Macromolecules*, **2014**, 47, 2984.
- [5] Wang, Y.; Chen, Y.; Gao, J. W.; Yoon, H. G.; Jin, L. Y.; Forsyth, M.; Dingemans, T. J.; Madsen, L. A., Highly Conductive and Thermally Stable Ion Gels with Tunable Anisotropy and Modulus, *Advanced Materials*, **2016**, 28, 2571.
- [6] Sarkar, N.; Kershner, L. D., Rigid rod water-soluble polymers, *Journal of Applied Polymer Science*, **1996**, 62, 393.
- [7] Ciferri, A. *Liquid crystallinity in polymers: principles and fundamental properties*; 1st ed.; VCH Publishers: New York, 1991.
- [8] Li, J.; Wilmsmeyer, K. G.; Hou, J. B.; Madsen, L. A., The role of water in transport of ionic liquids in polymeric artificial muscle actuators, *Soft Matter*, **2009**, 5, 2596.
- [9] Lodge, T. P., Materials science - A unique platform for materials design, *Science*, **2008**, 321, 50.
- [10] Schmidt-Rohr, K.; Chen, Q., Parallel cylindrical water nanochannels in Nafion fuel-cell membranes, *Nature Materials*, **2008**, 7, 75.
- [11] Goby, J. F.; Vanhoorne, P.; Jerome, R., Synthesis and preliminary characterization of model liquid crystalline ionomers, *Macromolecules*, **1996**, 29, 3376.

- [12] Schwarz, G.; Bodenthin, Y.; Tomkowicz, Z.; Haase, W.; Geue, T.; Kohlbrecher, J.; Pietsch, U.; Kurth, D. G., Tuning the Structure and the Magnetic Properties of Metallo-supramolecular Polyelectrolyte-Amphiphile Complexes, *Journal of the American Chemical Society*, **2011**, *133*, 547.
- [13] Bottcher, C.; Endisch, C.; Fuhrhop, J. H.; Catterall, C.; Eaton, M., High-yield preparation of oligomeric C-type DNA toroids and their characterization by cryoelectron microscopy, *Journal of the American Chemical Society*, **1998**, *120*, 12.
- [14] Lee, J. S. J.; Sokolovskii, R. O.; Berardi, R.; Zannoni, C.; Burnell, E. E., Orientational order of solutes in liquid crystals: The effect of distributed electric quadrupoles, *Chemical Physics Letters*, **2008**, *454*, 56.
- [15] Syvitski, R. T.; Burnell, E. E., Dipole-induced ordering in nematic liquid crystals fact or fiction?, *Chemical Physics Letters*, **1997**, *281*, 199.
- [16] Ao, G. Y.; Nepal, D.; Aono, M.; Davis, V. A., Cholesteric and Nematic Liquid Crystalline Phase Behavior of Double-Stranded DNA Stabilized Single-Walled Carbon Nanotube Dispersions, *ACS Nano*, **2011**, *5*, 1450.
- [17] Kantola, A. M.; Ahola, S.; Vaara, J.; Saunavaara, J.; Jokisaari, J., Experimental and quantum-chemical determination of the H-2 quadrupole coupling tensor in deuterated benzenes, *Physical Chemistry Chemical Physics*, **2007**, *9*, 481.
- [18] Li, J.; Park, J. K.; Moore, R. B.; Madsen, L. A., Linear coupling of alignment with transport in a polymer electrolyte membrane, *Nature Materials*, **2011**, *10*, 507.
- [19] Hou, J. B.; Zhang, Z. Y.; Madsen, L. A., Cation/Anion Associations in Ionic Liquids Modulated by Hydration and Ionic Medium, *Journal of Physical Chemistry B*, **2011**, *115*, 4576.
- [20] Hou, J. B.; Li, J.; Madsen, L. A., Anisotropy and Transport in Poly(arylene ether sulfone) Hydrophilic-Hydrophobic Block Copolymers, *Macromolecules*, **2010**, *43*, 347.
- [21] Walderhaug, H.; Soderman, O.; Topgaard, D., Self-diffusion in polymer systems studied by magnetic field-gradient spin-echo NMR methods, *Progress in Nuclear Magnetic Resonance Spectroscopy*, **2010**, *56*, 406.
- [22] Burnell, E. E.; de Lange, C. A. *NMR of Ordered Liquids*; 1st, Ed.; Springer: The Netherlands, 2003.
- [23] Wilmsmeyer, K. G.; Zhang, X. L.; Madsen, L. A., Switchable bistable ordering and real-time alignment dynamics in wormlike micelles, *Soft Matter*, **2012**, *8*, 57.
- [24] Chowdhury, S.; Madsen, L. A.; Frazier, C. E., Probing Alignment and Phase Behavior in Intact Wood Cell Walls Using H-2 NMR Spectroscopy, *Biomacromolecules*, **2012**, *13*, 1043.
- [25] Li, J.; Wilmsmeyer, K. G.; Madsen, L. A., Hydrophilic channel alignment modes in perfluorosulfonate ionomers: Implications for proton transport, *Macromolecules*, **2008**, *41*, 4555.
- [26] Li, J.; Wilmsmeyer, K. G.; Madsen, L. A., Anisotropic Diffusion and Morphology in Perfluorosulfonate Ionomers Investigated by NMR, *Macromolecules*, **2009**, *42*, 255.
- [27] Deloche, B.; Samulski, E. T., Short-Range Nematic-Like Orientational Order in Strained Elastomers - a Deuterium Magnetic-Resonance Study, *Macromolecules*, **1981**, *14*, 575.
- [28] Terzis, A. F.; Snee, P. T.; Samulski, E. T., Orientational order of water confined in anisotropic cavities, *Chemical Physics Letters*, **1997**, *264*, 481.

- [29] Price, W. S., Pulsed-field gradient nuclear magnetic resonance as a tool for studying translational diffusion .1. Basic theory, *Concepts in Magnetic Resonance*, **1997**, 9, 299.
- [30] Joabsson, F.; Nyden, M.; Linse, P.; Soderman, O., Pulsed field gradient NMR studies of translational diffusion in cylindrical surfactant aggregates, *Journal of Physical Chemistry B*, **1997**, 101, 9710.
- [31] Manning, G.; Joy, A.; Mathias, C. J.; McDonald, C. J.; MillarCraig, M. W., Double-blind, parallel, comparative multicentre study of a new combination of diltiazem and hydrochlorothiazide with individual components in patients with mild or moderate hypertension, *Journal of Human Hypertension*, **1996**, 10, 443.
- [32] Elabd, Y. A.; Hickner, M. A., Block Copolymers for Fuel Cells, *Macromolecules*, **2011**, 44, 1.
- [33] Kreuer, K.-D., Ion Conducting Membranes for Fuel Cells and other Electrochemical Devices, *Chemistry of Materials*, **2013**, 26, 361.
- [34] Nelson, E. J.; Samulski, E. T., Preparation of Cds Nanoparticles within an Ordered Polypeptide Matrix, *Materials Science & Engineering C-Biomimetic Materials Sensors and Systems*, **1995**, 2, 133.
- [35] Hou, J. B.; Madsen, L. A., New insights for accurate chemically specific measurements of slow diffusing molecules, *Journal of Chemical Physics*, **2013**, 138.
- [36] Chen, W. L.; Sato, T.; Teramoto, A., Interfacial tension between coexisting isotropic and nematic phases for a lyotropic polymer liquid crystal: Poly(n-hexyl isocyanate) solutions, *Macromolecules*, **1998**, 31, 6506.
- [37] Manning, G. S., The critical onset of counterion condensation: A survey of its experimental and theoretical basis, *Berichte Der Bunsen-Gesellschaft-Physical Chemistry Chemical Physics*, **1996**, 100, 909.
- [38] Manning, G. S., The counterion distribution in solutions of rod-shaped polyelectrolytes - Comments, *Journal of Polymer Science Part B-Polymer Physics*, **1996**, 34, 393.
- [39] Manning, G. S., Counterion condensation theory constructed from different models, *Physica A*, **1996**, 231, 236.
- [40] Park, J. K.; Li, J.; Divoux, G. M.; Madsen, L. A.; Moore, R. B., Oriented Morphology and Anisotropic Transport in Uniaxially Stretched Perfluorosulfonate Ionomer Membranes, *Macromolecules*, **2011**, 44, 5701.
- [41] Lingwood, M. D.; Zhang, Z. Y.; Kidd, B. E.; McCreary, K. B.; Hou, J. B.; Madsen, L. A., Unraveling the local energetics of transport in a polymer ion conductor, *Chemical Communications*, **2013**, 49, 4283.
- [42] Davis, J. H.; Bloom, M.; Butler, K. W.; Smith, I. C. P., The Temperature-Dependence of Molecular Order and the Influence of Cholesterol in Acholeplasma-Laidlawii Membranes, *Biochimica et Biophysica Acta*, **1980**, 597, 477.
- [43] Fernandez, D. I.; Le Brun, A. P.; Whitwell, T. C.; Sani, M. A.; James, M.; Separovic, F., The antimicrobial peptide aurein 1.2 disrupts model membranes via the carpet mechanism, *Physical Chemistry Chemical Physics*, **2012**, 14, 15739.
- [44] Samulski, E. T., Macromolecular Structure and Liquid Crystallinity, *Faraday Discussions*, **1985**, 79, 7.
- [45] Wu, Z. L.; Kurokawa, T.; Liang, S.; Furukawa, H.; Gong, J. P., Hydrogels with Cylindrically Symmetric Structure at Macroscopic Scale by Self-Assembly of Semi-rigid Polyion Complex, *Journal of the American Chemical Society*, **2010**, 132, 10064.

- [46] Kreuer, K. D., Proton conductivity: Materials and applications, *Chemistry of Materials*, **1996**, 8, 610.
- [47] Zhou, M. J.; Nemade, P. R.; Lu, X. Y.; Zeng, X. H.; Hatakeyama, E. S.; Noble, R. D.; Gin, D. L., New type of membrane material for water desalination based on a cross-linked bicontinuous cubic lyotropic liquid crystal assembly, *Journal of the American Chemical Society*, **2007**, 129, 9574.
- [48] Tran, H.; Gopinadhan, M.; Majewski, P. W.; Shade, R.; Steffes, V.; Osuji, C.; Campos, L. M., Monoliths of Semiconducting Block Copolymers by Magnetic Alignment, *Acs Nano*, **2013**, 7, 5514.
- [49] Majewski, P. W.; Gopinadhan, M.; Jang, W. S.; Lutkenhaus, J. L.; Osuji, C. O., Anisotropic Ionic Conductivity in Block Copolymer Membranes by Magnetic Field Alignment, *Journal of the American Chemical Society*, **2010**, 132, 17516.
- [50] Gopinadhan, M.; Majewski, P. W.; Choo, Y.; Osuji, C. O., Order-Disorder Transition and Alignment Dynamics of a Block Copolymer Under High Magnetic Fields by In Situ X-Ray Scattering, *Physical Review Letters*, **2013**, 110.
- [51] Park, M. J.; Balsara, N. P., Anisotropic Proton Conduction in Aligned Block Copolymer Electrolyte Membranes at Equilibrium with Humid Air, *Macromolecules*, **2010**, 43, 292.

Chapter 4

Double-Stranded Helical Conformation in PBDT Polyelectrolyte Solutions

4.1 Abstract

A synthetic sulfonated aramid polyanion, poly-2,2'-disulfonyl-4,4'-benzidine terephthalamide (PBDT), shown in **Figure 4.1a**, is a water-miscible system. PBDT forms a lyotropic nematic liquid crystal (LC) above a critical concentration $C^* = 2\%$ and has high ion density along the polymer backbone.^[1] We have described a basic understanding of the morphology of the PBDT aqueous solutions in previous publications.^[2] Herein, we will further describe a number of similarities between PBDT and DNA molecules in order to demonstrate the double helical conformation of this rigid-rod polyelectrolyte. Understanding the similarities between these two systems lays foundation for better applications of PBDT aqueous solutions in various aspects.

4.2 Introduction

The double-stranded helical conformation of DNA molecules, serves as the storage and transfer of genetic information for life, has been discovered for decades.^[3,4] Potential applications of helical polymers involve not only enantioselective and asymmetric catalysts for chemical reactions, but also novel scaffolds and templates for supramolecular self-assembly.^[5,6] The overwhelming importance of helix has encouraged chemists to construct multi-strand helical molecules. Over the previous decades, discoveries of single-strand helical macromolecules are not rare, however, only a few structural motifs for double helical oligomers, such as peptide nucleic acids^[7], amidinium-carboxylate salt bridges^[8-10], aromatic oligoamides^[11] and coordination polymers^[12-14], have been reported. The most widely used approaches to build double-

stranded helix include metal-directed self-assembly (ligand-containing) and hydrogen-bonding-driven self-assembly (interstrand hydrogen-bonding and aromatic-aromatic interactions).^[10,15] However, synthetic polymers with double helical conformations are still seldom reported other than isotactic poly(methyl methacrylate) (*it*-PMMA) and self-assembled oligomers.^[16,17] Herein, we describe an aromatic sulfonated polyamide that elaborately possesses the double helical conformation as compared to DNA molecules. The demonstration is a complementary verification from X-ray diffraction, ²³Na NMR, and molecular dynamics simulation.

4.3 Experimental

PBDT solutions. PBDT bulk polymer was dried under vacuum at room temperature for 2 days. Aqueous solutions with PBDT weight percentages (wt%) ranging from 4 to 20% were prepared by loading the prescribed amount of PBDT and D₂O into 5 mm NMR tubes. D₂O was used as received from Cambridge Isotope Laboratories (~99.9%). All of the sample tubes were flame-sealed immediately to prevent evaporation of water and were equilibrated at 80 °C in a water bath for 1 week to ensure complete dissolution and homogenization.

²³Na NMR: The Bruker Avance III WB 400 MHz (9.4 T) NMR was equipped with a 5 mm axial saddle ²³Na rf coil. A simple 90° r.f. pulse was applied for all measurements at 25°C.

X-ray Diffraction (XRD): The X-ray experiments were carried out on a Rigaku Oxford Diffraction Xcalibur Nova Single-Crystal Diffractometer equipped with an Onyx CCD detector and a Cu microsource operating at 49.5 kV and 80 mA at room temperature. The 20% PBDT aqueous solution was sealed in a capillary with 1.5 mm

diameter and 0.01 mm wall thickness and mounted on the edge of a steel pin. The sample to detector distance was 120 mm, providing the data at a scattering angle 2θ from 5° to 34° . The capillary was oriented at a 45° angle relative to the beamstop in order to minimize beamstop interference in the diffraction patterns. The sample was rotated 2° in ϕ (i.e. along the fiber axis). For each sample, a total of 200 images with 1200 s exposure time was collected and summed to increase signal-to-noise. The software CrysAlisPro (v1.171.37.35, Rigaku Oxford Diffraction, 2015, Rigaku Corporation, Oxford, UK) was used for data collection and analysis.

Small-Angle X-ray Scattering (SAXS). All SAXS experiments were operated on a Rigaku S-Max 3000 pinhole SAXS system, equipped with a copper rotating anode emitting X-rays with a wavelength λ of 0.154 nm (Cu $K\alpha$) and a sample-to-detector distance of 1600 mm. The relationship between pixel width and scattering vector q was determined by calibrating with a silver behenate standard sample. PBDT aqueous solutions with specific concentrations were sealed in capillaries with 1.5 mm diameter and 0.01 mm wall thickness. Before the SAXS measurements, the capillaries containing polymer solutions were placed axially along the field of a 7.1 T (300 MHz) NMR magnet to achieve uniaxial alignment. Then the capillaries were placed horizontally in the SAXS sample chamber with zero magnetic field. All 2D SAXS patterns were analyzed by the SAXSGUI software package (Rigaku Innovative Technologies, Inc.) to generate the integrated SAXS intensity $I(q)$ as a function of scattering vector q , where $q = (4\pi \sin \theta)/\lambda$. The angle θ refers to one-half of the total scattering angle.

MD simulation: The simulations of the polymer chains in gas were all done with CM3D. The force field was the Assisted Model Building with Energy Refinement

(AMBER), which is often used for simulating proteins and DNA. Periodic boundary conditions (PBC) were used for all simulations and a Nose-Hoover thermostat was used for simulations with a constant temperature.

4.4 Results and Discussion

4.4.1 Real X-ray Diffraction versus Simulated Diffraction Results

X-ray diffraction technique is commonly used to illustrate the crystalline or semi-crystalline structure of small molecules, proteins and macromolecules. In 1953, the DNA double helical configuration was firstly proposed by Watson and Crick^[3,4] based on the unique X-ray diffraction patterns on DNA fibers. Here, we also employed X-ray diffraction technique to study the packing structure and morphology of PBDT aqueous solutions. Since it is difficult for us to obtain highly aligned PBDT fibers, we try to run X-ray experiments on highly concentrated and magnetically oriented PBDT aqueous solutions. The 2D X-ray diffraction pattern for 20 wt% PBDT aqueous solution, shown in **Figure 4.1e**, is obtained by single crystal X-ray diffraction technique, without the in situ *B* field. The highly oriented fiber diffraction patterns indicate that the strong monodomain orientational order induced by *B* field is maintained after removal from the field. The main diffraction patterns are labeled with *A*, *B*, *C*, *D*, *E* and *F* (*A* = 5.6 Å, *B* = 8.4 Å, *C* = 16.8 Å, *D* ≈ 30 Å, *E* = 8 Å and *F* = 3.3 Å). The blue arrow shows the direction of the capillary in the instrument. Based on the diffraction patterns, we can elucidate the double helical conformation of PBDT chains in aqueous solutions as follow. In **Figure 4.1b**, the chemical repeat unit of PBDT can be considered as three subunits, including one $-(SO_3)^-_2-$ and two $-NHCO-$. The three subunits are mutually connected by one benzene ring. Thus, the chemical repeat unit length of PBDT is 16.8 Å (*C*), which is

composed of three subunits with equal length of 5.6 Å (A). The 2nd strand is shifted 8.4 Å ($B = 3A/2$) away from the 1st strand, the intermolecular hydrogen bonding (between $-(\text{SO}_3)^{-}_2-$ and $-\text{NHCO}-$) and the rotation of each subunit contribute to the formation of the double helical conformation. B is the distance between two $-(\text{SO}_3)^{-}_2-$ along the polymer chain. The length of hydrogen bonding is represented by F . **Figure 4.1c** mimics the self-assembly behavior of PBDT chains in H_2O with Na^+ counterions. For 20 wt% PBDT aqueous solution, the rod-rod distance is ~ 30 Å, represented by D . The diameter of the double helix is represented by E . In addition to the main diffraction patterns, we can see that the unique “X pattern” is similar as that of DNA fibers. In order to elucidate the “X pattern”, we propose a model with critical parameters in **Figure 4.1d**, and then we simulate the X-ray diffraction patterns (**Figure 4.1f**), using a package called “HELIX”. The detailed simulation parameters and the information about the package are included in the Supporting Information. The simulated results show high coincidence with the experimental results. The main difference is the absence of reflections on the meridian along the layer line number 1 and 2. The reason is that the simulation software cannot differentiate $-(\text{SO}_3)^{-}_2-$ and $-\text{NHCO}-$, thus the subunit length of B and C are absent in the simulated results. However, the layer line spacing agrees perfectly with the experimental X-ray diffraction patterns.

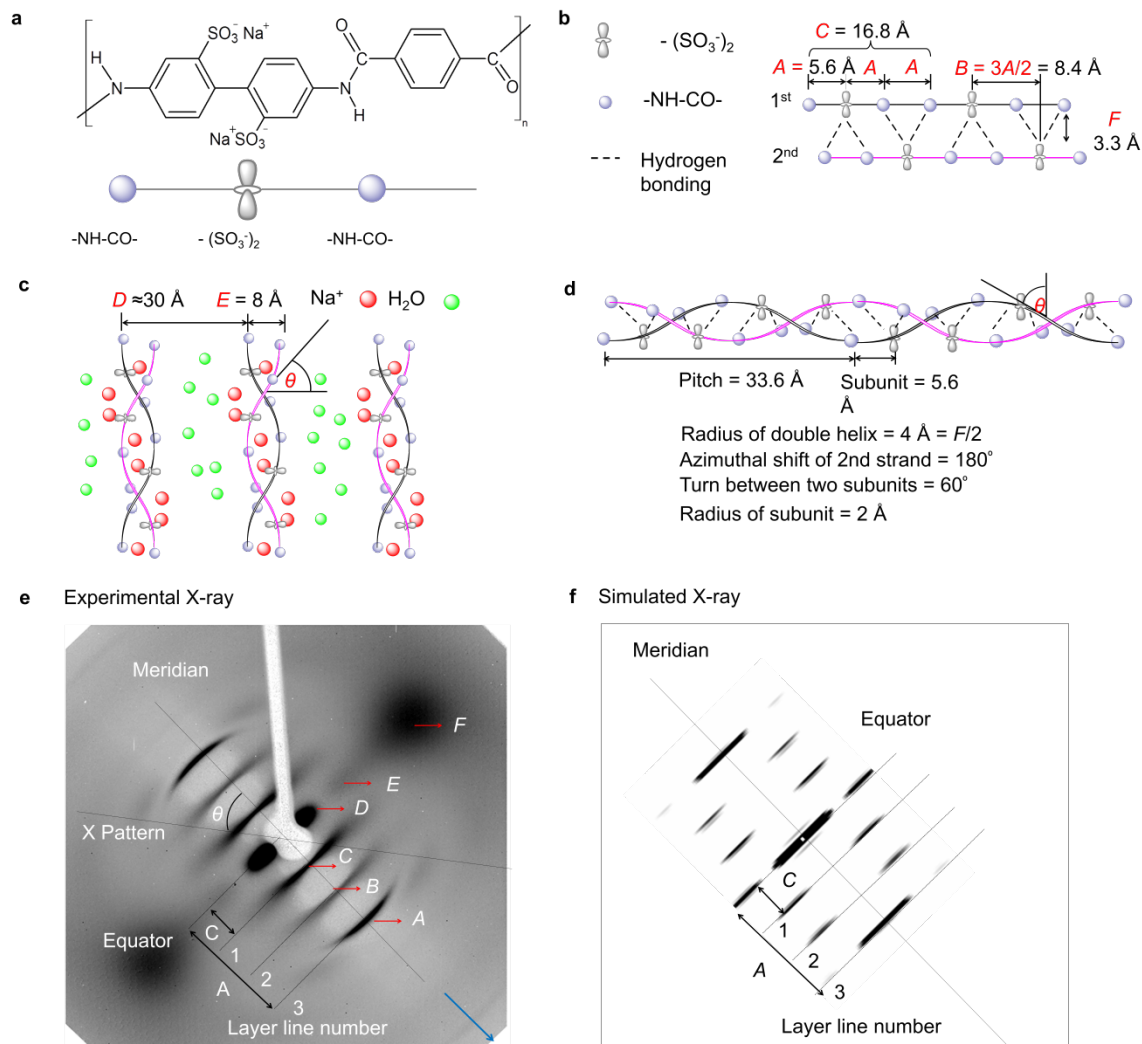


Figure 4.1. The experimental and simulation results of XRD for 20wt% PBDT aqueous solution. (a) The chemical repeat unit of PBDT. (b) The elucidation of hydrogen bonding and molecular packing for PBDT with double helical conformation. (c) The self-assembled morphology of PBDT aqueous solution. The red dots refer to the Na^+ counterions. The green dots are the water molecules. (d) The model packing and main parameters for the simulation. (e) The X-ray diffraction pattern for 20 wt% PBDT aqueous solution. The main diffractions are labelled and the tilt angle is θ . (f) The simulated X-ray diffraction patterns.

