

Investigation of Phase-Separated Polymeric Materials via X-ray Scattering Techniques

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Abstract

This dissertation presents a discussion of a variety of polymeric materials and their characterization via ultra-small, small, and wide-angle X-ray scattering methods (USAXS/SAXS/WAXS). Specifically, these experimental techniques are employed to investigate the phase separated morphologies that impart unique properties to each class of materials and allow for their use in advanced applications. It is crucial that the morphologies of polymeric materials are thoroughly characterized so that robust structure-property-processing relationships can be constructed. Chapter 2 of this dissertation discusses the fundamental principles of X-ray scattering, which form the basis for more complex experiments discussed throughout this dissertation. While historical, these foundational concepts of X-ray scattering are critical to highlight, due to instruments become increasingly more accessible and user-friendly. In Chapter 3, the origins of X-ray scattering in ion-containing polymers are discussed as it pertains to their unique hydrophilic/hydrophobic phase separated morphologies. These morphologies are becoming increasingly important to understand as ion-containing polymers increase in their commercial use. Chapter 4 discusses the use of USAXS experiments to understand the droplet size distributions of a filler in a polymer matrix and reveals that the liquid droplets in these composites can uniquely change size depending on their volume fraction in the composite. Chapter 5 discusses the use of SAXS and WAXS experiments to investigate the morphology of proton exchange membranes in hydrogen fuel cells. Ultimately, the results from X-ray scattering experiments provide strong evidence that

commercial polymers used to make these membranes can mix at the molecular level to form robust membranes. Chapter 6 presents the application of SAXS and WAXS experiments to probe morphologies of 3D-printed polyimide materials. Using a combination of scattering, microscopy, and computational methods, the differences between two chemical variants could be understood, and the origins of void formation were uncovered. Finally, in the Chapter 7 of this dissertation, a selection of other polymeric systems were studied via X-ray scattering methods. Since most of the work presented in this dissertation was collected on a laboratory scale instrument, these experiments display the capability of benchtop instruments to characterize a range of different materials without the need to access a beamline.

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General Audience Abstract

All plastics are polymers, and the term ‘polymer’ is defined as ‘many parts or segments.’ A single polymer is a long molecule consisting of multiple, repeating subunits known as ‘monomers’ which are defined as ‘single units.’ Many polymeric materials exhibit a phase separated morphology, meaning that certain regions of the material can become spatially separated from other parts of the material, like oil and water. This phenomenon gives many types of plastic their unique properties. In Chapter 4 of this dissertation, a soft polymer is blended with small droplets of metal, and the phase separation of the metal from the polymer provides the material with simultaneous electrical conductivity and flexibility. In Chapter 5 of this dissertation, polymer membranes are discussed for applications in clean energy technologies, and the phase separated structure of the membrane is responsible for the membrane’s ability to transport protons. In Chapter 6, strong and temperature resistant materials are discussed and again, their properties in part are traced back to phase separation within the material, in this case through the presence of crystallinity. In Chapter 7, the phase separation phenomena of many materials classes are explored, ranging from aerospace plastics to fibers to biological polymers.

While there are many ways to study the phase separated structures of polymeric materials, one of the best techniques involves using X-rays. X-rays are a form of electromagnetic radiation, like sunlight, but much have a much higher energy. X-rays can interact with materials based on the internal composition and structure of the material,

which many may be familiar with from medical imaging. In this case, X-rays can help produce an image of one's hand, revealing the internal structure of the body. In addition to absorbing or passing through materials, like one's hand, X-rays can also be scattered by materials, and X-ray scattering is the method that is used in this dissertation to study the internal structure of the materials on length scales smaller than the width of a human hair. Ultimately, throughout this dissertation, the power of X-ray scattering experiments is revealed as the experiments help provide information on many different phase separated polymeric materials. This improved understanding of materials at small length scales can help improve the design, processing, and performance of plastic materials in fields ranging from flexible electronics to clean energy membranes to aerospace materials.

*In loving memory of my late brother-in-law, Dylan L. Hensley, and my late grandpa,
“Papa” James Allen Swaim. I carry with me the precious memories of our time together
on this Earth and look forward to the day we are reunited.*

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List of Abbreviations

AFM	atomic force microscope/microscopy
AgBeh	silver behenate
APS	Advanced Photon Source
aPS	atactic polystyrene
CNC	cellulose nanocrystal
DMA	dynamic mechanical analysis
DNA	deoxyribosenucleic acid
DPA	diphenylacetone
DSC	differential scanning calorimetry
EGaIn	eutectic gallium indium
ENCC	electrosterically stabilized nanocellulose crystals
EPDM	ethylene-propylene-diene monomer
ESAXS	extra-small angle X-ray scattering
EW	equivalent weight
FIB	focused ion beam
FWHM	full width at half max
GaInSn	Galinstan
GI	grazing incidence
GnP	graphene nanoplatelets
HCH	hybrid copper halide
HOF	Herman's orientation factor
Hz	Hertz