4.4.2 Correlation between ^{23}Na NMR Spectroscopy and SAXS

Additionally, from the aspect of molecular dynamics, ^{23}Na -NMR has also been utilized to investigate the concentrated sodium-DNA solutions by Strzelecka and Rill.^[18,19] Triplet splittings of Na^+ counterions are attributed to the interaction between the Na electric quadrupole moment and the electric field gradient (*efg*) of the Na^+ in anisotropic ambient. The triplet splittings of Na^+ in concentrated DNA aqueous solutions are observed.^[18,19] The magnitude of the quadrupole splittings decreases with increasing DNA concentration at low temperatures, whereas increases with increasing concentration at high temperature. The temperature- and concentration- dependent changes in quadrupole splitting are consistent with an angle between the DNA helix axis and the principal component of the local *efg* tensor near the “magic angle” of 54.7° .^[18,19] By developing the same experimental design for the PBDT concentrated solutions, we observe similar results. As shown in **Figure 4.2a**, the quadrupole splitting of ^{23}Na will approximately converges to null with concentration around 10% at 25°C . The null concentration is also dependent on the temperature. One possible explanation of the abnormal quadrupole splitting is that the Na^+ ions form bridges between neighboring double helix, the intra-helical Na^+ interaction along the PBDT backbones and inter-helical Na^+ interaction between two rigid rods are averaged. As shown in Figure 2b, when the concentration increases, the rod-rod distance decreases, meanwhile the inter-helix Na^+ interaction is elevated with the decreasing Na^+ quadrupole splitting. As the concentration approaches around 9.5% (The intersection point, SI), this specific point will contribute to the magic angle between the PBDT helix axis and the principal component of the local *efg* tensor, shown in **Figure 4.2b**. With the concentration increases further, we can observe that the quadrupole splitting increases again. Based on

this deduction, we know that the ratio of the pitch length to the rod-rod distance is $1/\sqrt{2}$ when $C = 9.5\%$ at the null point with magic angle. The length of pitch along the rigid rod is $33.6 \text{ \AA}$, then the rod-rod distance should be around $48 \text{ \AA}$ under the condition of magic angle 54.7° , as shown in **Figure 4.2c**. Compared to our previous calculation results based on double helical model, the relationship between rod-rod distance (r) and the concentration (C) follows

$$r = 1.07C^{-0.5} + 0.6 \quad (4.1)$$

$r = 41 \text{ \AA}$ ($C = 0.095$), which agrees very well with the proposed $48 \text{ \AA}$.^[1] In order to further verify the model equation, we employ SAXS to investigate the rod-rod distance. As shown in Figure 1c, the rod-rod distance is $43 \text{ \AA}$ for 10% PBDT solution, which is very close to the values, obtained from the proposed model. Thus, as a complementary method for X-ray scattering, the Na quadrupole splitting results can also be utilized to verify the double helical conformation of PBDT aqueous solutions.

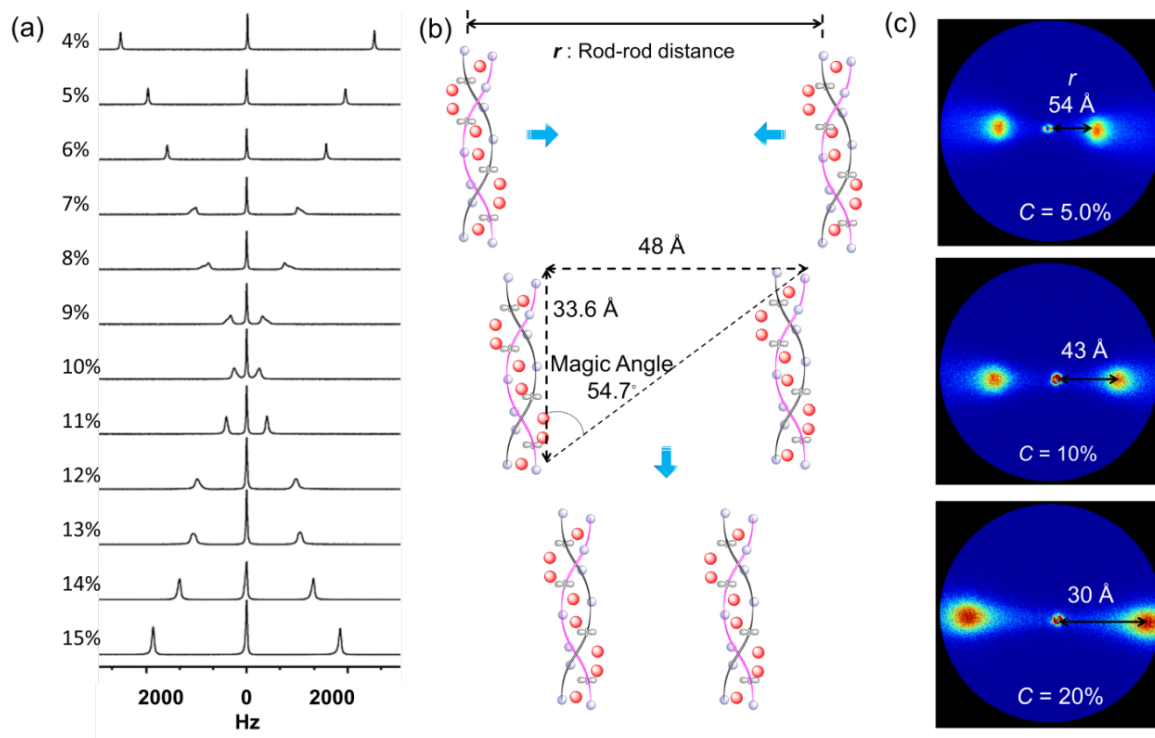


Figure 4.2. ^{23}Na NMR and SAXS results for PBDT aqueous solution with varying concentration. (a) Concentration-dependent ^{23}Na quadrupole spectra for PBDT aqueous solutions. (b) The configuration of the PBDT self-assembly behavior with increasing concentration. (c) The SAXS for concentration of 5%, 10% and 20%.

In addition to the concentration dependence of the quadrupole splitting, we also test the quadrupole splitting as a function of the temperature. We can also observe similar splitting pattern as compared to the concentration, the splitting decrease first and increase again with increasing temperature as shown in **Figure 4.3a**. This abnormal dependence is also seen in the aqueous solution of DNA molecules. **Figure 4.3b** shows the longitudinal (T_1) and transverse (T_2) relaxation of Na^+ counterions in the polymer solution. As reported previously, the inequality of T_1 and T_2 originates from fast motions (> 0.5 ns), such as counterion exchange, change of direction of the polyion segments, and counterion

diffusion along a curved polyion rod.^[20] However, we have not found any apparent difference of T_1 and T_2 relaxation time from **Figure 4.3b**. Thus, we may demonstrate that there is no fast Na^+ motion along a curved rod or fast internal motions in the rod. This demonstration agrees very well with the results based on the counterion condensation theory that has been reported in Chapter 3, where we have discussed about the association behavior of the Na^+ in PBDT aqueous solutions.

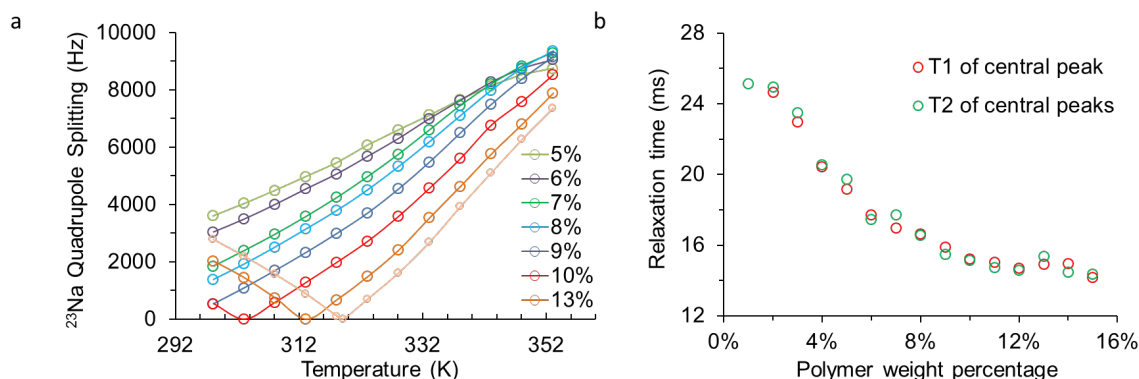


Figure 4.3. The ^{23}Na quadrupole splitting, T_1 and T_2 relaxation of Na^+ counterions in PBDT aqueous solutions. (a) The quadrupole splitting of ^{23}Na spectra as a function of the temperature. (b) The T_1 and T_2 relaxation as function of the polymer weight percentage in the PBDT polymer solution.

4.4.3 MD simulation to confirm the double helix structure of PBDT

In the last section, the PBDT configuration is further investigated by MD simulations to see how this polymer can form hydrogen bondings to other polymer chains when two or more chains are present. All these simulations were done with NVT ensembles. We will mainly talk about the simulation results done in vacuum. We also did the simulations of the PBDT chains in water. However, the interactions between the water molecules and

the PBDT chains are complicated. We will not discuss the details here. To simplify the model, we studied the PBDT with counterions of hydrogen. The polymer chains are three monomer units long. **Figure 4.4a** is the optimized structure of monomer of PBDT with counterion of hydrogen. Simulations were done for two and three chains with equal distance from each other at $t = 0$. The runtime for each simulation was at least 100 picoseconds. Multiple configurations for these polymers were seen in gas simulations but eventually, if the temperature was high enough (250 K), helices with two strands were observed. To form these helices, the main form of interaction between the chains is the hydrogen bonding between the oxygen of $-\text{SO}_3^-$ and the hydrogens of $-\text{NHCO}-$, as shown in **Figure 4.4b**. The first $-\text{SO}_3^-$ of the lower chain forms a hydrogen bond with the second $-\text{NHCO}-$ of the upper chain and the second $-\text{SO}_3^-$ of the lower chain forms a hydrogen bond with the first $-\text{NHCO}-$ of the upper chain. If the hydrogen bonds are not crossed as shown in Figure 4b, the helix cannot form neatly. While still equilibrating, amide-amide hydrogen bonding is also seen but this is never seen in the final helix configuration. Hydrogen bonding between acceptor (O) of $-\text{NHCO}-$ and donor (H) of $-\text{SO}_3\text{H}$ is never observed between the chains. **Figure 4.4c-f** show the simulation results by involving two PBDT chains and three PBDT chains. Both of them contribute to the double helical conformation after 100 ps. To form a complete pitch of the helix, 8 hydrogen bonds (4 pairs of crossed hydrogen bonding) between the 8 amide groups and the 8 sulfonate groups are required. The distance between two assembled sulfonate units is 8.4 Å. Thus, the simulated morphology based on the molecular dynamic simulation is also highly consistent with the model we proposed in the **Figure 4.1**.

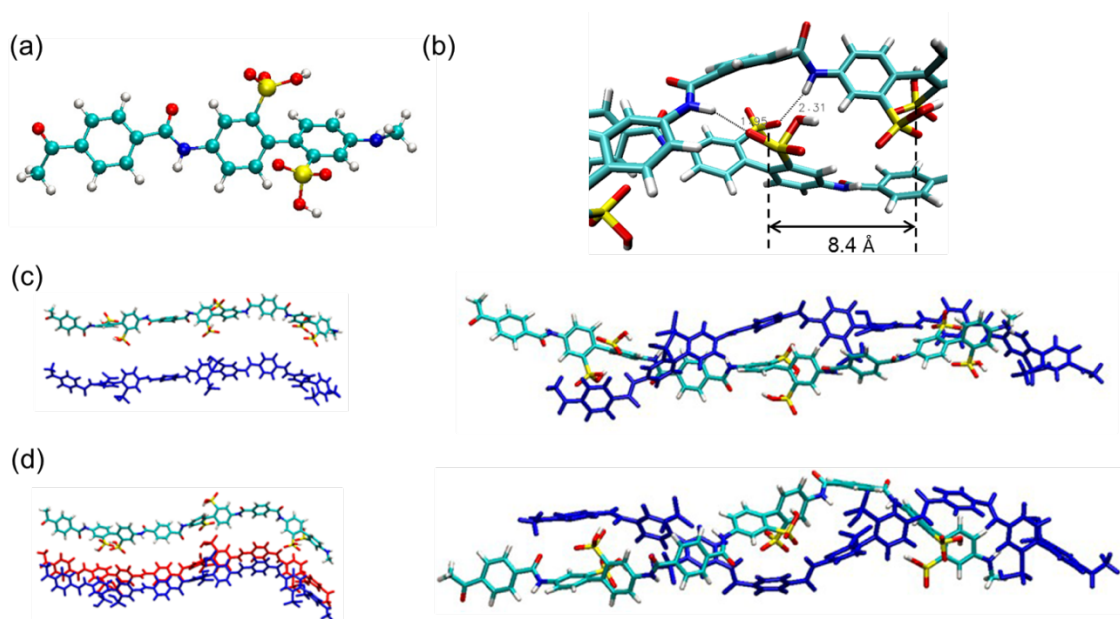


Figure 4.4. The molecular dynamic simulation of PBDT polymer chains. (a) The optimized monomer structure of the PBDT. (b) The crossed hydrogen bonding formed between the amide and sulfonate group. (c, d) The simulation result for two oligomers in 100ps in vacuum at $T = 300$ K. (e, f) The simulation result for three oligomers in 100ps in vacuum at $T = 300$ K.

4.5 Conclusion

In this chapter, we discuss the molecular configuration of PBDT chains in aqueous solutions. Based on the comparison of characterization techniques on the aqueous solutions, we found a number of similarities between PBDT and DNA molecules. This work not only resolve the configuration of the PBDT molecular chain, but also lay foundation for discovering broader applications based on the aqueous polymer solution. By using a combination of characterization methods, we can get a better understanding of

the molecular packing and the counterion association behavior that can be used to understand other polyelectrolyte systems.

References

- [1] Wang, Y.; Gao, J.; Dingemans, T. J.; Madsen, L. A., Molecular Alignment and Ion Transport in Rigid Rod Polyelectrolyte Solutions, *Macromolecules*, **2014**, *47*, 2984.
- [2] Gao, J.; Wang, Y.; Norder, B.; Garcia, S. J.; Picken, S. J.; Madsen, L. A.; Dingemans, T. J., Water and sodium transport and liquid crystalline alignment in a sulfonated aramid membrane, *Journal of Membrane Science*, **2015**, *489*, 194.
- [3] Watson, J. D.; Crick, F. H. C., Genetical Implications of the Structure of Deoxyribonucleic Acid, *Nature*, **1953**, *171*, 964.
- [4] Watson, J. D.; Crick, F. H. C., Molecular Structure of Nucleic Acids - a Structure for Deoxyribose Nucleic Acid, *Nature*, **1953**, *171*, 737.
- [5] Nakano, T.; Okamoto, Y., Synthetic helical polymers: Conformation and function, *Chemical Reviews*, **2001**, *101*, 4013.
- [6] Reggelin, M.; Doerr, S.; Klussmann, M.; Schultz, M.; Holbach, M., Helically chiral polymers: A class of ligands for asymmetric catalysis, *Proceedings of the National Academy of Sciences of the United States of America*, **2004**, *101*, 5461.
- [7] Nielsen, P. E., Peptide nucleic acid. A molecule with two identities, *Accounts of Chemical Research*, **1999**, *32*, 624.
- [8] Maeda, T.; Furusho, Y.; Sakurai, S. I.; Kumaki, J.; Okoshi, K.; Yashima, E., Double-stranded helical polymers consisting of complementary homopolymers, *Journal of the American Chemical Society*, **2008**, *130*, 7938.
- [9] Onouchi, H.; Okoshi, K.; Kajitani, T.; Sakurai, S. I.; Nagai, K.; Kumaki, J.; Onitsuka, K.; Yashima, E., Two- and three-dimensional smectic ordering of single-handed helical polymers, *Journal of the American Chemical Society*, **2008**, *130*, 229.
- [10] Tanaka, Y.; Katagiri, H.; Furusho, Y.; Yashima, E., A modular strategy to artificial double helices, *Angewandte Chemie-International Edition*, **2005**, *44*, 3867.
- [11] Huc, I., Aromatic oligoamide foldamers, *European Journal of Organic Chemistry*, **2004**, *17*.
- [12] Xiao, D.-R.; Wang, E.-B.; An, H.-Y.; Li, Y.-G.; Xu, L., Syntheses and Structures of Three Unprecedented Metal-Ciprofloxacin Complexes with Helical Character, *Crystal Growth & Design*, **2007**, *7*, 506.
- [13] Shen, Y. M.; Ma, N.; Wu, L. L.; Song, H. H., Structural diversity of four 1D chain coordination polymers based on chiral N-tosyl-L-glutamic acid: Effect of metal ions and N-donor ancillary ligands, *Inorganica Chimica Acta*, **2015**, *429*, 51.
- [14] Zhang, Q. N.; Sha, J. Q.; Yan, H.; Yang, Q. S.; Zhang, Y.; Li, L.; Wang, D. W.; Yang, X. N., Assembly of an unprecedented metal-pipemidic acid complex modifying octamolybdates containing like DNA spiral chain, *Solid State Sciences*, **2014**, *32*, 20.
- [15] Xia, Y. N.; Wu, B.; Liu, Y. Y.; Yang, Z. W.; Huang, X. J.; He, L.; Yang, X. J., A flexible bis(pyridylcarbamate) anion receptor: binding of infinite double-stranded phosphate, $[-\text{sulfate}-(\text{H}_2\text{O})_2-]_n$, and hydrogen-bridged helical perchlorate chain, *Crystengcomm*, **2009**, *11*, 1849.

- [16] Urbanek, S.; Tashiro, K.; Kitayama, T.; Hatada, K., Crystallite modulus of double-stranded helices of isotactic poly(methyl methacrylate): the X-ray measurement and the theoretical calculation, *Polymer*, **1999**, *40*, 3345.
- [17] Urbanek, S.; Tashiro, K.; Kitayama, T.; Hatada, K., Crystallite modulus of double-stranded helices of isotactic poly(methylmethacrylate): the x-ray measurement and the theoretical calculation, *Polymer*, **1999**, *40*, 3345.
- [18] Strzelecka, T. E.; Rill, R. L., Na-23 Nmr of Concentrated DNA Solutions - Salt Concentration and Temperature Effects, *Journal of Physical Chemistry*, **1992**, *96*, 7796.
- [19] Strzelecka, T. E.; Rill, R. L., A Na-23-Nmr Study of Sodium DNA Interactions in Concentrated DNA Solutions at Low-Supporting Electrolyte Concentration, *Biopolymers*, **1990**, *30*, 803.
- [20] Gustavsson, H.; Lindman, B.; Bull, T., Na-23 Nuclear Magnetic-Resonance in Polyanion Solution - Correlation Times and Quadrupole Coupling-Constants of Na⁺ Bound to Poly(Methacrylic Acid), *Journal of the American Chemical Society*, **1978**, *100*, 4655.

Chapter 5

Highly Conductive and Thermally Stable Ion Gels with Tunable Anisotropy and Modulus

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5.1 Abstract

In this chapter, we develop a new liquid-crystalline ion gel exhibiting unprecedented properties: conductivity up to 8 mS cm^{-1} , thermal stability to 300°C , and electrochemical window to 6.1 V , as well as adjustable transport anisotropy (up to $3.5\times$) and elastic modulus ($0.03\text{--}3 \text{ GPa}$). This ion gel is a combination of ionic liquid and magnetically oriented rigid-rod polyanion that provides widely tunable properties for use in diverse electrochemical devices.

5.2 Introduction

As key components of many energy storage and conversion technologies, polymer electrolyte materials allow for selective transport in diverse applications such as fuel cell membranes,^[1-3] battery separators,^[4] electro-responsive actuators,^[5] reverse-osmosis water purifiers,^[6] and solar cells.^[7] For rechargeable battery applications, solid-state polymer electrolytes deliver safer operation and mechanical stability without the leakage, volatility, or flammability issues usually associated with liquid-based electrolytes. However, current battery electrolytes are usually restricted to the use of volatile liquid electrolytes to provide efficient ion transport.^[8-11] Ion gels are polymeric networks swollen with a large volume fraction of ionic liquids (ILs).^[10,12-15] As promising

candidates for next-generation electrolytes, ion gels possess complementary features such as high ion mobility, excellent thermal stability, mechanical integrity (yet easy to cut and incorporate into devices), and conformable electrode-electrolyte contact.^[10,15-17] Moreover, applications of ion gels in fuel cells and electroactive actuators would benefit from a large or adjustable modulus while retaining anisotropic ionic mobility along a predetermined axis – properties that have remained out of reach for known ion gel electrolytes.^[9,10,18-20] In this letter, we describe a new liquid crystalline (LC) ion gel based on a rigid-rod polyanion and an IL that provides an unprecedented combination of tunable properties for use in a wide array of electrochemical devices, especially in fuel cells, ion batteries and electromechanical actuators. The fabrication method proposed here contributes to further development of materials requiring well-defined ordering for efficient transport of protons and ions in fuel cells and ion batteries.

Lodge *et al.* have studied morphology, ionic conductivity, modulus, viscoelasticity, gelation behavior, and capacitance of ion gels and membranes fabricated from diblock or triblock copolymers and swollen with ILs.^[13,18,21] Watanabe *et al.* have also successfully produced pyridinium and imidazolium salt-based ion gels by *in situ* polymerization of vinyl monomers in ILs.^[14,21] The resulting materials possess ionic conductivity up to 1 mS cm⁻¹ at room temperature, but have not exhibited useful macroscopic alignment and possess an undesirable tradeoff between elastic modulus and conductivity.^[10,12,18,22,23] In order to achieve aligned ion conduction pathways in macromolecular systems such as liquid crystal (LC) polymers and block copolymers, researchers have applied mechanical stretching,^[1,24] solution casting,^[25] and magnetic or electric fields.^[9,26,27] For example, after mechanical drawing, the benchmark polymer membrane Nafion[®] exhibits enhanced

water diffusion along the (in-plane) drawing axis.^[1,28] In contrast, membrane electrolytes with faster diffusion along the desired through-plane direction are seldom reported.^[10] Recently, Osuji *et al.* successfully applied a magnetic field (**B**-field) to achieve higher through-plane conductivity in membranes by introducing a smectic LC sequence to a poly(ethylene oxide)-based polymer.^[9] The resulting hot pressed membrane shows conductivity anisotropy of up to 450, whereas the ionic conductivity ($10^{-10} - 10^{-7} \text{ S cm}^{-1}$) along the alignment axis is limited by the solid hydrophilic phase of PEO.^[9] Furthermore, block-copolymer films have been developed for use as Li^+ battery electrolytes that provide high elastic (storage) modulus ($> 0.1 \text{ GPa}$ at $T < 125^\circ\text{C}$) to prevent macroscopic Li electrode dendrite formation,^[29] but these only exhibit conductivity in the range $10^{-8} - 10^{-5} \text{ S cm}^{-1}$.^[11,18] Above all, ion gel electrolytes with high ionic conductivity as well as high modulus offer promise in resolving safety and efficiency issues in Li-ion batteries and higher energy density Li-metal batteries.^[30]

In this report, we describe a new liquid crystal (LC) ion gel with the following exceptional combination of properties: transport anisotropy up to $3.5\times$, high ionic conductivity (up to 8 mS cm^{-1}), widely tunable modulus ($0.03 - 3 \text{ GPa}$) and high thermal stability (up to 300°C). This material is formed by combining an ionic liquid with a rigid-rod polyanion in the presence of a magnetic (**B**) field. Based on this unique combination of component precursors, this material not only breaks the usual trade off between ionic conductivity and modulus, but also exhibits macroscopic alignment in the as-formed ion gels. Lyotropic LC phases can be formed from rigid-rod polyelectrolytes including natural biopolymers (DNA,^[31] collagen,^[32] polypeptides^[33]) and synthetic polymers such as poly(2,2'-disulfonyl-4,4'-benzidine terephthalamide) (PBDT).^[34] Such LCs can display

strong monodomain alignment in a **B**-field, and can thus act as assembly templates for developing long-range-ordered structures.^[35-38] In this work, the synthetic sulfonated aramid polyanion PBDT, shown in **Figure 5.1**, is a water-miscible system that forms a lyotropic LC phase above a critical concentration $C^* = 1.2$ wt% and has high ion density along the polymer backbone.^[34,39] The IL shown in **Figure 5.1** contains the cation 1-ethyl-3-methyl imidazolium $[\text{C}_2\text{mim}]^+$ and the anion trifluoromethanesulfonate $[\text{TfO}]^-$. In order to obtain the ion gel (**Figure 5.1a**), we place the pure IL $[\text{C}_2\text{mim}][\text{TfO}]$ above a magnetically aligned aqueous PBDT seed solution. Through ion exchange between the two phases, the LC ion gel forms in the bottom seed solution over approximately 24 hours as shown in **Figure 5.1c**. To systematically study the LC ion gel, we fabricate four gel samples with increasing PBDT mass percentage in the (dried) gel relative to the total gel mass, with $(m_{\text{PBDT}}/(m_{\text{PBDT}} + m_{\text{IL}})) = 5\%, 11\%, 15\%, \text{ and } 21\%$. The corresponding initial mass percentage $(m_{\text{PBDT}}/(m_{\text{PBDT}} + m_{\text{H}_2\text{O}}))$ of the aqueous PBDT seed solutions are 2%, 3%, 4% and 5%, respectively. The formation process is driven by three aspects: 1) molecular diffusion induced by the concentration gradients of water and IL among the two phases, 2) ion exchange between Na^+ counterions of PBDT and $[\text{C}_2\text{mim}]^+$ of the IL, and 3) a hydrogen-bonding network driven largely by specific water–ion interactions. In **Figure 5.1b**, we present the composition and assembly of the formed LC ion gel without water present, which will be corroborated using X-ray diffraction later. Magnetically aligned PBDT chains serve as the host matrix for the distributed guest IL. The guest IL transports preferentially along the aligned matrix thus yielding higher ionic conduction along this predetermined axis as opposed to the perpendicular directions. Thus we can conveniently regulate the orientation and degree of alignment in the ion gels by

reorienting the $\mathbf{B}$ direction and varying the concentration of the initial seed solutions, respectively. As observed previously, the shape anisotropy of the container used to form the gel can induce significant alignment in PBDT solutions, removing the need for a large $\mathbf{B}$ -field to produce gel alignment and thus enabling simple manufacture and convenient application.^[34]

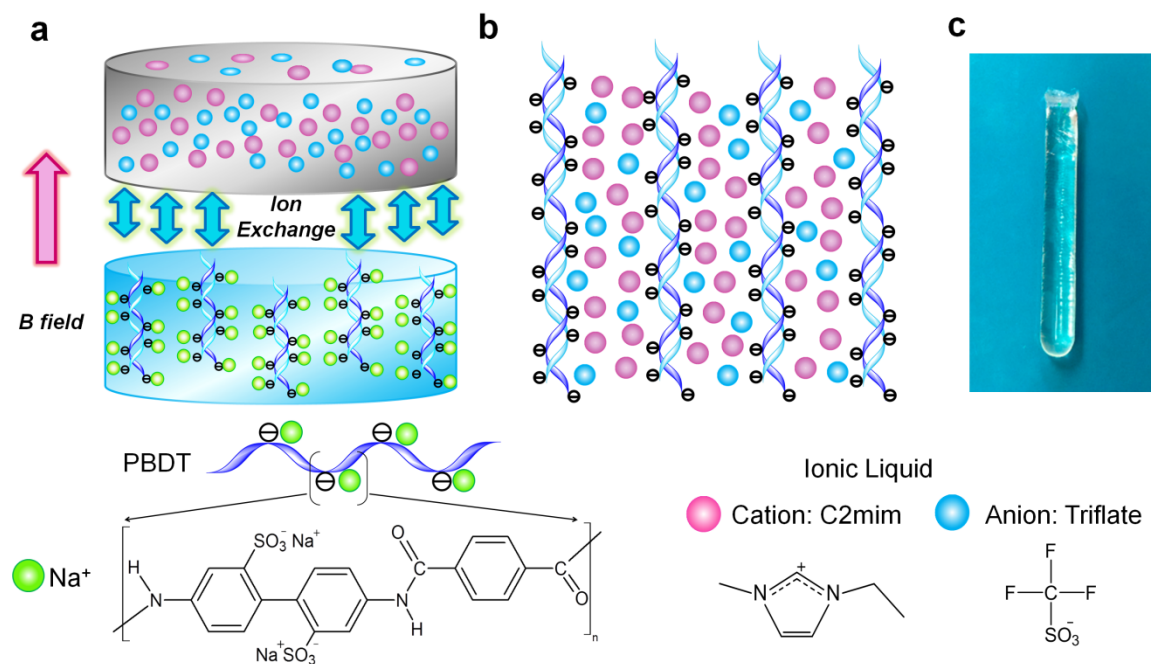


Figure 5.1. Liquid crystalline ion gels formed from a rigid-rod sulfonated aramid polymer and an ionic liquid. **(a)** Formation scheme of the anisotropic PBDT LC ion gel through ion exchange between the top IL and the bottom PBDT aqueous seed solution ($C \geq 2\%$) in a magnetic field $B \geq 7.1$ T. **(b)** Schematic of dried PBDT IL gel with IL dispersed in aligned PBDT polymer matrix. **(c)** PBDT IL gel with water present as formed in the bottom PBDT aqueous seed solution.

5.3 Experimental

Materials: Poly 2,2'-disulfonyl-4,4'-benzidine terephthalamide (PBDT) with Na^+ counterions was synthesized by interfacial condensation. The M_n , M_w , and PDI (M_w/M_n) were 7900, 17300, and 2.2, respectively, as determined by GPC in sulfuric acid solvent. Aqueous solutions with PBDT weight percentage (wt%) ranging from 1% – 5% were prepared by loading the prescribed amount of PBDT and deionized H_2O into 5mm NMR tubes. 1-ethyl-3-methyl imidazolium $[\text{C}_2\text{mim}]^+$ trifluoromethanesulfonate $[\text{TfO}]^-$ was purchased from Solvent Innovation GmbH (Cologne, Germany) with purity > 99%.

Preparation of PBDT IL gel: NMR tubes with PBDT solutions were equilibrated in a magnetic field of 7.1 T for 24 hours. Tests also showed that $B \geq 0.5$ T was sufficient to highly align the gels. $[\text{C}_2\text{mim}][\text{TfO}]$ with the same volume as the polymer solution was slowly pipetted on top of the polymer solutions. After 24 hours ion exchange in the magnetic field, the gel was formed in the bottom phase of the polymer solution and the residual water/IL supernatant above was poured off.

Pulsed-field-gradient (PFG) NMR Diffusometry: The pulsed-gradient stimulated-echo sequence (PGSTE) was applied for all diffusion measurements at 25°C (± 0.1). A Bruker Avance III widebore 400 MHz (9.4 T) NMR was equipped with a Micro5 pulsed-field-gradient diffusion/microimaging probe having a maximum gradient value of 300 G/cm (at 60 A current) along X, Y, and Z axes and a 5 mm $^1\text{H}/^2\text{H}$ rf coil. All parameters for the PFG diffusometry experiments have been calibrated and optimized as reported earlier.^[1,40,41]

Polarized Optical Microscopy (POM) and Scanning Electronic Microscopy (SEM): Aligned samples were examined in transmission mode with crossed polarizers at 200 $\times$ magnification with a polarized optical microscope (Meiji Technology MX9430) equipped

with a digital camera (Infinity Cannon). Pixel values from recorded POM micrographs were averaged to provide transmission intensities. Transmission intensities were normalized by the beam intensity I_0 , which was measured with the polarizer and analyzer parallel and without sample present. SEM was performed using a LEO (Zeiss) field-emission SEM. Samples were prepared by freeze fracture after immersion in liquid nitrogen.

X-ray Diffraction (XRD): XRD experiments were carried out on a Rigaku Oxford Diffraction Xcalibur Nova Single-Crystal Diffractometer equipped with an Onyx CCD detector and a Cu microsource operating at 49.5 kV and 80mA at room temperature. The gel was cut to a diameter of 0.2 mm and mounted on the edge of a steel pin, such that the gel extended above the steel pin and into the X-ray beam. The sample-to-detector distance was 120 mm, giving data at scattering angle 2θ from 5° to 34° . The gel sample was oriented at a 45° angle relative to the beamstop in order to minimize beamstop interference in the diffraction patterns. The sample was rotated 2° in phi (i.e. along the fiber axis). For each sample, a total of two-hundred images with 120 s exposure time was collected and summed to increase signal-to-noise. The software CrysAlisPro (v1.171.37.35, Rigaku Oxford Diffraction, 2015, Rigaku Corporation, Oxford, UK) was used for data collection and analysis.

Conductivity Measurements and Cyclic Voltammetry: Gel samples were sandwiched between two electrode stages connected to a Solartron gain-phase 1260 and a Solartron electrochemical interface 1287 operating in a 100 Hz – 10 MHz frequency range at amplitude 100 mV. Conductivity of the gel samples was calculated using a value of electrical resistance obtained by fitting the data to a single equivalent circuit model using

Zplot[®]. Cyclic voltammetry experiments were performed to determine the electrochemical windows of prepared PBDT gel electrolytes. Target material was sandwiched between a 1.6 mm diameter Cu working electrode and a Pt plate, which was used as both the counter and the reference electrode (i.e. a two-electrode setup). The Pt pseudo reference potential was further internally calibrated by ferrocene redox potential. All scans were performed in an Argon-filled glovebox ($\text{H}_2\text{O} < 0.0$ ppm, $\text{O}_2 < 10$ ppm) at 25°C with 20 mV s⁻¹ scan rate using a Biologic SP-200 controlled by EC-Lab (ver. 10.40) software.

Thermal and Mechanical Properties: Thermal properties were measured by a Pyris Diamond TGA (PerkinElmer) and a Sapphire DSC (PerkinElmer) with a 10°C min⁻¹ ramp under N₂ atmosphere. The thermal mechanical properties were measured in tensile mode (along gel alignment axis for 21% sample) using a Diamond DMTA (PerkinElmer) with a temperature range of -75 to 450°C and frequencies of 0.1, 1, and 10 Hz at heating rate of 2.5°C min⁻¹ under air atmosphere.

5.4 Results and Discussion

5.4.1 Morphological Alignment Evidenced by SEM, POM, and XRD

Here we describe multi-scale anisotropic properties of the gels using key microscopy and diffraction methods. The SEM image in **Figure 5.2a** for 21% PBDT IL gel shows a micron-scale fibrillar-structure oriented parallel to **B**. POM confirms this anisotropy for the gels with > 5% PBDT content, where the average transmission intensity of the observed POM images demonstrates strong macroscopic alignment along **B** for 11%, 15%, and 21% gel samples. **Figure 5.2b** shows smooth modulation in light transmission

as a function of ϕ angle between the alignment axis of 21% PBDT IL gel and the plane polarization of incident light. Adjacent minima and maxima are separated by 45° , with a sinusoidal periodicity of 90° .

We also employ X-ray diffraction to investigate molecular structure correlations in the ion gels. Figure 2c, 2d, and 2e show diffraction patterns for 5%, 15% and 21% PBDT IL gel, respectively. We observe that the grey amorphous halo at $2\theta = 12^\circ$ to 24° scattering angle contributes a large fraction of the intensity for all three diffraction patterns. We assign this halo to the amorphous IL since it is the main component of the ion gel, and verify this by collecting the diffraction pattern of the pure IL as shown in **Figure 5.3**. The remaining diffraction peaks are thus attributed to the diffraction of aligned PBDT chains. To eliminate the effect of the IL halo, we subtract a scaled intensity (scale factor = 0.62) version of **Figure 5.2c** from **Figure 5.2e** using MATLAB[®]. For comparison, we include additional figures with varying scale factor in **Figure 5.4**. The difference pattern, shown in **Figure 5.2f**, represents predominantly diffraction of aligned PBDT chains in 21% PBDT IL gel. The main diffraction peaks are labeled A, B, C and D, with decreasing characteristic lengths ($A = 10 \sim 17 \text{ \AA}$, $B = 8.0 \text{ \AA}$, $C = 3.3 \text{ \AA}$, $D = 8.4 \text{ \AA}$). The blue arrow denotes the gel alignment axis. The spots and arcs of Figure 2f further confirm the highly oriented fibrillar structures in the ion gel. Based on these analyses, we develop a model for the LC ion gel morphology with IL dispersed in aligned PBDT matrix, shown in **Figure 5.2g**. A is regarded as the d -spacing between rigid-rods. The broad dimension of A indicates that the distance between the rigid rods is not uniformly distributed. We assign B and C to the width of the rigid rod backbone and the width with the pendant sulfonate groups, respectively, and assignment to more specific

structure is under further development. Additionally, the chemical repeat unit length of PBDT is 1.68 nm based on previous WAXD results on PBDT bulk membrane.^[34,42] The characteristic length D (8.4 Å) is half of the chemical repeat unit, which strongly indicates, as previously suggested, that PBDT molecular dimers are assembled as the rigid-rod building blocks in the water precursor solution and thus in the ion gel.^[34] Within one chemical repeat unit, the two sulfonate groups are considered to be one unit, since they are close to each other. The “X” pattern in Figure 2f, which can be observed in the diffraction pattern of DNA,^[33,43] and in other double helix fibers,^[44] also strongly indicates a helical dimer conformation of PBDT chains. In our previous report, we proposed a self-assembled double-helix conformation of PBDT chains using a combination of a nematic LC model and SAXS results.^[34] Thus, D represents the distance between two neighboring sulfonate units along the proposed double helix and θ is the tilt angle of the helix. The double helical conformation likely originates from intermolecular hydrogen bonding, as well as the biased rotation of benzene rings in the PBDT chains.^[34] Further XRD interpretation and refinement of this helix-dimer model using more advanced X-ray analysis and molecular simulations will form the subject of another near future publication. In these ion gel systems, the PBDT dimeric units provide extremely rigid and long coherence length polymeric units (≥ 10 nm) to provide easy alignment of the gel matrix.

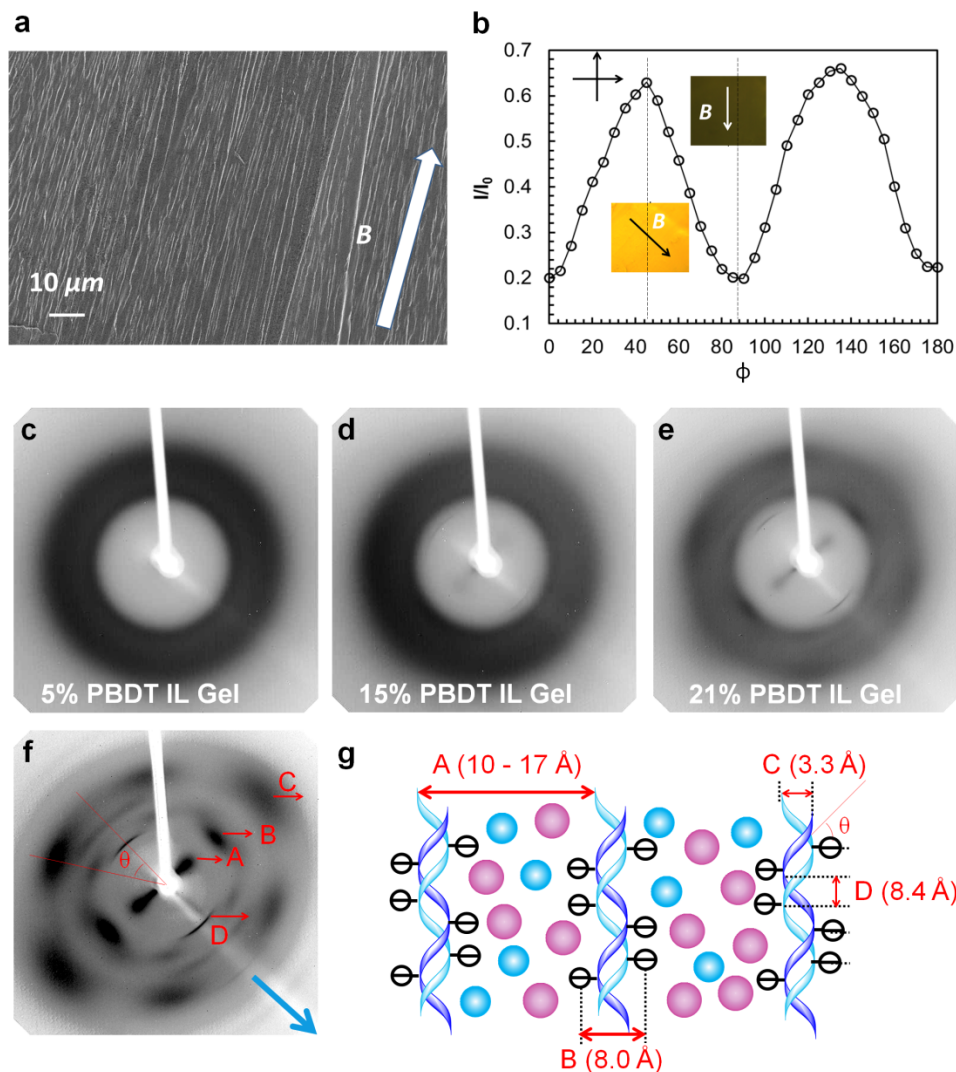


Figure 5.2. Morphological alignment and semi-crystalline structure of LC ion gels. **(a)** SEM image of nitrogen freeze-fractured side-on surface of 21% PBDT IL gel. **(b)** Transmitted light intensity of aligned gel sample under crossed polarizers as a function of the angle ϕ between the alignment of the sample and the analyzer, showing periodic variation every 90° and thus strong alignment along the **B** direction. **(c, d, and e)** X-ray diffraction patterns for 5%, 15%, and 21% PBDT IL gel, respectively. **(f)** Difference image of c) and e) to remove the amorphous halo due to IL scattering. The blue arrow displays the mounting direction of the sample fiber and gel alignment axis. The main

scattering parameters are labeled A, B, C and D. (g) Diagram of the PBDT IL gel with specified dimensions based on the scattering parameters.

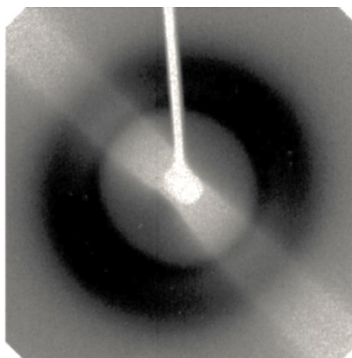


Figure 5.3. X-ray diffraction pattern of neat IL [C2mim][Triflate] in a capillary with 1.5 mm diameter and 0.01 mm wall thickness.

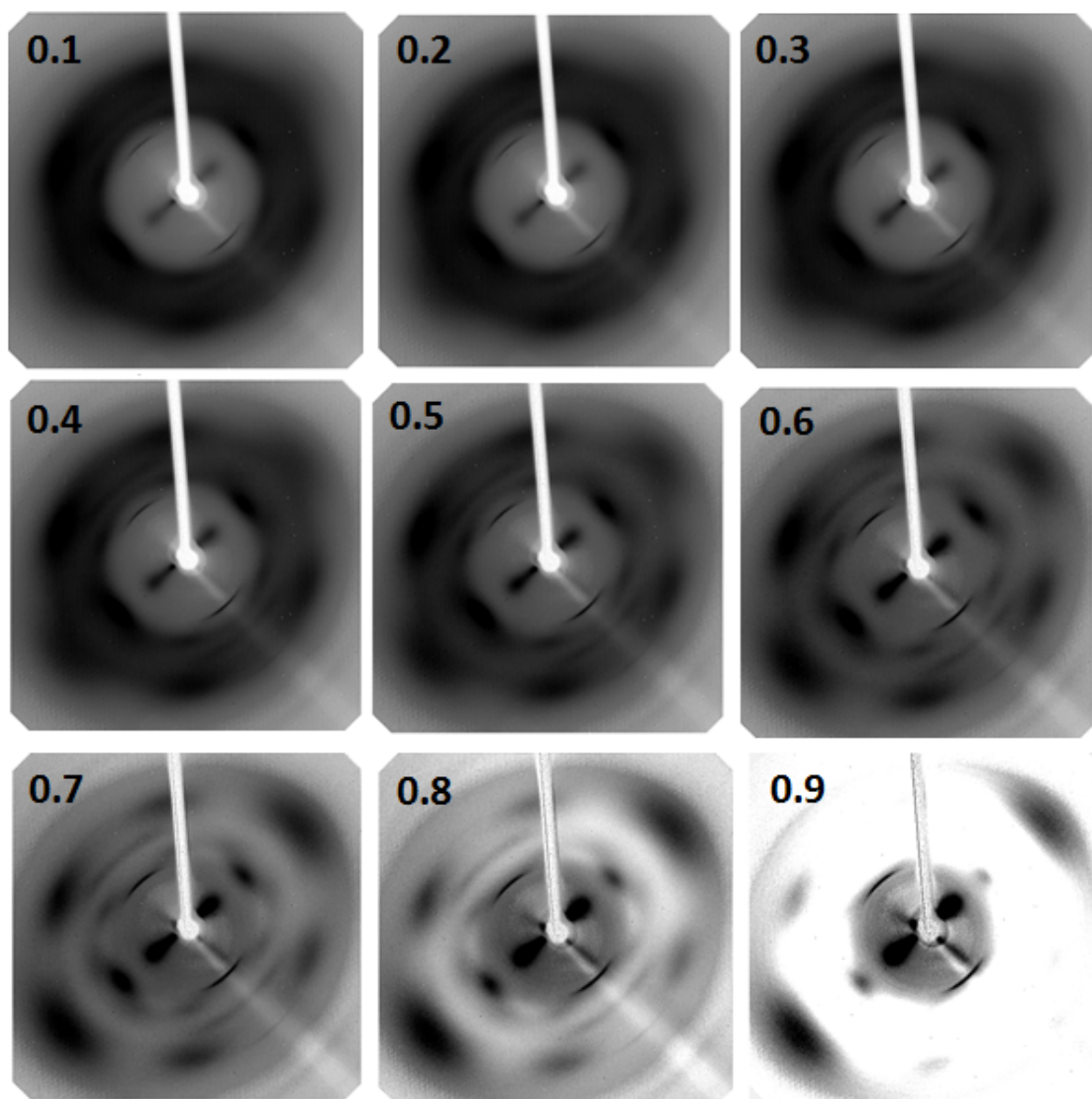


Figure 5.4. X-ray diffraction pattern of neat IL [C2mim][Triflate] in a capillary with 1.5 mm diameter and 0.01 mm wall thickness.

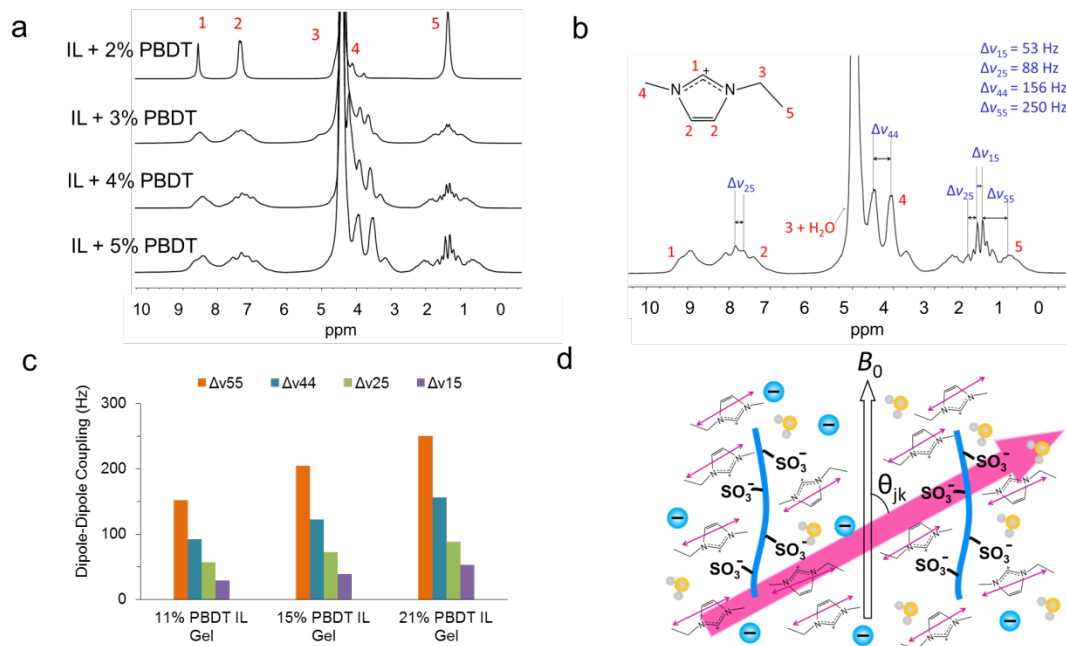


Figure 5.5. (a) The dipole-dipole splitting of the PBDT IL gel with increasing polymer content from ¹H NMR. (b) The detailed assignment of the dipole-dipole splitting. (c) The dipole-dipole splitting of the cation molecules. (d) The cartoon to mimic the orientational order of cation molecules in the PBDT IL gel.

Figure 5.5a shows the proton NMR spectra of cations in PBDT IL gels with increasing polymer content of 5%, 11%, 15%, and 21%, respectively. For 5% PBDT IL gel, one can observe ordinary peaks representing [C₂mim]⁺ and H₂O. However, featured couplings are generated in spectra for 11%, 15%, and 21% PBDT IL gels. The splittings are attributed to the intramolecular dipole-dipole coupling of the probed [C₂mim]⁺. The highly aligned PBDT backbones are particularly essential as the host matrix for orienting guest IL molecules. The diffusion and rotation of the probed cations in the aligned system are anisotropic, thus contribute to the nonzero direct intramolecular dipole-dipole coupling. **Figure 5.2b, d** displays the specific splitting information of the coupled spins

in the $[C_{2mim}]$. The secular dipole-dipole coupling of the same isotopic species spin i and spin j is expressed as

$$\Delta\nu_{ij} = b_{ij} \frac{1}{2} (3 \cos^2 \Theta_{jk} - 1), \quad (5.1)$$

where Θ_{jk} is the angle between the magnetic field and the orientation of the two spin pairs. b_{ij} is the dipole-dipole coupling constant, which depends on the distance r_{ij} between the spins. As shown in **Figure 5.5c**, the splittings are getting larger with increasing PBDT polymer content, indicating elevating anisotropy and alignment of the gel samples.

As introduced previously, ^2H NMR is also very critical technique to study the anisotropic dynamics of the polymeric materials. We also detect the quadrupole splitting of the D_2O molecules in the ion gels with polymer content, such as 5%, 11%, 15% and 21%. **Figure 5.6a** shows the ^2H spectra of the ion gels that verify the anisotropic structure in the ion gels. In addition, we can also observe that the quadrupole splitting is decreasing with increasing water content in the gels showing the increased orientation order of the probe molecules (**Figure 5.6b**).

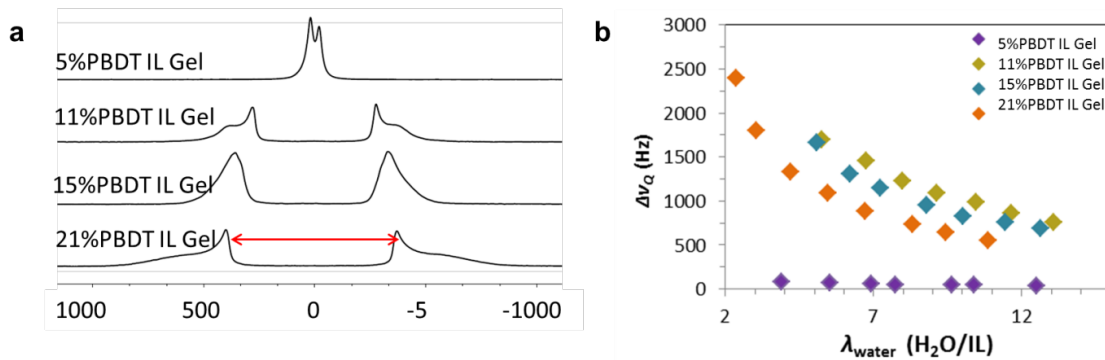


Figure 5.6. (a) The ^2H NMR spectra of the PBDT IL Gel. (b) The quadrupole splitting in the ion gel as a function of the water content in the ion gels.

5.4.2 Anisotropic Diffusion and Conductivity of Ions inside PBDT-IL Gels

Besides direct observation of the morphological anisotropy, we also employ multi-axis pulsed-field-gradient (PFG) NMR diffusometry to quantify diffusion and its anisotropy for H_2O , $[\text{C}_2\text{mim}]^+$, and $[\text{TfO}]^-$ in the ion gels. We measure diffusion along two orthogonal directions, $D_{\parallel}$ (parallel with the gel alignment axis) and $D_{\perp}$, and we define diffusion anisotropy as the ratio $D_{\parallel}/D_{\perp}$. **Figure 5.7a** shows $D_{\text{H}_2\text{O}}$ in the ion gels as a function of PBDT content for the two directions at $\lambda_{\text{H}_2\text{O}} = 12$ and 25°C , where $\lambda_{\text{H}_2\text{O}}$ is the mole ratio of H_2O to IL in the ion gels. We measure $D_{\text{H}_2\text{O}}$ at $\lambda_{\text{H}_2\text{O}} = 12$ here because that is the equilibrium concentration of H_2O at the completion of gel formation, a phenomenon we discuss further below. For gels with 11%, 15%, and 21% PBDT we observe $D_{\parallel}/D_{\perp}$ up to 1.7 for H_2O , while the 5% PBDT IL gel shows isotropic diffusion ($D_{\parallel}/D_{\perp} = 1$), as shown in **Figure 5.7a**. Additionally, we investigate cation and anion diffusion for the gels under dry conditions, since water must be strictly controlled for high energy density (*e.g.*, lithium ion) batteries. After vacuum drying the gels for 48 hours at 80°C , proton NMR spectra confirm that H_2O is at sufficiently low levels as to not significantly influence ion conductivity or diffusion (see also **Figure 5.11**).^[45,46] **Figure 5.7b** shows diffusion coefficients ($\sim 10^{-11} \text{ m}^2/\text{s}$) of $[\text{C}_2\text{mim}]^+$ and $[\text{TfO}]^-$ in the dry ion gels at 25°C . The cation and anion diffusion rates decrease only slightly with increasing PBDT content ($\leq$ a factor of 2) compared to the pure IL. Thus these gels provide a large ionic transport advantage compared to other solid-state non-swelling polymer electrolytes, which have cation and anion $D < 10^{-12} \text{ m}^2 \text{ s}^{-1}$.^[47-49] In **Figure 5.7b**, $D_{\parallel}/D_{\perp}$ approaches 2.7 and 1.8 for anions and cations, respectively. A likely explanation for the smaller diffusion anisotropy of $[\text{C}_2\text{mim}]^+$ than that of $[\text{TfO}]^-$ is that $[\text{C}_2\text{mim}]^+$ ions

tend to associate with the PBDT sulfonate groups and are thus easier to transport between PBDT chains. We observe that the distance between rigid rods are 1 - 2 nm from X-ray diffraction, thus allowing an easy pathway for cations to move transverse to the rigid rods. Conversely, dissociated $[\text{TfO}]^-$ are repelled by the sulfonate groups along the PBDT chains and are thus more effectively confined to move along the chain axes. We also observe that the diffusion of $[\text{C}_2\text{mim}]^+$ is faster than that of $[\text{TfO}]^-$, likely due to ion association phenomena in $[\text{C}_2\text{mim}][\text{TfO}]$ previously reported.^[47,50] In order to further probe thermal stability of the gel anisotropy, we also investigate the transport properties at 80°C, which is the highest temperature allowed for our NMR probe (**Figure 5.7c**). The diffusion anisotropies remain the same as at 25°C, whereas the diffusion rates increase by a factor of 4 for both cations and anions.^[51] We further observe no thermal transition in DSC (**Figure 9c and d**) on second heating until $\geq 300^\circ\text{C}$, indicating that this material is a LC gel at least up to 300°C.

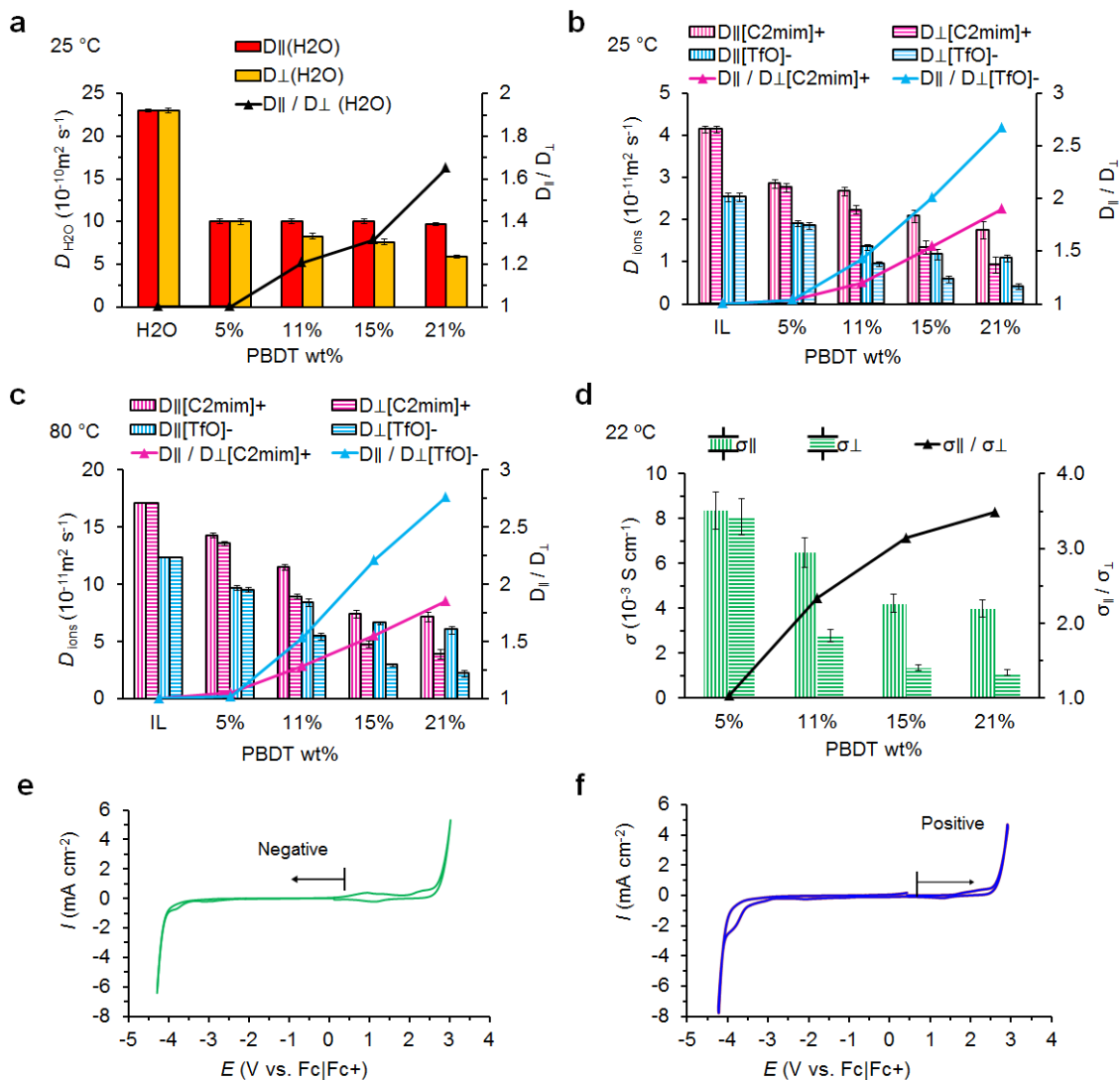


Figure 5.7. Anisotropic ion diffusion and conductivity, and electrochemical window of LC ion gels. **(a)** D_{H_2O} in hydrated ($\lambda_{H_2O} = 12$) PBDT IL gels with increasing PBDT polymer content as compared to pure H₂O at 25°C. The solid line shows the corresponding diffusion anisotropy. **(b)** Diffusion coefficients of $[C_2mim]^+$ and $[TfO]^-$ in dried PBDT IL gels with increasing PBDT polymer content as compared to pure IL at 25°C. The solid lines show the corresponding diffusion anisotropy for $[C_2mim]^+$ and $[TfO]^-$, respectively. **(c)** $D_{[C_2mim]^+}$ and $D_{[TfO]^-}$ in dried PBDT IL gels with increasing PBDT polymer content as compared to pure IL at 80°C. **(d)** Ionic conductivity of the ion

gels at 22°C as a function of increasing PBDT polymer content for the two orthogonal directions ($\sigma_{\perp}$ and $\sigma_{\parallel}$). The black line shows the corresponding conductivity anisotropy. **(e, f)** CV tests for 5% PBDT IL gel with initially negative and positive scan directions, respectively.

Table 5.1. Dimensions of the cuboid ion gel samples and the corresponding resistance obtained from IS.

PBDT IL Gel	Length (mm)	Width (mm)	Height (mm)	$A_{\parallel}$ (mm ²)	$A_{\perp}$ (mm ²)	$R_{\parallel}$ (Ω)	$R_{\perp}$ (Ω)
5%	2.54	1.70	1.32	2.25	4.32	1450	410
11%	3.43	1.78	0.89	1.58	6.10	3340	524
15%	3.00	1.40	0.94	1.32	4.20	5360	1670
21%	2.26	1.60	1.17	1.87	3.61	3020	2830

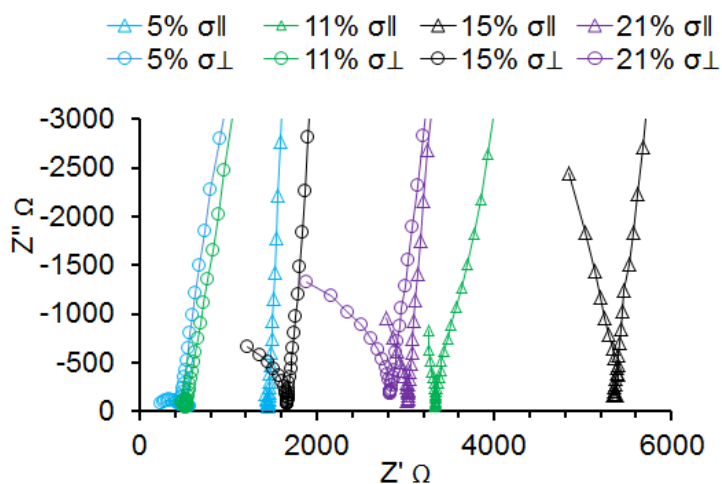


Figure 5.8. Nyquist plots for the ion gels in the two orthogonal directions. The experimental parameters used are 100 Hz to 10 MHz frequency range at 100 mV amplitude.

In terms of the frequency, we utilized the range 100Hz – 10MHz. Based on the Nyquist plot shown in **Figure 5.8**, the conductivity is captured by the high frequency end. The low frequency tails are straight, indicating the frequency is low enough to reach the diffusion controlled conduction behaviors, i.e., no further semi-circle is observed after the first touchdown. Highly conductive materials such as ion gels tend to show conduction behavior at the high frequency end (MHz). The incomplete semi-circles in **Figure 5.8** originate from the limitation of the high frequency for the instrument (10 MHz), but the data is still clear and fits perfectly to a single conductivity process.

In terms of the amplitude, we used 100 mV. Judging from the large electrochemical window and high conductivity of the LC ion gels, 100mV amplitude is suitable for these measurements. Based on previous literature for solid electrolytes and ion gels with similar electrochemical windows and ionic composition to our LC ion gels, 100mV has been widely utilized to ensure large enough current response to overcome instrument noise.^[52,53]

To study ionic conductivity and electrochemical window of the ion gels, we have employed impedance spectrometry (IS) and cyclic voltammetry (CV), respectively. We sliced the as-formed ion gels (cylinders of ~ 3 mm diam) to obtain cuboid samples with dimensions shown in **Table 5.1**. We calculate ionic conductivity σ using measured resistance R from IS using

$$\sigma = \frac{d}{R \times A}, \quad (5.2)$$

where d is the distance between two electrodes and A is the cross-sectional area of the sample. We measure the ionic conductivities for two orthogonal directions by changing the orientation of the gel samples between the electrodes. **Figure 5.7d** shows the ionic

conductivity for the four samples at ambient temperature. The observed ionic conductivity (standard deviation $\leq 10\%$, 3 replicates) lies in the range 1 to 8 mS/cm, which is $10^2 - 10^4$ times higher than that of previously known non-swelling PEO-based polymer electrolytes with high modulus,^[9,54-56] and is comparable to or larger than previous (much softer) ion gels.^[12,22] Furthermore, the PBDT ion gels approach σ for the pure IL ($\sigma = 11 \text{ mS cm}^{-1}$ at 22°C).^[52] In accordance with NMR diffusometry measurements, the 5% PBDT IL gel shows no conductivity anisotropy, and with increasing PBDT content the conductivity anisotropy increases from 1 to 3.5. Thus, these LC ion gels exhibit not only high ionic conductivity, but also can be tuned to have substantially faster ion transport along a predetermined direction. **Figure 5.7e, f** show the electrochemical windows of the gels characterised by cyclic voltammetry. A small (less than 1 mA cm^{-2}) and broad reduction event starting at -3.6 V vs. $\text{Fc} | \text{Fc}^+$ (ferrocene) reference followed by a strong main decomposition peak at -4 V , are observed in the cathodic scan of 5% PBDT IL gel. Following this, during the anodic sweep, we observe a broad oxidation peak at $+1 \text{ V}$, corresponding to the main reduction peak since this peak is not observed when the scan begins in the positive direction. During the first anodic scan, the 5 wt% PBDT gel shows no obvious oxidation reaction until 2.5 V vs $\text{Fc} | \text{Fc}^+$, at which point the current exhibits exponential increase. Therefore, the electrochemical window is approximately 6.1 V , which offers great promise for these ion gels to enable enhanced high energy density devices. Ispas et al.^[57] reported the electrochemical window of neat $[\text{C2mim}][\text{TfO}]$ to be 5.4 V . It is smaller than the 6.1 V observed by cyclic voltammetry (CV) for the present gel electrolyte based on the same IL. There are two reasons that can account for this difference. (1) We measured the reduction and

oxidation limits in two separate CV runs, which prevents reduction or oxidation products formed during the experiment from interfering with the intrinsic electrochemical behavior of the gel itself. (2) By introducing the charged and structured polymer network (the sulfonated aramid polyanion PBDT), the electrochemical stability of the IL based gel presumably becomes enhanced due to the strong interactions between the IL and PBDT chains as discussed in the paper.

5.4.3 Thermal and Mechanical Properties of PBDT-IL Gels

Many advanced electrochemical devices require greater mechanical rigidity and high-temperature stability than afforded by common Li-ion battery electrolytes. Here we employ dynamic thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) to study the ion gels. **Figure 5.9a and b** present TGA results (green lines) for 5% and 21% PBDT IL gel. The decomposition temperature of the ion gels from the derivative weight loss curves (blue lines) is 350°C, indicating that these gels can enable devices with extreme temperature tolerance. The DSC results in **Figure 5.9c and d**, show a heat-cool-heat cycle in the range -100°C to 300°C, and further emphasize the gels' high thermal stability. The peak during the 1st heating process from -10°C to 40°C corresponds to the melting of IL and melting of a small amount of residual H₂O. We attribute the broad peak near 200°C to the evaporation of this residual strongly associated H₂O inside the ion gels. During the 1st cooling step, the only observable transition at -40°C represents the crystallization of IL. In the 2nd heating process, we observe no thermal transition in the range 10°C to 300°C, which confirms the exceptional thermal stability.

Figure **5.9e and f** show dynamic mechanical thermal analysis (DMTA) results in tension mode for the 5% and 21% ion gels, respectively. The sharp modulus drop in the temperature range of -40°C to -10°C reflects the melting of absorbed IL. Above the IL melting temperature, we observe that the 21% PBDT IL gel is much stiffer, with an elastic modulus of 3 GPa, compared to 30 MPa for 5% PBDT IL gel. The high modulus in aligned ion gels originates from the highly oriented aromatic polyamide backbones of PBDT in analogy to that observed in (chemically similar) Kevlar® fiber. Clearly we can modulate PBDT content to tune the modulus of the ion gels over at least a factor of 100 in order to, *e.g.*, combat Li dendrite formation,^[29] and/or obtain desired device stiffness or mechanical response.^[58] Importantly, this significant increase (and tunability) in elastic modulus comes at only a modest cost in ion conductivity ($\leq$ a factor of two).

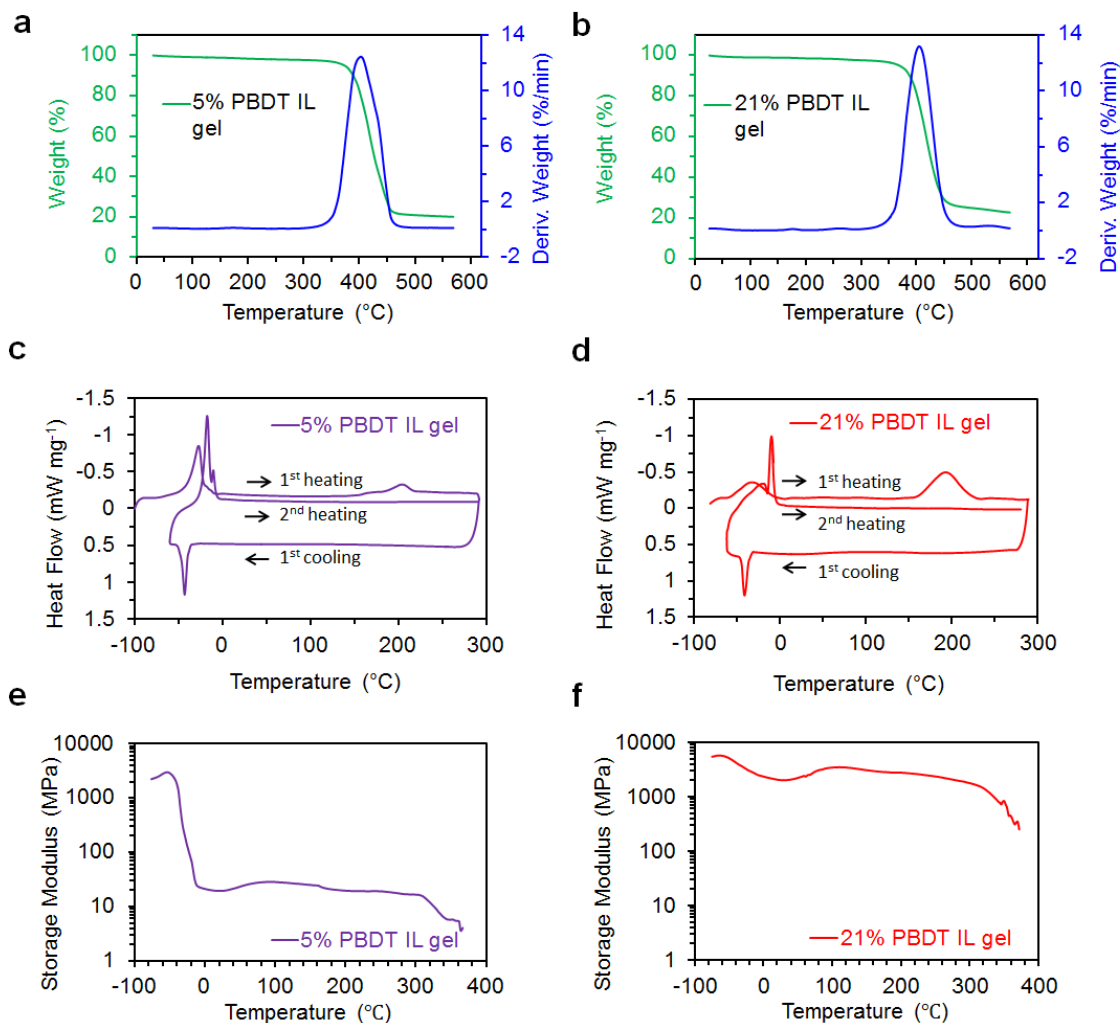


Figure 5.9. Thermal and mechanical properties of LC ion gels. **(a, b)** TGA for 5% and 21% PBDT IL gels at heating rate = $10^{\circ}\text{C min}^{-1}$. **(c, d)** DSC for 5% and 21% PBDT IL gels at heating rate = $10^{\circ}\text{C min}^{-1}$. **(e, f)** DMTA under tension for 5% and 21% PBDT IL gels at frequency = 1 Hz, showing elastic modulus as a function of temperature at heating rate = $2.5^{\circ}\text{C min}^{-1}$.

In order to confirm the thermal stability of the aligned structure in the ion gels after evaporation of residual strongly associated H_2O , we have employed POM and IS to verify the high thermal stability of the oriented gel structure as shown in **Figure 5.10**.

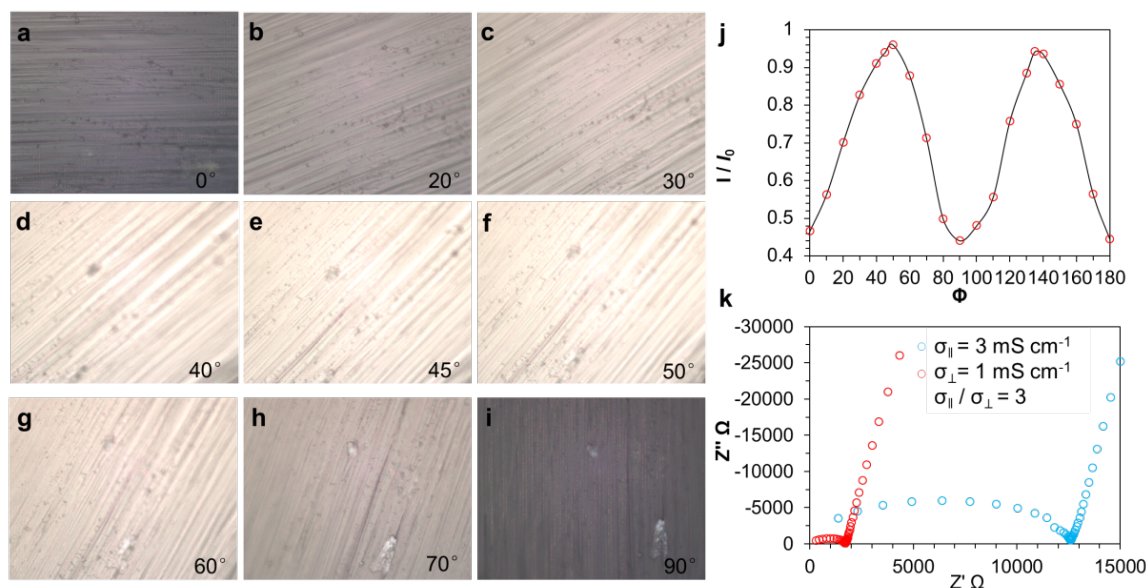


Figure 5.10. (a-i) POM images of the bulk 15 wt% ion gel vacuum dried at 200°C, with varying angle ϕ labelled on the image. ϕ is the angle between the alignment axis of the gel and the plane polarization of the incident light. (j) Transmitted light intensity of the aligned gel as a function of angle ϕ . (k) The Nyquist plot shows the anisotropic ionic conductivity of the gel at room temperature after vacuum drying at 200°C. The ionic conductivity along the alignment axis $\sigma_{\parallel} = 3 \text{ mS cm}^{-1}$, whereas the ionic conductivity perpendicular to the alignment axis $\sigma_{\perp} = 1 \text{ mS cm}^{-1}$.

5.4.4 Hydrogen Bonding Network in Gel Formation Mechanism

Many factors determine gel formation, including molecular diffusion, electrostatic interactions, Van der Waals forces, and hydrogen bonding.^[37,59] Gelation is phenomenon of liquid – solid transition with a bond percolation transition. At the gelation point, infinite clusters are created that spans the whole system. Gel contains a heterogeneous system, with mobile solvents immobilized in a polymer network. Gel features solid-like properties, such as the shape integrity and specific mechanical modulus. However, the

main component of gel comes from the liquid phase. Gelation can be mainly divided into physical gelation and chemical gelation.

With respect to physical gelation, the network created by physical crosslinks attributes to polymer micelles, helix formation, entanglement, microphase separation and hydrogen or ionic bonds. Gelation process can be induced by temperature, pH, salt concentration and so on.^[4]

To achieve molecular alignment in physical gels, we can employ aligned templates, such as phase separated block copolymers and rigid rod polymers. In addition, we can also utilize external mechanical stretch, magnetic or electric fields to achieve the desired physical alignment.

For PBDT IL gel in my project, many factors determine the final gel, including Van der Waals forces, electrostatic interactions and hydrogen bondings. In terms of the molecular characteristics, the long persistent length and the high aspect ratio of PBDT chains play essential roles in the formation of gels. In terms of the physical driving forces, the external magnetic field is required to transfer the LC phase of PBDT solution from multidomain LC to monodomain LC. Also, the electrostatic interaction between the polymer chains and the ionic liquids are also essential in forming the stable ion gels.

To form a stable alignment in a gel, the inter-molecular interactions, such as Van der Waals forces (short-range or hard sphere excluded volume), electrostatic interaction and the hydrogen bonding should be high enough to maintain the alignment structure in the gel compared to the thermal fluctuation (kT) at certified temperature.

Here, we propose that a specific hydrogen bonding network is formed between the IL and PBDT ions and H_2O in a specific range of water content as indicated in **Figure 5.11**.

[TfO][−] and SO₃[−] groups are strong electron donors, which tend to form hydrogen bonds with H₂O molecules. As reported by Luebke and coworkers, water molecules have two counteracting effects on dynamics in some ILs, *e.g.*, [C₂mim][acetate].^[60] On one hand, adding water will expand the distance between [C₂mim]⁺ and [acetate][−] thus accelerating ion diffusion. On the other hand, water can form a hydrogen bonding network with [acetate][−], which will reduce the ion diffusion rate. We believe a similar counteracting effect also occurs in our LC ion gel system based on of water–[TfO][−] interactions. In order to verify the importance of the hydrogen bonding interaction, we also attempted to use oriented PBDT D₂O seed solutions to generate the ion gels, but failed to obtain well-formed gels. This can be attributed to the difference between H₂O and D₂O, where hydrogen bonding in H₂O is stronger and with shorter bond length compared to that of D₂O.^[61,62] Based on these indicators, we thus suggest that a hydrogen bonding network of ideal distances between H₂O, IL, and PBDT ions (a thermodynamic minimum) serves to reject water and excess ions from the PBDT-IL-H₂O solution in order to form the final gel and leave a stable supernatant salt solution above.

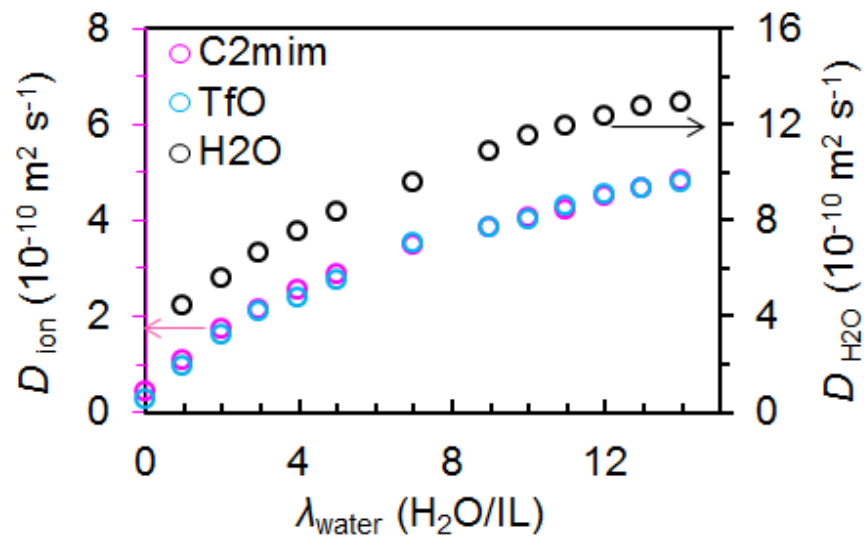


Figure 5.11. Diffusion coefficients of H₂O, [C₂mim]⁺ and [TfO][−] as a function of $\lambda_{\text{H}_2\text{O}}$ in the mixture solution of IL with H₂O. Note that the ion diffusion coefficients will not drop substantially below the lowest $\lambda_{\text{H}_2\text{O}}$ point on these curves, even if a small amount of water ($\lambda_{\text{H}_2\text{O}} < 0.5$) is still present.^[45,46]

5.4.5 ²³Na NMR study of Na⁺ Concentration in PBDT-IL Ion Gels

Figure 5.12 briefly illustrates fabrication of the PBDT ion gel. The ion gel can be obtained by an ion exchange process between the ionic liquid (IL) [C₂mim][TfO] and the 4wt% PBDT aqueous seed solution (with 100% Na⁺ counterions). This process yields a dried ion gel with 15 wt% PBDT, in the middle of the range explored computationally in this paper.

To quantify the relative concentration of Na⁺ (C_{Na^+}) in the as-fabricated ion gels, we employ a simple and robust pulse-acquire sequence of ²³Na NMR to measure abundance of Na⁺ in the PBDT ion gel (Green region in **Figure 5.12**) as compared to that in the PBDT seed solution (Blue region in **Figure 5.12**).

Additionally, we also use a predetermined NaCl aqueous solution (0.036 mol/kg) to quantify the absolute concentration of Na^+ in the ion gels for the corresponding molecular dynamics simulations. The acquisition parameters are maintained constant for all the NMR experiments, and the NMR spectra and peak integrals are shown in **Figure 5.13**. We also measure the 90° pulse time for the three samples to ensure the experimental accuracy in determining spin concentration without the effect of differential probe coil sensitivity.

Table 5.2 shows detailed sample information and calculated results for Na^+ concentration. C_{Na^+} (0.056 mol/kg) in the as-formed ion gel is nearly half that in the PBDT seed solution (0.12 mol/kg). We have repeated this experiment for gels with lower PBDT content (down to 5 wt% in the dried gel) with similar C_{Na^+} results.

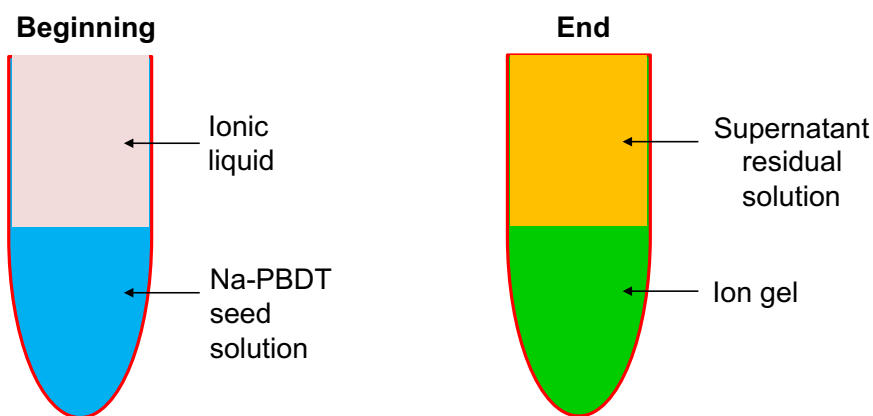


Figure 5.12. The fabrication process for the ion gel sample. At the beginning, we slowly pipette the pure IL [C2mim][TfO] on top of the 4wt% Na-PBDT seed solution. At the end, the system has ion gel formed in the bottom phase and the supernatant residual solution on the top phase.

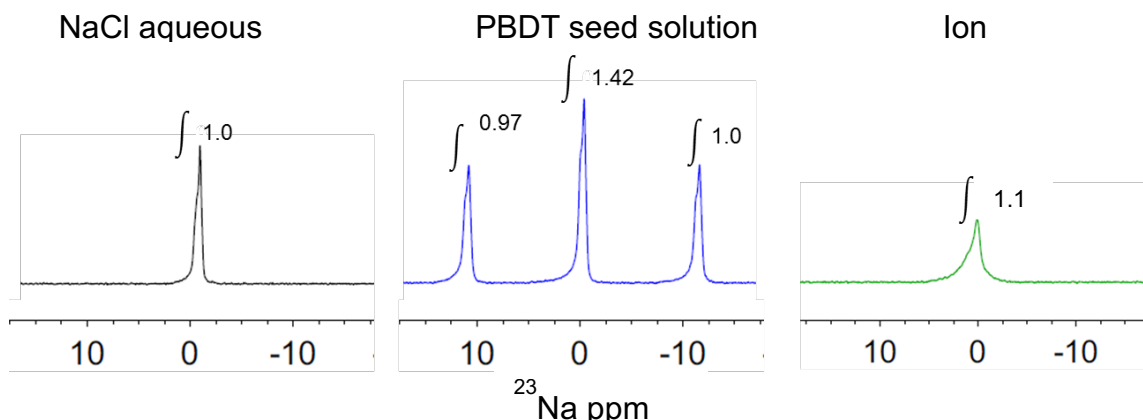


Figure 5.13. ^{23}Na spectra for NaCl aqueous solution, PBDT seed solution and hydrated PBDT ion gel, respectively (left to right). Note the presence of the 3 peaks in the PBDT seed solution are due to the nuclear quadrupole splitting of the ^{23}Na ions, which are partially ordered by the aligned polymer chains in the spectrometer magnetic field.

Table 5.2. Detailed sample information, measured 90° pulse times and calculated concentrations. The concentration of NaCl aqueous solution is a predetermined reference to which the others are compared to determine unknown Na^+ concentrations. NMR peak integrals (relative areas) are shown in Figure S6. Error in concentration is $\leq \pm 10\%$.

Sample	90° pulse time (μs)	Weight (mg)	Peak area (relative)	Concentration (mol/kg)
NaCl Aqueous sol	8.5	100	1.0	0.036
PBDT seed sol	8.5	100	3.4	0.12
Ion gel	8.5	71.3	1.1	0.056

5.5 Conclusion

In summary, we have described a highly conductive and thermally stable ion gel with tunable anisotropy and modulus by absorbing ionic liquids (ILs) into magnetically aligned liquid crystalline (LC) polyelectrolyte solutions of poly 2,2'-disulfonyl-4,4'-benzidine terephthalamide (PBDT). The ion gel alignment reveals itself in macroscopic optical anisotropy and enhanced ion transport along the gel alignment axis as opposed to perpendicular directions, as evidenced by polarized optical microscopy, scanning electron microscopy, X-ray diffraction, pulsed-field-gradient NMR diffusometry, and impedance spectroscopy. Ionic conductivity at ambient temperature along the gel alignment axis is a factor $10^2 - 10^4$ higher than known solid-state polymer electrolytes, and the gel modulus is a factor $10 - 10^3$ higher than previous IL-polymer electrolytes with comparable conductivity. We propose a gel formation mechanism driven by a thermodynamically favored hydrogen bonding network among water and ions. The concentration of PBDT seed solution and the **B**-field direction form the two essential factors for flexible tailoring of final gel features. Moreover, using the concepts developed here one can explore electrolyte formation using a wide array of ionic liquids, non-aqueous co-solvents for gel formation, and other rigid-rod polyelectrolytes, in order to produce enhanced combinations of properties. We expect these safe, robust, tunable, and highly conductive ion gels to enable critical and groundbreaking electrochemical device applications.

References

- [1] Li, J.; Park, J. K.; Moore, R. B.; Madsen, L. A., Linear coupling of alignment with transport in a polymer electrolyte membrane, *Nature Materials*, **2011**, *10*, 507.
- [2] Miyatake, K.; Chikashige, Y.; Higuchi, E.; Watanabe, M., Tuned polymer electrolyte membranes based on aromatic polyethers for fuel cell applications, *Journal of the American Chemical Society*, **2007**, *129*, 3879.

- [3] Peckham, T. J.; Holdcroft, S., Structure-Morphology-Property Relationships of Non-Perfluorinated Proton-Conducting Membranes, *Advanced Materials*, **2010**, *22*, 4667.
- [4] Liu, X.; Wu, D.; Wang, H.; Wang, Q., Self-Recovering Tough Gel Electrolyte with Adjustable Supercapacitor Performance, *Advanced Materials*, **2014**, *26*, 4370.
- [5] Kong, L. R.; Chen, W., Carbon Nanotube and Graphene-based Bioinspired Electrochemical Actuators, *Advanced Materials*, **2014**, *26*, 1025.
- [6] Gin, D. L.; Noble, R. D., Designing the Next Generation of Chemical Separation Membranes, *Science*, **2011**, *332*, 674.
- [7] Chen, C.-L.; Teng, H.; Lee, Y.-L., In Situ Gelation of Electrolytes for Highly Efficient Gel-State Dye-Sensitized Solar Cells, *Advanced Materials*, **2011**, *23*, 4199.
- [8] Armand, M.; Endres, F.; MacFarlane, D. R.; Ohno, H.; Scrosati, B., Ionic-liquid materials for the electrochemical challenges of the future, *Nature Materials*, **2009**, *8*, 621.
- [9] Majewski, P. W.; Gopinadhan, M.; Jang, W. S.; Lutkenhaus, J. L.; Osuji, C. O., Anisotropic Ionic Conductivity in Block Copolymer Membranes by Magnetic Field Alignment, *Journal of the American Chemical Society*, **2010**, *132*, 17516.
- [10] Lodge, T. P., Materials science - A unique platform for materials design, *Science*, **2008**, *321*, 50.
- [11] Jangu, C.; Savage, A. M.; Zhang, Z.; Schultz, A. R.; Madsen, L. A.; Beyer, F. L.; Long, T. E., Sulfonimide-Containing Triblock Copolymers for Improved Conductivity and Mechanical Performance, *Macromolecules*, **2015**, *48*, 4520.
- [12] He, Y.; Boswell, P. G.; Bühlmann, P.; Lodge, T. P., Ion Gels by Self-Assembly of a Triblock Copolymer in an Ionic Liquid†, *Journal of Physical Chemistry B*, **2006**, *111*, 4645.
- [13] Virgili, J. M.; Nedoma, A. J.; Segalman, R. A.; Balsara, N. P., Ionic Liquid Distribution in Ordered Block Copolymer Solutions, *Macromolecules*, **2010**, *43*, 3750.
- [14] Susan, M. A. B. H.; Kaneko, T.; Noda, A.; Watanabe, M., Ion Gels Prepared by in Situ Radical Polymerization of Vinyl Monomers in an Ionic Liquid and Their Characterization as Polymer Electrolytes, *Journal of the American Chemical Society*, **2005**, *127*, 4976.
- [15] Cho, J. H.; Lee, J.; He, Y.; Kim, B. S.; Lodge, T. P.; Frisbie, C. D., High-Capacitance Ion Gel Gate Dielectrics with Faster Polarization Response Times for Organic Thin Film Transistors, *Advanced Materials*, **2008**, *20*, 686.
- [16] Le Bideau, J.; Ducros, J. B.; Soudan, P.; Guyomard, D., Solid-State Electrode Materials with Ionic-Liquid Properties for Energy Storage: the Lithium Solid-State Ionic-Liquid Concept., *Advanced Functional Materials*, **2011**, *21*, 4073.
- [17] Meyer, W. H., Polymer electrolytes for lithium-ion batteries, *Advanced Materials*, **1998**, *10*, 439.
- [18] Schulze, M. W.; McIntosh, L. D.; Hillmyer, M. A.; Lodge, T. P., High-Modulus, High-Conductivity Nanostructured Polymer Electrolyte Membranes via Polymerization-Induced Phase Separation, *Nano Letters*, **2014**, *14*, 122.
- [19] Yoon, J.; Cho, S.; Kim, J.-H.; Lee, J.; Bi, Z.; Serquis, A.; Zhang, X.; Manthiram, A.; Wang, H., Vertically Aligned Nanocomposite Thin Films as a Cathode/Electrolyte Interface Layer for Thin-Film Solid Oxide Fuel Cells, *Advanced Functional Materials*, **2009**, *19*, 3868.

- [20] Liu, W.-w.; Lu, C.; Liang, K.; Tay, B. K., A three dimensional vertically aligned multiwall carbon nanotube/NiCo₂O₄ core/shell structure for novel high-performance supercapacitors, *Journal of Materials Chemistry A*, **2014**, *2*, 5100.
- [21] Ueki, T.; Watanabe, M., Macromolecules in ionic liquids: Progress, challenges, and opportunities, *Macromolecules*, **2008**, *41*, 3739.
- [22] Tang, B. X.; White, S. P.; Frisbie, C. D.; Lodge, T. P., Synergistic Increase in Ionic Conductivity and Modulus of Triblock Copolymer Ion Gels, *Macromolecules*, **2015**, *48*, 4942.
- [23] Ueno, K.; Hata, K.; Katakabe, T.; Kondoh, M.; Watanabe, M., Nanocomposite ion gels based on silica nanoparticles and an ionic liquid: Ionic transport, viscoelastic properties, and microstructure, *Journal of Physical Chemistry B*, **2008**, *112*, 9013.
- [24] Wu, Z. L.; Sawada, D.; Kurokawa, T.; Kakugo, A.; Yang, W.; Furukawa, H.; Gong, J. P., Strain-Induced Molecular Reorientation and Birefringence Reversion of a Robust, Anisotropic Double-Network Hydrogel, *Macromolecules*, **2011**, *44*, 3542.
- [25] Lee, M.; Park, J. K.; Lee, H. S.; Lane, O.; Moore, R. B.; McGrath, J. E.; Baird, D. G., Effects of block length and solution-casting conditions on the final morphology and properties of disulfonated poly(arylene ether sulfone) multiblock copolymer films for proton exchange membranes, *Polymer*, **2009**, *50*, 6129.
- [26] Gasa, J. V.; Weiss, R. A.; Shaw, M. T., Structured polymer electrolyte blends based on sulfonated polyetherketoneketone (SPEKK) and a poly(ether imide) (PEI), *Journal of Membrane Science*, **2008**, *320*, 215.
- [27] Gopinadhan, M.; Majewski, P. W.; Choo, Y.; Osuji, C. O., Order-Disorder Transition and Alignment Dynamics of a Block Copolymer Under High Magnetic Fields by In Situ X-Ray Scattering, *Physical Review Letters*, **2013**, *110*.
- [28] Park, J. K.; Li, J.; Divoux, G. M.; Madsen, L. A.; Moore, R. B., Oriented Morphology and Anisotropic Transport in Uniaxially Stretched Perfluorosulfonate Ionomer Membranes, *Macromolecules*, **2011**, *44*, 5701.
- [29] Schausser, N. S.; Harry, K. J.; Parkinson, D. Y.; Watanabe, H.; Balsara, N. P., Lithium Dendrite Growth in Glassy and Rubbery Nanostructured Block Copolymer Electrolytes, *Journal of the Electrochemical Society*, **2014**, *162*, A398.
- [30] Xu, W.; Wang, J.; Ding, F.; Chen, X.; Nasybulin, E.; Zhang, Y.; Zhang, J.-G., Lithium metal anodes for rechargeable batteries, *Energy & Environmental Science*, **2014**, *7*, 513.
- [31] Livolant, F.; Levelut, A. M.; Doucet, J.; Benoit, J. P., The Highly Concentrated Liquid-Crystalline Phase of DNA Is Columnar Hexagonal, *Nature*, **1989**, *339*, 724.
- [32] Giraud-Guille, M.-M.; Besseau, L.; Martin, R., Liquid crystalline assemblies of collagen in bone and in vitro systems, *Journal of Biomechanics*, **2003**, *36*, 1571.
- [33] Okoshi, K.; Kamee, H.; Suzaki, G.; Tokita, M.; Fujiki, M.; Watanabe, J., Well-defined phase sequence including cholesteric, smectic A, and columnar phases observed in a thermotropic LC system of simple rigid-rod helical polysilane, *Macromolecules*, **2002**, *35*, 4556.
- [34] Wang, Y.; Gao, J.; Dingemans, T. J.; Madsen, L. A., Molecular Alignment and Ion Transport in Rigid Rod Polyelectrolyte Solutions, *Macromolecules*, **2014**, *47*, 2984.
- [35] Mitov, M.; Portet, C.; Bourgerette, C.; Snoeck, E.; Verelst, M., Long-range structuring of nanoparticles by mimicry of a cholesteric liquid crystal, *Nature Materials*, **2002**, *1*, 229.

- [36] Wu, Z. L.; Kurokawa, T.; Sawada, D.; Hu, J.; Furukawa, H.; Gong, J. P., Anisotropic Hydrogel from Complexation-Driven Reorientation of Semirigid Polyanion at Ca^{2+} Diffusion Flux Front, *Macromolecules*, **2011**, *44*, 3535.
- [37] Shigekura, Y.; Chen, Y. M.; Furukawa, H.; Kaneko, T.; Kaneko, D.; Osada, Y.; Gong, J. P., Anisotropic polyion-complex gels via template polymerization, *Advanced Materials*, **2005**, *17*, 2695.
- [38] Yang, W.; Furukawa, H.; Gong, J. P., Highly Extensible Double-Network Gels with Self-Assembling Anisotropic Structure, *Advanced Materials*, **2008**, *20*, 4499.
- [39] Wu, Z. L.; Arifuzzaman, M.; Kurokawa, T.; Le, K.; Hu, J.; Sun, T. L.; Furukawa, H.; Masunaga, H.; Gong, J. P., Supramolecular Assemblies of a Semirigid Polyanion in Aqueous Solutions, *Macromolecules*, **2013**, *46*, 3581.
- [40] Li, J.; Wilmsmeyer, K. G.; Madsen, L. A., Anisotropic Diffusion and Morphology in Perfluorosulfonate Ionomers Investigated by NMR, *Macromolecules*, **2009**, *42*, 255.
- [41] Hou, J. B.; Li, J.; Madsen, L. A., Anisotropy and Transport in Poly(arylene ether sulfone) Hydrophilic-Hydrophobic Block Copolymers, *Macromolecules*, **2010**, *43*, 347.
- [42] Gao, J.; Wang, Y.; Norder, B.; Garcia, S. J.; Picken, S. J.; Madsen, L. A.; Dingemans, T. J., Water and sodium transport and liquid crystalline alignment in a sulfonated aramid membrane, *Journal of Membrane Science*, **2015**, *489*, 194.
- [43] Watson, J. D.; Crick, F. H. C., Molecular Structure of Nucleic Acids - a Structure for Deoxyribose Nucleic Acid, *Nature*, **1953**, *171*, 737.
- [44] Albrecht, M., "Let's twist again" - Double-stranded, triple-stranded, and circular helicates, *Chemical Reviews*, **2001**, *101*, 3457.
- [45] Li, J.; Wilmsmeyer, K. G.; Hou, J. B.; Madsen, L. A., The role of water in transport of ionic liquids in polymeric artificial muscle actuators, *Soft Matter*, **2009**, *5*, 2596.
- [46] Fadeeva, T. A.; Husson, P.; DeVine, J. A.; Costa Gomes, M. F.; Greenbaum, S. G.; Castner, E. W., Interactions between water and 1-butyl-1-methylpyrrolidinium ionic liquids, *Journal of Chemical Physics*, **2015**, *143*, 064503.
- [47] Hou, J. B.; Zhang, Z. Y.; Madsen, L. A., Cation/Anion Associations in Ionic Liquids Modulated by Hydration and Ionic Medium, *Journal of Physical Chemistry B*, **2011**, *115*, 4576.
- [48] Bhattacharja, S.; Smoot, S. W.; Whitmore, D. H., Cation and Anion Diffusion in the Amorphous Phase of the Polymer Electrolyte (Peo) 8licf3so3, *Solid State Ionics*, **1986**, *18-9*, 306.
- [49] Shi, J.; Vincent, C. A., The Effect of Molecular-Weight on Cation Mobility in Polymer Electrolytes, *Solid State Ionics*, **1993**, *60*, 11.
- [50] Zhang, Z. Y.; Madsen, L. A., Observation of separate cation and anion electrophoretic mobilities in pure ionic liquids, *Journal of Chemical Physics*, **2014**, *140*.
- [51] Lingwood, M. D.; Zhang, Z.; Kidd, B. E.; McCreary, K. B.; Hou, J.; Madsen, L. A., Unraveling the local energetics of transport in a polymer ion conductor, *Chemical Communications*, **2013**, *49*, 4283.
- [52] Zhang, S. J.; Sun, N.; He, X. Z.; Lu, X. M.; Zhang, X. P., Physical properties of ionic liquids: Database and evaluation, *Journal of Physical and Chemical Reference Data*, **2006**, *35*, 1475.
- [53] Jin, L. Y.; Howlett, P. C.; Pringle, J. M.; Janikowski, J.; Armand, M.; MacFarlane, D. R.; Forsyth, M., An organic ionic plastic crystal electrolyte for rate capability and

- stability of ambient temperature lithium batteries, *Energy & Environmental Science*, **2014**, 7, 3352.
- [54] Yuan, R.; Teran, A. A.; Gurevitch, I.; Mullin, S. A.; Wanakule, N. S.; Balsara, N. P., Ionic Conductivity of Low Molecular Weight Block Copolymer Electrolytes, *Macromolecules*, **2013**, 46, 914.
- [55] Devaux, D.; Bouchet, R.; Gle, D.; Denoyel, R., Mechanism of ion transport in PEO/LiTFSI complexes: Effect of temperature, molecular weight and end groups, *Solid State Ionics*, **2012**, 227, 119.
- [56] Bouchet, R.; Phan, T. N. T.; Beaudoin, E.; Devaux, D.; Davidson, P.; Bertin, D.; Denoyel, R., Charge Transport in Nanostructured PS-PEO-PS Triblock Copolymer Electrolytes, *Macromolecules*, **2014**, 47, 2659.
- [57] Ispas, A.; Polleth, M.; Ba, K. H. T.; Bund, A.; Janek, J., Electrochemical deposition of silver from 1-ethyl-3-methylimidazolium trifluoromethanesulfonate, *Electrochimica Acta*, **2011**, 56, 10332.
- [58] Lin, J.; Jain, V.; Madsen, L.; Montazami, R.; Heflin, J.; Li, J.; Liu, Y.; Zhang, Q.; Wang, D.; Liu, S., Ion transport and storage of ionic liquids in ionic polymer conductor network composites, *Applied Physics Letters*, **2010**, 96, 223503.
- [59] Hu, X.; Vatankeh-Varnoosfaderani, M.; Zhou, J.; Li, Q.; Sheiko, S. S., Weak Hydrogen Bonding Enables Hard, Strong, Tough, and Elastic Hydrogels, *Advanced Materials (Weinheim, Germany)*, **2015**, n/a.
- [60] Shi, W.; Damodaran, K.; Nulwala, H. B.; Luebke, D. R., Theoretical and experimental studies of water interaction in acetate based ionic liquids, *Physical Chemistry Chemical Physics*, **2012**, 14, 15897.
- [61] Schott, H., Direct comparison of the strength of hydrogen bonds formed by H₂O and D₂O, *Journal of Macromolecular Science, Part B*, **1988**, 27, 119.
- [62] Soper, A. K.; Benmore, C. J., Quantum differences between heavy and light water, *Physical Review Letters*, **2008**, 101.

Chapter 6

Ionic Liquid Based Polymer Electrolytes with Tunable Modulus for Non-flammable and Dendrite-free Li-metal Batteries

6.1 Abstract

Use of Li metal in battery anodes has been investigated for several decades, but has not found practical use. This presents opportunities for development of next-generation higher energy density Li batteries, such as Li-metal, Li-sulfur and Li-air batteries. Notably, low coulombic efficiency and dendrite growth on the Li metal surface along with limited battery cycle life prevent its commercial application. In this project, we have developed a series of solid-state ion gel electrolytes with high Li density based on a two-step fabrication method and lithium bis(fluorosulfonyl)imide (LiFSI) as the doping salt. This heterogeneous salt doping has shown potential for stabilizing Li metal deposition. This ionic liquid-based gel electrolyte possesses high ionic conductivity (~ 1 mS/cm) and non-flammability while maintaining a high (up to ~ 1 GPa) modulus to suppress unfavorable Li dendrite growth. We observe stable cycling of this gel electrolyte at current density ≤ 1 mA cm⁻², which is rarely reported for previous solid-state electrolytes. By tuning modulus and Li salt concentration in these gel electrolytes, we conclude that stable deposition of Li metal is closely correlated with the high modulus of the gel electrolyte as well as the salt concentration. Finally, we demonstrate a new fabrication method to obtain thin (~ 100 μ m) gel electrolyte membranes with controllable thickness and smooth surfaces, thus showing promise for application in advanced Li batteries.

6.2 Introduction

Among the myriad energy storage technologies, the lithium-ion battery plays an important role due to its relatively high specific energy.^[1,2] Currently, Li-ion batteries are widely used in portable devices and electric vehicles. However, Li-ion batteries have almost reached the theoretical energy density limit (387 Wh.Kg^{-1}).^[1-3] In order to increase the capacity of Li batteries, researchers have proposed two main directions. First, researchers have been working to discover high energy density cathode materials. For example, Li-air and Li-S batteries have been heavily investigated in recent decades.^[1,4,5] However, it is still difficult to control the irreversible and complex interfacial reactions between electrodes and electrolytes. Second, we can replace the Li graphite composite anode material with pure Li metal in order to increase the energy density by up to a factor of 2 or 3.^[1-3,6] However, dendrite growth on the Li metal surface during charging has prevented practical applications. In general, both of these methods require a suitable electrolyte to combat irreversible reactions and dendrite growth during repeated charge and discharge cycles.^[1,7,8] To alleviate these problems, solid-state polymer electrolytes not only provide high modulus to block dendrite growth on the anodes, but also deliver safer (non-flammable) operation compared to organic liquid electrolytes.^[7,9-11] Here, we describe an advanced solid-state electrolyte based on a sulfonated aramid rigid-rod polymer, an ionic liquid (IL), and a lithium salt, showing potential to resolve these issues.

Previous researchers have developed a number of IL-based gel electrolytes that share the non-flammability of ionic liquids as well as the mechanical integrity of a polymeric or inorganic supporting matrix.^[10,12-14] Based on the type of supporting material incorporated into these electrolytes, researchers have developed two main gel electrolytes, termed “ion gels” and “ionogels”.^[13-15] An “ion gel” is a polymer matrix swollen with a

large volume fraction of IL.^[10,16] An “ionogel” is developed based on immobilization of ILs in a thermally stable inorganic matrix, such as SiO₂ and TiO₂.^[14,15,17] A large number of papers have discussed the potential applications of both gel types for high energy density Li batteries.^[14,18-21] However, only rarely can researchers demonstrate strong battery cycling performance without doping the gels with volatile organic electrolytes.^[14,21-23] Organic electrolytes can greatly improve the ionic conductivity of the system, but introduce the inconvenience and complexity of a volatile liquid component while also diminishing safety against overheating and fire.^[2,3,24,25] Here we describe a class of gel electrolytes based on pure IL without any organic solvents. This all new class of ion gels maintains high ionic conductivity and high thermal stability while possessing sufficient modulus to serve as separators in batteries.

Doping with Li salts has been widely applied to Li battery electrolyte in order to balance the Li⁺ compensation in the reactions between electrodes and electrolytes.^[26-31] Recently, researchers have discovered many advantages of LiFSI as an additive salt.^[29,32,33] The counterion FSI⁻ can provide a stable SEI layer and reversible capacity for a graphitized negative electrode at ambient temperature.^[34] In this project, we employ IL electrolytes (ILEs) containing the N-propyl-N-methylpyrrolidinium [C₃mpyr]⁺ bis(fluorosulfonyl)imide [FSI]⁻ IL combined with a variable amount of LiFSI as an additive salt. This ILE has enabled safe charge-discharge cycling of commercially viable batteries for 1000 cycles, and with coulombic efficiency > 99.5%.^[34] However, the electrode used in these batteries needs to be pretreated with the ILE and some cycles need to be performed to achieve a stable response.^[34] As reported previously, the Li⁺ partial conductivity (as assessed by NMR diffusometry on the various mobile ions) in this ILE

achieves a peak value at a relatively high salt concentration (~ 50 mol%).^[35] Thus, in this work, we have mainly studied this ILE with relatively high Li salt concentration. **Table 6.1** shows the concentration of the ILEs we used. By incorporating this ILE into our newly fabricated PBDT ion gel, we demonstrate the fabrication of a solid-state electrolyte with high Li density that promises to suppress Li dendrite growth on the metal anode. The gel fabrication process requires two steps as shown in **Figure 6.1**: (1) We obtain the "raw" ion gel based on the interfacial ion exchange process between a sulfonated aromatic polyamide (PBDT H₂O solution) and an IL ([C₂mim][BF₄]) as reported previously.^[10] (2) We then ion exchange the raw ion gel by immersing the raw ion gel in the pre-mixed ILEs shown in **Table 6.1**. According to this two-step fabrication method, we can obtain solid-state electrolytes that show significant potential to resolve outstanding issues in Li metal batteries such as dendrite growth and risk of fire. The key to step 1 is that both the IL and ionic polymer are soluble in the same solvent (water). Note that we are exploring variable temperature fabrication as well as other solvent systems (e.g., ethylene glycol, DMSO and their water mixtures) that can expand the range of ion gels made directly by a one-step process. The addition of step 2 allows a wide range of IL and Li-salt mixtures to be exchanged into the gel matrix in order to adjust the properties of the gel for batteries or other desired applications. Step 1 of **Figure 6.1** illustrates the concepts involved in the formation and morphology of the raw ion gel, which, when incorporating the C₂mimBF₄ IL, is composed of locally aligned PBDT domains dispersed with guest IL molecules. The raw ion gel is macroscopically isotropic, whereas it shows local microscale LC alignment. This alignment originates from the highly aligned PBDT chains. We propose that the domain boundaries formed at the

interfaces between individually aligned domains might allow for higher Li density and faster Li transport as compared to within the domains. We are currently employing an array of characterization methods to study the morphology and Li distribution in the doped ion gels, as described below.

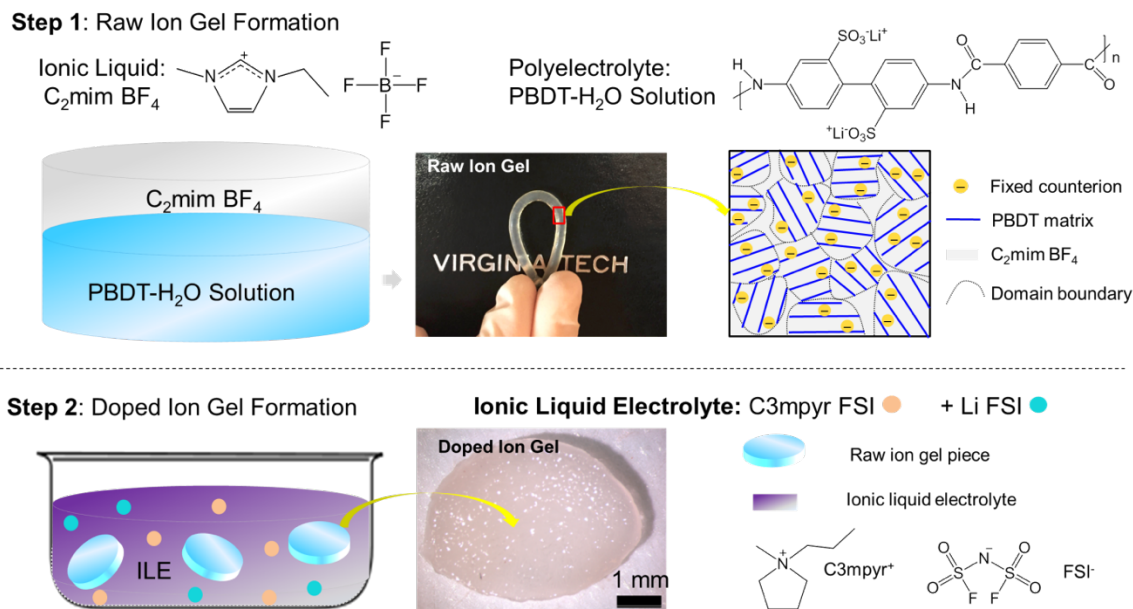


Figure 6.1. Fabrication processes used to form the solid-state ion gel electrolytes. **Step 1** shows fabrication of the raw ion gel sample. This gel is obtained based on an interfacial ion exchange between a water-soluble IL (C_2mimBF_4) and an aqueous polyelectrolyte solution (PBDT).^[10] An interfacial layer is initially formed at the interface between the two solutions, then cations and anions of IL will permeate downward through the interfacial layer while the water and Li^+ counterions in the bottom solution phase will transport upward into the IL phase. **Step 2** shows the second ion exchange process of immersing the sliced ion gel inside the Li-salt and IL electrolyte (ILE), where in this case the ILE is $\text{C}_3\text{mpyrFSI}$ mixed with a predetermined concentration of LiFSI .

6.3 Experimental

Materials: Poly 2,2'-disulfonyl-4,4'-benzidine terephthalamide (PBDT) was synthesized by interfacial condensation polymerization. Aqueous solutions with PBDT weight percentage (wt%) ranging from 2% - 4% were prepared by loading the prescribed amount of PBDT and deionized H₂O into 5mm and 8mm NMR tubes. 1-ethyl-3-methyl imidazolium tetrafluoroborate ([C₂mim][BF₄], purity > 99%) was purchased from Solvent Innovation GmbH (Cologne, Germany).

Ionic Liquid Electrolyte: N-propyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide (C₃mpyrFSI, purity > 99.9%) was purchased from Solvionic. Lithium bis(fluorosulfonyl)imide (LiFSI, purity >99.5%) was sourced from Suzhou Fluolyte Co., Ltd., China. Lithium metal was sourced from China Energy Lithium Co. Ltd. (purity > 99.9%). IL electrolytes in this paper were prepared by adding the prescribed amount of LiFSI to C₃mpyrFSI IL at room temperature in an Ar-filled glove box (< 0 ppm O₂ and < 10 ppm H₂O). We prepared ILEs with varying ratio of IL to Li salt as shown in **Table 1**.

Preparation of PBDT IL gel: C₂mimBF₄ with the same volume as the PBDT polymer seed solution was slowly pipetted on the top of each PBDT solution. After 24 hours ion exchange, the gel was formed in the bottom polymer solution phase and the residual water/IL supernatant was poured off. After vacuum drying the ion gel at 50°C, we obtained the raw ion gel electrolytes. We then immersed the ion gels in the ILEs for at least one day at room temperature.

¹H and ¹⁹F NMR and Pulsed-field-gradient (PFG) NMR Diffusometry: The pulsed-gradient stimulated-echo sequence (PGSTE) was applied for all diffusion measurements.

A Bruker Avance III widebore 400 MHz (9.4 T) NMR was equipped with a diff60 pulsed-field-gradient diffusion probe having a maximum gradient value of 2000 G/cm (at 33 A) along the Z axis and 5 mm ^7Li and 8 mm $^1\text{H}/^{19}\text{F}$ rf coils. All parameters for the NMR diffusometry experiments have been calibrated and optimized as reported earlier.^[36]

X-ray Diffraction (XRD): XRD experiments were carried out on a Rigaku Oxford Diffraction Xcalibur Nova Single-Crystal Diffractometer equipped with an Onyx CCD detector and a Cu microsource operating at 49.5 kV and 80 mA at room temperature. The gel was sliced to a thickness ~ 1 mm and mounted on the edge of a steel pin, such that the gel extended above the steel pin and into the X-ray beam. The sample-to-detector distance was 50 mm, giving data at scattering angle 2θ from 5° to 42° . The sample was rotated 2° along phi direction. For each sample, a total of 6 images each with 30 s exposure time was collected and summed to increase signal-to-noise ratio. The software CrysAlisPro (v1.171.37.35, Rigaku Oxford Diffraction, 2015, Rigaku Corporation, Oxford, UK) was used for data collection and analysis.

Cyclic Voltammetry: A 1.5 mm diameter Ni working electrode and a Li metal foil counter electrode were employed for cyclic voltammetry. The CV measurements were performed against $\text{Li}|\text{Li}^+$ redox potential.^[35] All scans were performed in an Argon-filled glovebox ($\text{H}_2\text{O} < 0.0$ ppm, $\text{O}_2 < 10$ ppm) at 25°C with 20 mV s^{-1} scan rate using a Biologic SP-200 controlled by EC-Lab (ver. 10.40) software.

Symmetric lithium metal coin cells: These CR2032 type cells were prepared with two 10 mm^2 diameter lithium disk electrodes in an Ar-filled glove box. The coin cells were used for impedance spectroscopy, and cycling measurements. A VMP3 (BioLogic) system and a Neware system were used for battery testing. The ionic conductivity was

operated over a 1kHz - 10MHz frequency range at 50 mV. Conductivity of the gel samples was calculated using a value of electrical resistance obtained by fitting the data to an equivalent circuit model using EC-Lab (ver. 10.40) software[®].

6.4 Results and Discussion

6.4.1 Chemical Composition, Ion Transport and Activation Energy

According to the two-step fabrication method, we can obtain a solid-state ion gel electrolyte with tunable modulus and efficient Li^+ transport. The chemical composition of products after each step can be qualitatively and quantitatively verified based on ^1H and ^{19}F NMR spectroscopy. Here, we mainly investigate three gel samples with polymer weight percentage ($m_{\text{PBDT}}/(m_{\text{PBDT}} + m_{\text{IL}})$) of 5%, 10% and 15%. The corresponding initial mass percentage ($m_{\text{PBDT}}/(m_{\text{PBDT}} + m_{\text{H}_2\text{O}})$) of the aqueous PBDT seed solutions are 2%, 3%, and 4%, respectively. **Figure 6.2a** shows the ^1H spectra for C_2mim^+ and C_3mpyr^+ in the free liquid state. **Figure 6.2b** exhibits the ^1H spectra for C_2mim^+ in the raw ion gels obtained by **step 1** in **Figure 6.1**. **Figure 6.2c** compares the ^1H spectrum in the raw ion gel (black) to the doped ion gel (blue). The peak linewidth in the doped ion gel is much broader compared to the raw ion gel, which indicates lower tumbling rate and shorter T_2 relaxation time for ions in the doped ion gel. In terms of the anions in the system, **Figure 6.2d** shows the ^{19}F spectra for $[\text{BF}_4]^-$ (-150 ppm) and $[\text{FSI}]^-$ (60 ppm) in the free liquid state. **Figure 6.2e** displays the ^{19}F spectra for anions in the doped ion gels. By integrating the peak areas of BF_4^- and FSI^- in the ^{19}F spectra, we can quantify the relative ratio of anions ($[\text{BF}_4^-]/[\text{FSI}^-]$) in the doped ion gel electrolytes. **Figure 6.2f** compares the ^{19}F spectrum for anions in the raw ion gel (black) to the doped ion gel (blue). The broader

linewidth of ^{19}F spectra in the doped ion gel also indicates shorter relaxation time for both anions, $[\text{BF}_4]^-$ and $[\text{FSI}]^-$.

We can thus conclude that the cations and anions in the doped ion gels have more restricted motions compared to the ions in the raw ion gels. It is known that ion transport, ion association and Li transport mechanism in electrolyte materials are critical for development of next-generation battery electrolytes. Based on the temperature dependence of D_{Li^+} , D_{cations} and D_{anions} obtained from NMR diffusometry, we can investigate the diffusion coefficients and corresponding activation energies for the ions present in the ion gels. As shown in **Figure 6.3a-b**, we measure the diffusion coefficients and activation energies of C_2mim^+ and BF_4^- in the raw ion gels. Based on the fitting results using the Arrhenius equation,

$$D = D_0 e^{-\frac{E_a}{RT}}, \quad (6.1)$$

where D is the diffusion coefficient of the measured particles, D_0 is the pre-exponential factor, E_a is the activation energy of the transport process, R is universal gas constant and T is the absolute temperature, we observe that the activation energies of $[\text{C}_2\text{mim}]^+$ and $[\text{BF}_4]^-$ increase with polymer content in the raw ion gels. Thus we can conclude that the PBDT matrix tend increase the local energetic barriers that governs ion transport.^[37] Conversely, as shown in **Figure 6.3c-d**, in the doped ion gel, the activation energy of Li^+ is diminished with increasing polymer content, indicating smaller local energetic barriers for Li^+ transport. This surprising phenomenon may originate from the introduction of a two-phase system, where a heterogeneous structure exists in the doped ion gels.^[7,26,38] We will discuss this phenomenon further in the next section. In addition to Li^+ transport in the doped ion gel, we have begun study on the IL ions and we observe D_{cation} ($[\text{C}_3\text{mpyr}]^+$

and [C₂mim]) in the doped ion gel is $6.2 \times 10^{-12} \text{ m}^2/\text{s}$ at 25°C, which is 10 times lower than $D_{\text{C}_2\text{mim}^+}$ in the raw ion gel. The motions of anions ([BF₄]⁻ and [FSI]⁻) appear to be more restricted ($T_2 < 1 \text{ ms}$), and so far we cannot measure their diffusion. All of these chemical identification and ion transport investigations allow us to propose a new model for morphology in the Li-doped ion gels.

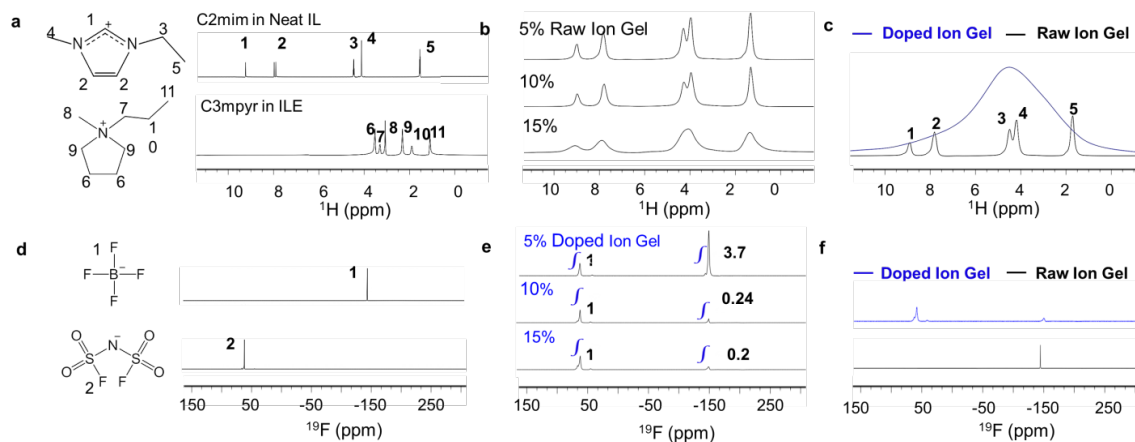


Figure 6.2. Molecular structure and quantitative identification of cations and ions in ion gels based on ¹H and ¹⁹F NMR spectra. (a) ¹H spectra of cations in neat IL ([C₂mim][BF₄]) and ILEs (3.2 mol kg⁻¹ LiFSI in [C₃mpyr][FSI]). (b) ¹H spectra of C₂mim⁺ in raw ion gels with polymer percentage of 5%, 10% and 15%, respectively. (c) ¹H spectra of raw ion gel (black) and doped ion gel (blue). (d) ¹⁹F spectra of anions in neat IL ([C₂mim][BF₄]) and ILEs (3.2 mol kg⁻¹ LiFSI in [C₃mpyr][FSI]). (e) ¹⁹F spectra in doped ion gels. (f) ¹⁹F spectra of raw ion gel (black) and doped ion gel (blue).

Table 6.1. Salt concentration in the ionic liquid electrolytes (ILEs)

LiFSI conc in IL (mol kg ⁻¹)	Molar ratio of each ion relative to total ion content		
	Li ⁺	[C ₃ mpyr] ⁺	[FSI] ⁻
0 (neat IL)	0	0.50	0.50
1.6	0.17	0.33	0.50
3.2	0.25	0.25	0.50

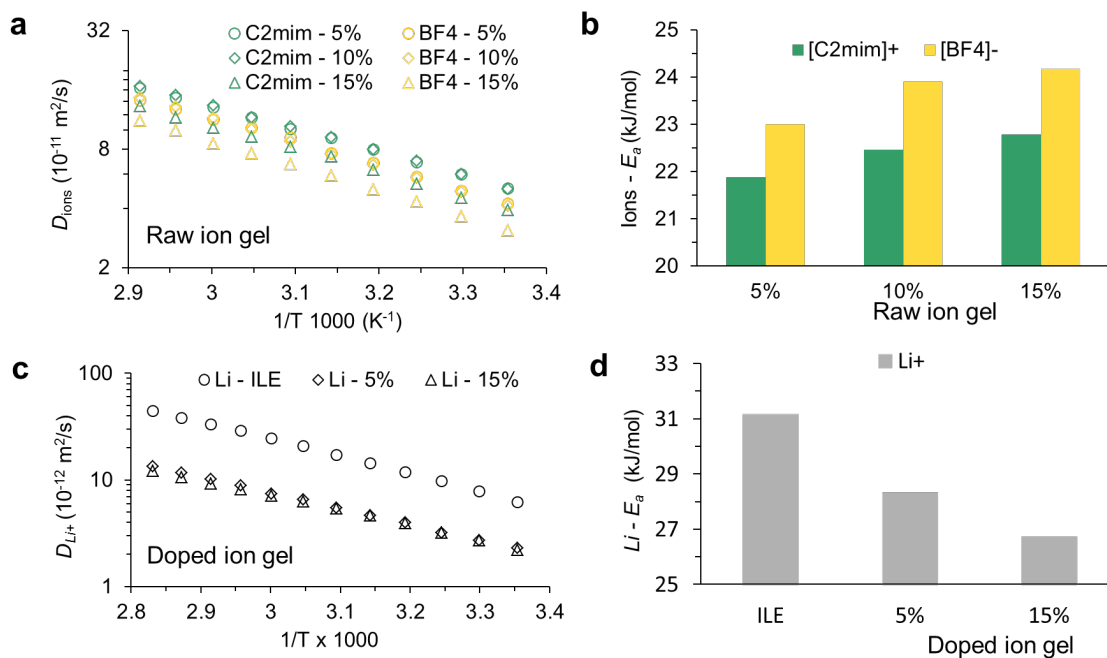


Figure 6.3. Diffusion coefficients and activation energies of ions in the raw and doped ion gels. (a,b) Diffusion coefficients of cation ($[\text{C}_2\text{mim}]^+$) and anion ($[\text{BF}_4]^-$) in the raw ion gels obtained from step 1 in Figure 6.1 and the corresponding activation energies. (c,d) Diffusion coefficients of Li^+ after the ion exchange based on step 2, and the corresponding activation energies. The errors for diffusion are smaller than the symbol size and the errors for E_a are approximately ± 1 kJ/mol.

In order to obtain more information about the gel morphology, we also employ X-ray diffraction to investigate the molecular packing in the doped ion gel as compared to the raw ion gel. As shown in **Figure 6.4a** and **d**, we observe an amorphous halo at $2\theta = 12^\circ$ to 30° scattering angle for the 10% raw ion gel. We assign this halo to the amorphous IL $[\text{C}_3\text{mpyr}][\text{BF}_4]$ in the raw ion gel. After immersing the raw ion gel in the ILEs, we can

obtain a Li-doped solid-state electrolyte. In **Figure 6.4b and e**, the XRD pattern of the 10% Li-doped ion gel indicates the existence of some crystalline structures. The diffraction pattern is a mixture of LiFSI and LiBF₄. Based on the illustration of the raw ion gel shown in **Figure 6.4c**, we also propose a possible mechanism to explain the morphology in the doped ion gel (**Figure 6.4f**). The cations, C₃mpyr⁺ and C₂mim⁺, are partially trapped by polymer-fixed counterions in the solid PBDT matrix, thus partially dissociating the anions (FSI)⁻ and [BF₄]⁻ out of the ion pairs. The released [BF₄]⁻ or [FSI]⁻ then combine with Li⁺, and these could preferentially partition into the grain boundaries, which would then contain an excess of the salts LiBF₄ and/or LiFSI. The grain boundaries are likely located in the original domain boundaries in the raw ion gels, as introduced in **Figure 6.1**. Furthermore, the grain boundaries could contribute to an ion conductive network that can transport Li⁺. We might also expect a higher Li⁺ transference number, which would provide better battery cycling performance and charge/discharge rates. However, this idea requires further investigation by electrophoretic NMR, which can provide the highest accuracy measurements of Li⁺ transference number in polymer and liquid electrolytes.^[39] Furthermore, we are planning to conduct a range of solid-state NMR techniques to quantify the types and amounts of Li salts in polymer domains, in domain boundaries, and possibly in macroscopically phase-separated regions of these Li-doped ion gel systems. Investigation of transport mechanisms, domain or boundary heterogeneities, and ion interactions in this proposed hetero-structure will be essential for us to discover and optimize next-generation Li-ion conductors.

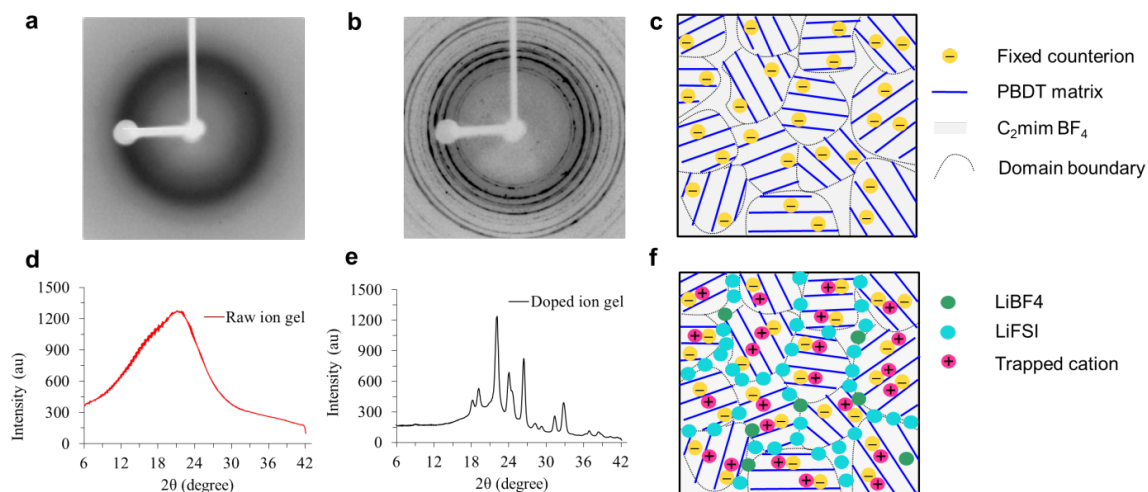


Figure 6.4. The XRD pattern for raw ion gel and doped ion gel. (a-c) The XRD pattern for raw ion gel. (d-f) The XRD pattern for doped ion gel.

6.4.2 Cyclic Voltammetry and Solid-electrolyte Interface (SEI) Formation

We have so far introduced diffusion coefficients, ion associations and morphological structure in these Li-doped ion gel electrolytes. In order to apply this new electrolyte in real devices, we require more information about the cycling performance of electrochemical cells based on this new class of solid-state electrolyte. By assembling the gel electrolytes in Li metal symmetric cells, we investigate various factors that will determine the cycling performance, such as Li salt concentration, modulus of the electrolyte separators, applied current density and cycle time.

To evaluate the Li plating (negative scan) and stripping (positive scan) behavior of the Li metal electrodes by using our newly developed solid-state electrolytes, we employ cyclic voltammetry with scan rate of 50 mV s^{-1} , where the working electrode is a Ni disk (1.7 mm^2) and Li metal is both the reference and counter electrode (see **Figure 6.5**). We

can extract the coulombic efficiency (CE) from the integrated area of the oxidation peak as compared to the reduction peak. **Figure 6.5f** shows the corresponding CE values as a function of cycle number. We can observe that 5% and 15% ion gel doped with 3.2 mol.kg^{-1} ILE show increased coulombic efficiency at higher cycle number. Conversely, ILE exhibits decreasing CE. This may be attributed to the formation of a SEI layer and better surface homogeneity, thus ensuring better performance in batteries. In contrast to the stable current density I in the pure ILE shown in **Figure 6.5a**, the Li-doped ion gels display varying current density, which further indicates the formation of SEI layers on the Li metal surface.

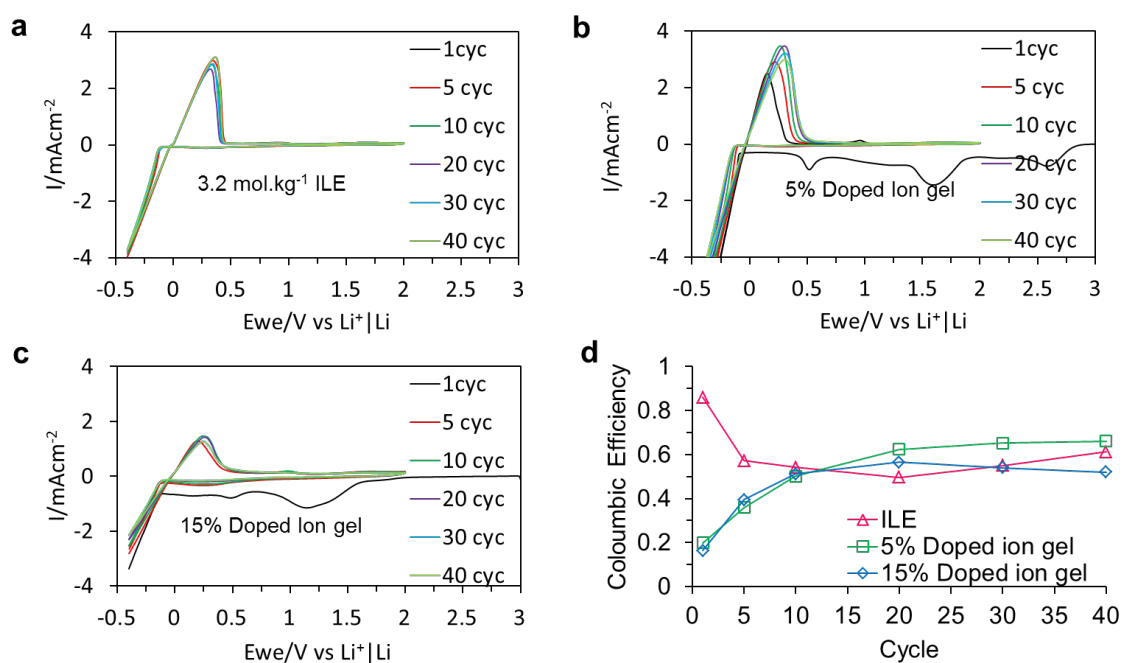


Figure 6.5. Cyclic voltammograms (Ni working electrode 50 mVs^{-1} , room temperature) for pure ILE and ILE-PBDT ion gels. (a) 3.2 mol.kg^{-1} , (b) 5% doped ion gel, (c) 15% doped ion gel (d) The corresponding coulombic efficiency as a function of cycle number from (a-c).

By employing the Li symmetric cell, we can observe voltage vs. cycling number in the doped ion gels at different current densities from 0.01 mA cm^{-2} to 0.3 mA cm^{-2} , as shown in **Figure 6.6**. The overpotential remains relatively stable at specific current density and is proportional to the salt concentration used to exchange the ion gels. The overpotential is commonly inversely proportional to the ionic conductivity of the electrolyte.^[2,35] We observe that the ion gel doped with 3.2 mol kg^{-1} ILE shows the most stable cycling performance (**Figure 6.6 a and c**), possibly because of a relatively high Li^+ transference number or superior SIE later, as discussed above, or due to the higher Li^+ density in the electrolyte, although the ionic conductivity is not the highest.^[35,40] Thus, we demonstrate that the cycling performance of Li symmetric cell is dependent not only on the ionic conductivity of the electrolyte, but also on the Li^+ ion concentration. We will investigate these possible effects using further cycling, cell autopsy, and NMR spectroscopy and diffusometry studies. Furthermore, we will work to determine the correct Li concentration in ILEs in order to optimize the corresponding cycling performance. The results shown in **Figure 6.6 b and d** are corresponding impedance spectra collected before each cycle test at a different current density. The first touchdown shows the resistance of the bulk electrolyte and the second touchdown shows the resistance of the electrode surface. The resistance of the bulk electrolytes stays constant for all the ion gel samples, whereas the interfacial resistance is changing with increasing cycling numbers, indicating SEI layer formation at the interface.

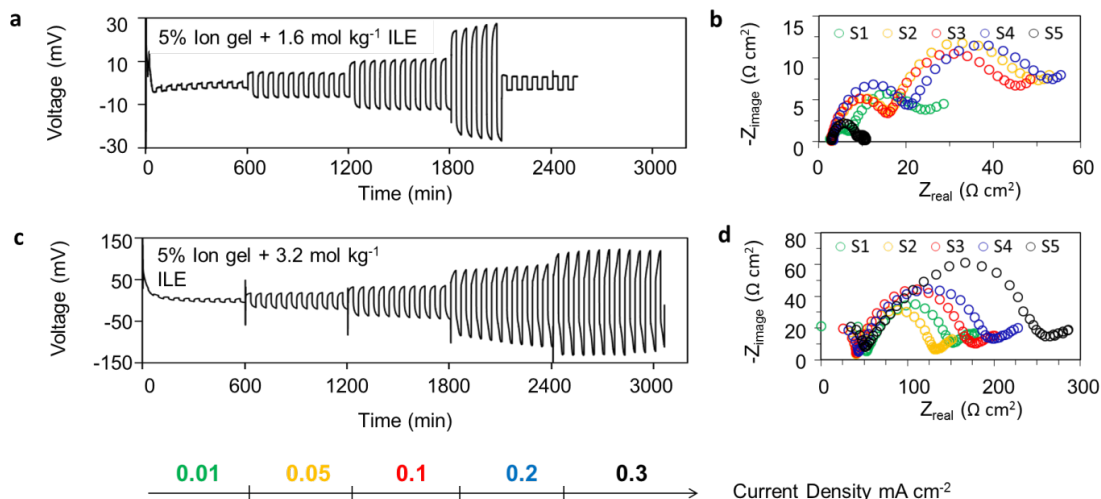


Figure 6.6. Voltage versus time and corresponding impedance spectra scanned before each variation of current density (0.01, 0.05, 0.1, 0.2, 0.3 mAcm⁻²) for a symmetric lithium cell where each half cycle lasts 30 min. (a,b) 5% PBDT ion gel with 1.6 mol.kg⁻¹ ILE, (c,d) 5% PBDT ion gel with 3.2 mol.kg⁻¹ ILE.

Figure 6.7 shows the comparison of two gel samples with different polymer content (5% and 15% PBDT), where we observe that ion gels with higher polymer content display more stable cycling and can withstand current density up to 1mA/cm². This current density has seldom been achieved by solid-state electrolyte materials.^[2,14] To understand the relationship between the modulus of the electrolytes and the cycling performance of the battery, we also investigate the modulus of the doped ion gel based on nanoindentation experiments (**Figure 6.7e** and **f**). These nanoindentation curves record the load placed on the indenter tip as the tip is displaced into the sample. The load is removed when it achieves a predetermined value. The slope angle of the curve at the starting point of the unloading indicates the stiffness of the material. As shown in **Figure 6.7f**, we observe that the 15% doped ion gel displays higher (uncorrected) modulus

compared to the raw ion gels. We will perform further analysis of this nanoindentation data to extract accurate modulus values. However, we may initially conclude that the modulus of the electrolyte correlates with the battery cycling performance. As mentioned previously, the modulus of the gels can be easily tuned by varying the polymer content. Thus, we will discuss more about the correlation between the modulus of the gels and the long-term cycling performance as follows.

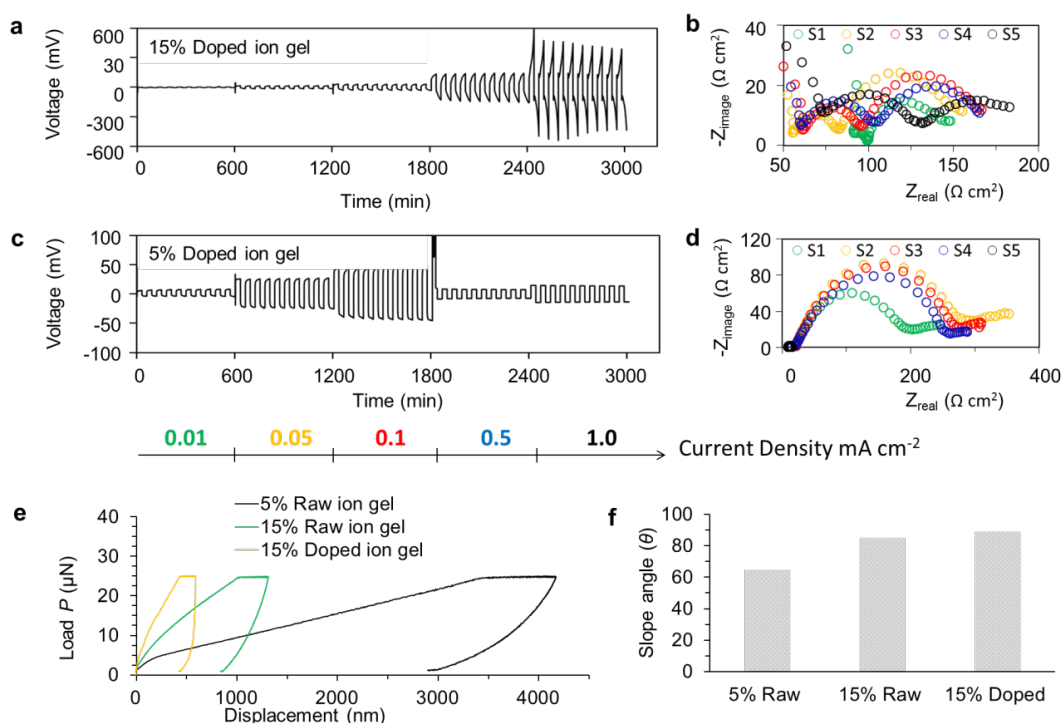


Figure 6.7. Battery cycling and mechanical modulus for Li-doped ion gels. Parts (a) through (d) show voltage versus time, as well as corresponding impedance spectra scanned before each variation of current density for symmetric lithium cells where each half-cycle lasts 30 mins. (a,b) 15% PBDT Li-doped ion gel with current density up to 1.0 mA cm⁻². (c,d) 5% ion gel with current density up to 1.0 mA cm⁻². (e) Nanoindentation curves for 5% raw ion gel, 15% raw ion gel and 15% doped ion gel. (f) Slope angles for tangent lines of the curve just below the unloading point.

6.4.3 Long-term Li Symmetric Cell Cycling Performance

In addition to the preliminary cycling results shown in the last section, **Figure 6.8** shows the long-term cycling performance of the gel electrolytes with increasing polymer content and as a function of current density. Based on the comparison between the 5% and 15% Li-doped ion gel at different current densities, such as 0.05, 0.1 and 0.2 mAcm⁻², we can observe that the 15% ion gel with higher modulus shows higher stable cycling number. Thus, we conclude that the Li dendrite growth can be further suppressed by increasing the modulus of the electrolyte, although this conclusion requires further direct investigation of the electrode surfaces by SEM. In addition, based on the cycling performance shown in **Figure 6.8**, we cannot observe the overpotential phenomenon that indicates Li dendrite formation, which is usually observed in organic electrolytes with high charge-discharge rate.^[35,40] This strongly suggests that these gel electrolytes can be applied in a new generation of safer and higher capacity battery materials.

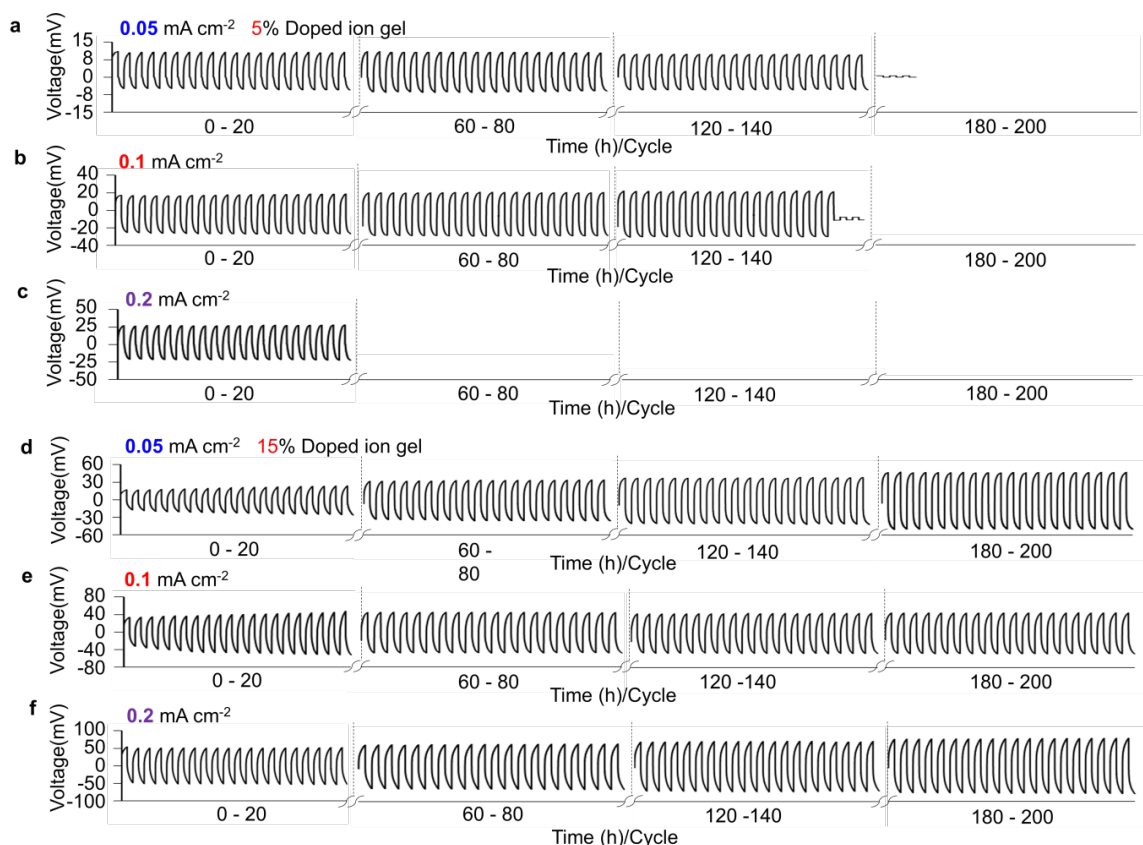


Figure 6.8. Voltage-time profiles for Li symmetric cells incorporating Li-doped ion gel electrolytes. (a) 0.05 mA.cm^{-2} for 5% PBDT Li-doped ion gel, (b) 0.1 mA.cm^{-2} for 5% ion gel, (c) 0.2 mA.cm^{-2} for 5% ion gel, (d) 0.05 mA.cm^{-2} for 15% exchanged PBDT ion gel, (e) 0.1 mA.cm^{-2} for 5% ion gel, (f) 0.2 mA.cm^{-2} for 15% ion gel. We can observe that the 15% doped ion gel exhibits higher stable cycling number than that of 5% doped ion gel.

6.4.4 Fabrication of Thin Gel Membranes and Arbitrary Gel Shapes

We have introduced the fabrication of a new solid-state ion gel electrolyte, as well as various methods to investigate its associated structure-property relationships. For broader application, it is still valuable to build new fabrication techniques to create larger scale

gels in thin film (membrane) format. Fabrication of this gel in membrane form will soon be used as a solid-state electrolyte in full battery pouch cells, and eventually should be applicable in, e.g., portable electronics, grid storage, or electric vehicle batteries. **Figure 6.9** depicts our new film fabrication method. This method can enable fabrication of smooth and uniform ion gel membranes that can be directly employed in battery assembly. Based on this fabrication technique, we can simply control the thickness of the gel membrane by varying the volume of the IL and polymer solution and the pressure applied on the glass substrates. Here is a brief explanation of the detailed steps for this technique.

Step 1: Coat the thin glass coverslip with IL solution.

Step 2: Coat the thick glass slide substrate with PBDT aqueous solution.

Step 3: Quickly flip the glass coverslip and put it on the top of the thick glass substrate, and the ion gel forms at the interface.

Step 4: Remove the top glass coverslip, vacuum dry the ion gel, and peel it off from the glass substrate.

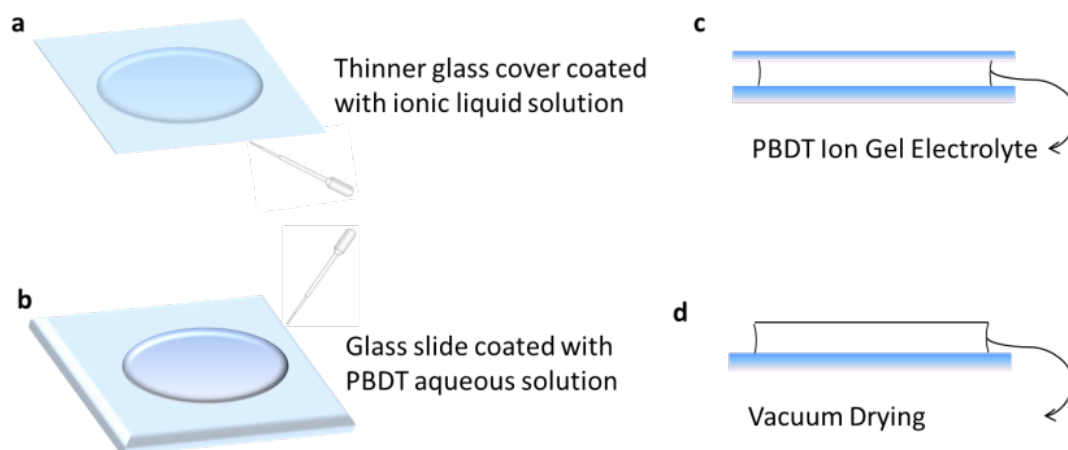


Figure 6.9. Fabrication process to form thin ion gel membrane. (a) Thin glass coverslip coated uniformly with IL solution. (b) Thick glass slide substrate coated with PBDT solution. (c) Place the glass cover on top of the glass slide. (d) After waiting for gel formation (seconds to minutes), remove the top glass cover and vacuum dry the ion gel formed on the glass slide. Different flat or contoured surfaces may be used (e.g., PTFE for less adhesion) for either substrate, as well as different temperatures, solvents, ILs, etc.

Additionally, we propose that we can develop arbitrary shapes of this material through the use of additive manufacturing (3D printing). **Figure 6.10** illustrates 3D printing using a pair of nozzles, where one distributes a small amount (droplet or pixel) of PBDT solution, followed by a top coating of IL (or IL-salt mixture) to form a pixel of thin gel. By raster scanning this pair of nozzles in a desired programmed pattern and metering the stopped-flow of the two liquids, any complex 3D scaffold structure can in principle be printed. In thin films (sub-micron to tens of microns), we estimate the gel will form on millisecond or faster time scales and thus the gel pixels can be built up rapidly. Thus, this gel can be patterned into any shape for use in broad applications,

which may include ionically conductive coatings, distributed electrolyte batteries or microbatteries, medical electrolytes for interfacing with implants or biosensors, or intricately structured mechanical actuators.

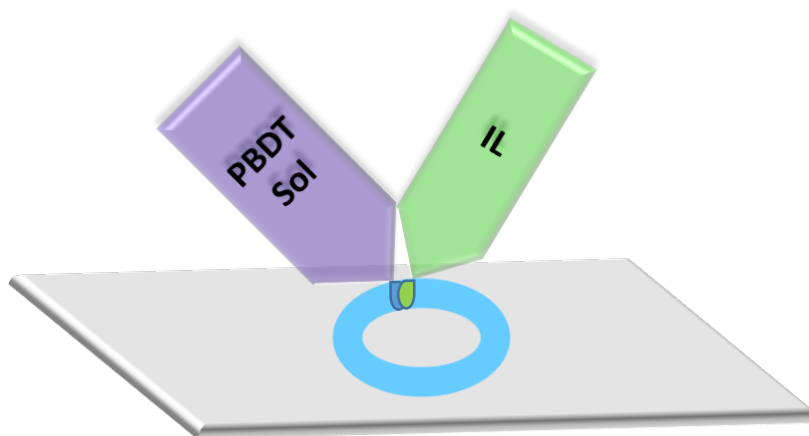


Figure 6.10. 3D printing technique by using the combination of PBDT aqueous solution and ILs metered out of two separate nozzles in order to generate complex shapes of ion gel materials.

6.4.5 Different Ionic Liquids Used for Ion Gel Formation

In addition to the ILs we have described in this project, we can also fabricate a series of ion gels based on different combinations of ILs and PBDT aqueous solution. **Table 6.2** summarizes the ion gel fabrication results. By carefully selecting the type of IL, we can develop a series of ion gels with tunable properties, such as modulus, conductivity, birefringence, fluorescence, as well as anisotropy in a range of properties. These properties encourage development of broader applications for these newly developed gel materials, including artificial muscles, optical sensors, fuel cell membranes and reverse osmosis membranes.

Table 6.2. Demonstrated fabrication of PBDT ion gels based on different ILs.

Ionic Liquid	Formation of Gels	Observations
C ₂ mim TfO	Y	Gel formed in the bottom solution
C ₂ mim BF ₄	Y	Gel formed in the bottom solution
C ₂ mim TFSI	N	Immiscible
C ₂ mim Acetate	Y	Gel formed in the bottom solution
C ₄ mim TfO	Y	Gel formed in the bottom solution
C ₄ mim BF ₄	Y	Gel formed in the bottom solution
C ₄ mim TFSI	N	Immiscible
C ₄ mim DCA	Y	Gel formed in the bottom solution
C ₆ mim TfO	Y	Cloudy gel in the bottom solution
C ₆ mim BF ₄	Y	Cloudy gel in the bottom solution
C ₃ mpyr TfO	N	Highly viscous solution
C ₃ mpyr TFSI	N	Immiscible
C ₃ mpyr DCA	N	Highly viscous solution

6.5 Conclusion

In this chapter, we describe the material development, ion transport, morphology and electrochemical properties of an IL-based polymer gel electrolyte that shows potential to serve as a next generation electrolyte material for a range of electrochemical devices, notably high energy density batteries such as Li-S, Li-air or Na batteries. The two-step fabrication method proposed in the paper is essential to generate highly conductive separators with tunable modulus and adjustable metal ion type and content. By controlling polymer content, modulus of the gel electrolyte, Li salt concentration and applied current density in electrochemical cells, we have explored the main factors that determine the cycling stability of these systems in Li-metal batteries. In addition, we have described several unique fabrication methods for making these ion gels in various forms and with a range of compositions. These studies have thus shown great promise for

flexible integration of these next-generation electrolytes into a number of real world applications.

References

- [1] Bruce, P. G.; Freunberger, S. A.; Hardwick, L. J.; Tarascon, J. M., Li-O-2 and Li-S batteries with high energy storage *Nature Materials*, **2012**, *11*, 19.
- [2] Lu, Y. Y.; Tu, Z. Y.; Archer, L. A., Stable lithium electrodeposition in liquid and nanoporous solid electrolytes, *Nature Materials*, **2014**, *13*, 961.
- [3] Qian, J. F.; Henderson, W. A.; Xu, W.; Bhattacharya, P.; Engelhard, M.; Borodin, O.; Zhang, J. G., High rate and stable cycling of lithium metal anode, *Nature Communications*, **2015**, *6*.
- [4] Krause, A.; Dörfler, S.; Piwko, M.; Wisser, F. M.; Jaumann, T.; Ahrens, E.; Giebeler, L.; Althues, H.; Schädlich, S.; Grothe, J.; Jeffery, A.; Grube, M.; Brückner, J.; Martin, J.; Eckert, J.; Kaskel, S.; Mikolajick, T.; Weber, W. M., High Area Capacity Lithium-Sulfur Full-cell Battery with Prelithiated Silicon Nanowire-Carbon Anodes for Long Cycling Stability, *Scientific Reports*, **2016**, *6*, 27982.
- [5] Lu, J.; Jung Lee, Y.; Luo, X.; Chun Lau, K.; Asadi, M.; Wang, H.-H.; Brombosz, S.; Wen, J.; Zhai, D.; Chen, Z.; Miller, D. J.; Sub Jeong, Y.; Park, J.-B.; Zak Fang, Z.; Kumar, B.; Salehi-Khojin, A.; Sun, Y.-K.; Curtiss, L. A.; Amine, K., A lithium–oxygen battery based on lithium superoxide, *Nature*, **2016**, *529*, 377.
- [6] Liang, Z.; Lin, D. C.; Zhao, J.; Lu, Z. D.; Liu, Y. Y.; Liu, C.; Lu, Y. Y.; Wang, H. T.; Yan, K.; Tao, X. Y.; Cui, Y., Composite lithium metal anode by melt infusion of lithium into a 3D conducting scaffold with lithiophilic coating, *Proceedings of the National Academy of Sciences of the United States of America*, **2016**, *113*, 2862.
- [7] Maier, J., Nanoionics: ion transport and electrochemical storage in confined systems, *Nature Materials*, **2005**, *4*, 805.
- [8] Lin, D. C.; Zhuo, D.; Liu, Y. Y.; Cui, Y., All-Integrated Bifunctional Separator for Li Dendrite Detection via Novel Solution Synthesis of a Thermostable Polyimide Separator, *Journal of the American Chemical Society*, **2016**, *138*, 11044.
- [9] Sakuda, A.; Hayashi, A.; Tatsumisago, M., Sulfide Solid Electrolyte with Favorable Mechanical Property for All-Solid-State Lithium Battery, *Scientific Reports*, **2013**, *3*, 2261.
- [10] Wang, Y.; Chen, Y.; Gao, J. W.; Yoon, H. G.; Jin, L. Y.; Forsyth, M.; Dingemans, T. J.; Madsen, L. A., Highly Conductive and Thermally Stable Ion Gels with Tunable Anisotropy and Modulus, *Advanced Materials*, **2016**, *28*, 2571.
- [11] Elia, G. A.; Hassoun, J.; Kwak, W. J.; Sun, Y. K.; Scrosati, B.; Mueller, F.; Bresser, D.; Passerini, S.; Oberhumer, P.; Tsiouvaras, N.; Reiter, J., An Advanced Lithium–Air Battery Exploiting an Ionic Liquid-Based Electrolyte, *Nano Letters*, **2014**, *14*, 6572.
- [12] Armand, M.; Endres, F.; MacFarlane, D. R.; Ohno, H.; Scrosati, B., Ionic-liquid materials for the electrochemical challenges of the future, *Nature Materials*, **2009**, *8*, 621.
- [13] Lodge, T. P., Materials science - A unique platform for materials design, *Science*, **2008**, *321*, 50.

- [14] Wu, F.; Chen, N.; Chen, R. J.; Zhu, Q. Z.; Ban, J.; Li, L., "Liquid-in-Solid" and "Solid-in-Liquid" Electrolytes with High Rate Capacity and Long Cycling Life for Lithium-Ion Batteries, *Chemistry of Materials*, **2016**, 28, 848.
- [15] Lu, Y. Y.; Korf, K.; Kambe, Y.; Tu, Z. Y.; Archer, L. A., Ionic-Liquid-Nanoparticle Hybrid Electrolytes: Applications in Lithium Metal Batteries, *Angewandte Chemie-International Edition*, **2014**, 53, 488.
- [16] Ueki, T.; Watanabe, M., Macromolecules in ionic liquids: Progress, challenges, and opportunities, *Macromolecules*, **2008**, 41, 3739.
- [17] Horowitz, A. I.; Panzer, M. J., High-performance, mechanically compliant silica-based ionogels for electrical energy storage applications, *Journal of Materials Chemistry*, **2012**, 22, 16534.
- [18] Manuel Stephan, A., Review on gel polymer electrolytes for lithium batteries, *European Polymer Journal*, **2006**, 42, 21.
- [19] Lodge, T. P.; Ueki, T., Mechanically Tunable, Readily Processable Ion Gels by Self-Assembly of Block Copolymers in Ionic Liquids, *Accounts of Chemical Research*, **2016**, 49, 2107.
- [20] Zhang, S.; Ueno, K.; Dokko, K.; Watanabe, M., Recent Advances in Electrolytes for Lithium-Sulfur Batteries, *Advanced Energy Materials*, **2015**, 5.
- [21] Le Bideau, J.; Ducros, J. B.; Soudan, P.; Guyomard, D., Solid-State Electrode Materials with Ionic-Liquid Properties for Energy Storage: the Lithium Solid-State Ionic-Liquid Concept., *Advanced Functional Materials*, **2011**, 21, 4073.
- [22] Wang, S.; Hsia, B.; Carraro, C.; Maboudian, R., High-performance all solid-state micro-supercapacitor based on patterned photoresist-derived porous carbon electrodes and an ionogel electrolyte, *Journal of Materials Chemistry A*, **2014**, 2, 7997.
- [23] Li, X. W.; Li, S. J.; Zhang, Z. X.; Huang, J.; Yang, L.; Hirano, S., High-performance polymeric ionic liquid-silica hybrid ionogel electrolytes for lithium metal batteries, *Journal of Materials Chemistry A*, **2016**, 4, 13822.
- [24] Jeon, J. D.; Kwak, S. Y., Variable-temperature Li-7 solid-state NMR investigation of Li-ion mobility and its correlation with conductivity in pore-filling polymer electrolytes for secondary batteries, *Macromolecules*, **2006**, 39, 8027.
- [25] Kao, H. M.; Chang, P. C.; Chao, S. W.; Lee, C. H., Li-7 NMR, ionic conductivity and self-diffusion coefficients of lithium ion and solvent of plasticized organic-inorganic hybrid electrolyte based on PPG-PEG-PPG diamine and alkoxysilanes, *Electrochimica Acta*, **2006**, 52, 1015.
- [26] Bhattacharyya, A. J.; Dolle, M.; Maier, J., Improved Li-battery electrolytes by heterogeneous doping of nonaqueous Li-salt solutions, *Electrochemical and Solid State Letters*, **2004**, 7, A432.
- [27] Christie, A. M.; Lilley, S. J.; Staunton, E.; Andreev, Y. G.; Bruce, P. G., Increasing the conductivity of crystalline polymer electrolytes, *Nature*, **2005**, 433, 50.
- [28] MacFarlane, D. R.; Forsyth, M., Plastic crystal electrolyte materials: New perspectives on solid state ionics, *Advanced Materials*, **2001**, 13, 957.
- [29] Alarco, P. J.; Abu-Lebdeh, Y.; Armand, M., Highly conductive, organic plastic crystals based on pyrazolium imides, *Solid State Ionics*, **2004**, 175, 717.
- [30] Zhang, L.; Chaloux, B. L.; Saito, T.; Hickner, M. A.; Lutkenhaus, J. L., Ion Conduction in Poly(ethylene oxide) Ionically Assembled Complexes, *Macromolecules*, **2011**, 44, 9723.

- [31] Porcarelli, L.; Gerbaldi, C.; Bella, F.; Nair, J. R., Super Soft All-Ethylene Oxide Polymer Electrolyte for Safe All-Solid Lithium Batteries, ***Scientific Reports***, **2016**, *6*.
- [32] Matsumoto, H.; Sakaebe, H.; Tatsumi, K.; Kikuta, M.; Ishiko, E.; Kono, M., Fast cycling of Li/LiCoO₂ cell with low-viscosity ionic liquids based on bis(fluorosulfonyl)imide [FSI](-), ***Journal of Power Sources***, **2006**, *160*, 1308.
- [33] Zaghib, K.; Charest, P.; Guerfi, A.; Shim, J.; Perrier, M.; Striebel, K., Safe Li-ion polymer batteries for HEV applications, ***Journal of Power Sources***, **2004**, *134*, 124.
- [34] Basile, A.; Bhatt, A. I.; O'Mullane, A. P., Stabilizing lithium metal using ionic liquids for long-lived batteries, ***Nature Communications***, **2016**, *7*.
- [35] Yoon, H.; Best, A. S.; Forsyth, M.; MacFarlane, D. R.; Howlett, P. C., Physical properties of high Li-ion content N-propyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide based ionic liquid electrolytes, ***Physical Chemistry Chemical Physics***, **2015**, *17*, 4656.
- [36] Li, J.; Park, J. K.; Moore, R. B.; Madsen, L. A., Linear coupling of alignment with transport in a polymer electrolyte membrane, ***Nature Materials***, **2011**, *10*, 507.
- [37] Lingwood, M. D.; Zhang, Z. Y.; Kidd, B. E.; McCreary, K. B.; Hou, J. B.; Madsen, L. A., Unraveling the local energetics of transport in a polymer ion conductor, ***Chemical Communications***, **2013**, *49*, 4283.
- [38] Kaskhedikar, N.; Karatas, Y.; Cui, G.; Maier, J.; Wiemhofer, H. D., Nanocomposites based on borate esters as improved lithium-ion electrolytes, ***Journal of Materials Chemistry***, **2011**, *21*, 11838.
- [39] Zhang, Z. Y.; Madsen, L. A., Observation of separate cation and anion electrophoretic mobilities in pure ionic liquids, ***Journal of Chemical Physics***, **2014**, *140*.
- [40] Yoon, H.; Howlett, P. C.; Best, A. S.; Forsyth, M.; MacFarlane, D. R., Fast Charge/Discharge of Li Metal Batteries Using an Ionic Liquid Electrolyte, ***Journal of the Electrochemical Society***, **2013**, *160*, A1629.

Chapter 7

Summary and Future Work

7.1 Summary

This dissertation describes the development and characterization of advanced polymer electrolyte materials for next generation of energy storage and conversion devices such as batteries, fuel cells, artificial actuators and reverse osmosis membranes.

We focus on investigating an aromatic sulfonate polyelectrolyte poly (2,2'-disulfonyl-4,4'-benzidine terephthalamide) (PBDT). This rigid-rod polyelectrolyte is the molecular foundary for the ionic liquid-based gel electrolyte developed in the project. The aqueous solution of PBDT forms a lyotropic LC phase above a critical concentration $C^* = 1.2$ wt% and has high ion density along the polymer backbone. We employ pulsed-field-gradient (PFG) NMR diffusometry, ^2H NMR spectroscopy, polarized optical microscopy, and small-angle X-ray scattering to determine relationships between counterion transport, dynamic coupling of water, and molecular alignment in aqueous solutions of PBDT. These studies promise to open new pathways to understanding a range of anisotropic polymer systems including aligned polymer electrolyte membranes, wood composites, aligned hydrogels, liquid crystals and stretched elastomers.

From the perspective of molecular configuration and liquid crystalline structure, we further propose that PBDT elaborately possesses a double helical conformation as similar to DNA molecules. The demonstration is based on a complementary investigation of X-ray diffraction, ^{23}Na NMR, and molecular dynamics simulation. This double helical structure endows the unique properties of PBDT aqueous solutions that can be employed to design versatile materials.

As the main achievement in this research project, we primarily develop an ionic liquid-based polymer gel electrolyte that possesses following exceptional combination of properties: transport anisotropy up to 3.5x, high ionic conductivity transport anisotropy up to 3.5x, high ionic conductivity (up to 8 mS cm⁻¹), widely tunable modulus (0.03 – 3 GPa) and high thermal stability (up to 300°C). This material is formed by combining an ionic liquid with PBDT aqueous solution in the presence of a magnetic (**B**) field. Based on this unique combination of component precursors, this material not only breaks the usual tradeoff between ionic conductivity and modulus, but also provides controllable macroscopic alignment in the as-formed ion gels.

Furthermore, in order to investigate the real performance of the developed gel electrolyte, we test its corresponding electrochemical properties by assembling the electrolytes in Li symmetric coin cells. Use of Li metal in battery anodes has been investigated for several decades, but has not found practical use because of low coulombic efficiency and dendrite growth on the Li metal surface along with limited battery cycle life. This ionic liquid-based solid state electrolyte possesses high ionic conductivity and excellent thermal stability while maintaining enough modulus to suppress the unfavorable Li dendrite growth. We observe stable cycling of this gel electrolyte at current density $\leq 1\text{mA cm}^{-2}$, which is rarely reported for previous solid-state electrolytes. By tuning the modulus and the Li salt concentration in the gel electrolytes, we conclude that the deposition of Li metal is closely correlated with the modulus of the gel electrolyte. In addition, we further demonstrate a new fabrication method to obtain ultrathin ($\sim 100\text{ }\mu\text{m}$) gel electrolyte membrane with controllable thickness and smooth surface that showing promise for more practical applications in electrochemical devices.

7.2 Future Work

We have talked about fabrication and characterization of this new class of PBDT ion gel electrolytes. However, the real mechanism hidden behind the gel formation has not been fully investigated. The gel forming mechanism is essential for developing more other gel materials. By elaborately selecting the precursor polymer solutions as well as the type of ionic liquid, we can achieve more functionality in the resulted polymer electrolytes. Meanwhile, the investigation of ion association, polymer chain conformation and dynamic coupling in the polymeric systems is also critical to develop more advanced materials with comprehensive and tunable properties.

Based on the investigation of this newly developed PBDT ion gel electrolytes, we believe that it is highly possible to apply these solid-state gel electrolytes in next-generation Li batteries. Beforehand, we still require substantial testing and modification to better fit this system into some commercialized products.

In addition to the gel forming mechanism and the potential application in battery fields, it is also desirable and valuable for us to discover many other applications for this gel electrolyte, such as mechanical actuators, fuel cell membranes and reverse osmosis membranes. This unique platform by combining ionic liquid and polyelectrolyte is promising for us to develop more advanced materials that can be fit in more energy storage and conversion devices.