ICTAS	Institute for Critical Technology and Applied Science
IPN	interpenetrating network
LaB ₆	lanthanum hexaboride
LLDPE	linear low density polyethylene
LM	liquid metal
LSC	long sidechain
NIST	National Institute of Standards and Technology
NSF	National Science Foundation
MCL	Materials Characterization Laboratory
MC	Monte Carlo
NaCl	sodium chloride
NMR	nuclear magnetic resonance
NVP	N-vinylpyrrolidone
PDMS	poly(dimethyl siloxane)
PEEK	poly(ether ether ketone)
PEI	poly(ether imide)
PEKK	poly(ether ketone ketone)
PFSI	perfluorosulfonate ionomer
PFSA	perfluorosulfonic acid
PPS	poly (phenylene sulfide)
PS	polysalt
PTFE	poly(tetrafluoroethylene)
rGO	randomly mixed graphene oxide

RH	relative humidity
RRM	region of restricted mobility
SANS	small-angle neutron scattering
SAXS	small-angle X-ray scattering
SALLS	small-angle laser light scattering
SEM	scanning electron microscope/microscopy
SLD	scattering length density
sPS	syndiotactic polystyrene
TEM	transmission electron microscope/microscopy
TFE	tetrafluoroethylene
TGA	thermogravimetric analysis
TIPS	thermally induced phase separation
TPU	thermoplastic polyurethane
UHMWPE	ultra-high molecular weight polyethylene
USAXS	ultra-small angle X-ray scattering
UV	ultraviolet
VP	vat photopolymerization
WAXS	wide-angle x-ray scattering

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Chapter 1. Introduction

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1.1 Dissertation Overview

This dissertation details the characterization of phase separated polymeric materials using ultra-small, small, and wide-angle X-ray scattering experimental techniques (USAXS/SAXS/WAXS). Though broadly defined, phase separation encompasses many different morphologies of polymeric materials, with examples including crystallinity, porosity, nanofillers, and ion-conducting channels. While there are many ways to characterize phase separation processes, X-ray scattering techniques remain among the best experiments to access the nanometer length scales involved. In **Chapter 2** of this dissertation, the fundamental principles of X-rays are discussed, along with how they are used in common experiments. **Chapter 2** provides a practical guide to X-ray scattering experiments, based on fundamental principles, which can support new users who seek to use X-ray scattering techniques to characterize their own systems. The key features of materials that are required to successfully conduct X-ray scattering experiments are discussed. Finally, X-ray scattering techniques are compared with other commonly utilized experimental techniques that probe similar length scales.

In **Chapter 3**, a historical understanding of scattering by a unique class of phase separated polymers known as ionomers is discussed. Ion-containing polymers (i.e., ionomers) exhibit nanoscale phase due to the polarity differences between their

hydrophilic, acidic sidechains and their hydrophobic, perfluorinated polymer backbones. Their phase separated morphology leads to a remarkable capacity to conduct protons, making them a central component in sustainable energy technologies such as hydrogen fuel cell vehicles. In **Chapter 3**, the fundamentals of X-ray scattering of ionomers are discussed, including the origin of the signature SAXS “ionomer peak” observed in countless scattering profiles of ionomers. Finally, theories on the origins of scattering at ultra-small angles are discussed, which could yield additional insights into the hierarchical morphologies of ionomers.

In **Chapter 4**, a class of phase separated materials known liquid metal nanocomposites is studied using USAXS experiments for the first time. In this work, characterizing the ultra-small angle scattering profile was necessary to study the composite morphology, as the droplet sizes were greater than 100 nanometers and thus outside of the conventional SAXS range. In alignment with the work discussed in **Chapter 3**, these results highlight the importance of investigating the origins of scattering at ultra-small angles when experimentally possible. In **Chapter 4**, the droplet size distributions of liquid metal in a PDMS matrix were characterized as a function of the volume fraction of liquid filler using several size distribution methods from the USAXS data, along with complementary size distribution from scanning electron microscopy image analysis. This study was the first study to characterize the droplet sizes within liquid metal composites via X-ray scattering and showed that the droplet size could increase from the original size when they are incorporated into PDMS.

In **Chapter 5**, SAXS and WAXS experiments are used to characterize the morphology of commercial ionomer blends. This chapter presents the first comprehensive

study of integrated membranes consisting of two different commercial perfluorosulfonic acid (PFSA) ionomers and the relationships between the blend composition, the morphologies, and the physical properties of the membranes. Small and wide-angle X-ray scattering experiments were crucial to these studies; They confirmed that the hydrophilic and hydrophobic phases within the phase separated morphology of the membrane consisted of both PFSA, as the dimensions of these domains followed strict rule-of-mixtures properties. This work has direct industrial impacts as it demonstrates that commercial PFSA products can be blended into a robust integrated membrane which will be necessary when recycling PFSA waste from mixed streams. This chapter demonstrated the power of SAXS techniques to ascertain very small dimensional changes (less than 1 nanometer) in the domain sizes of the phase separated morphologies of polymeric materials.

In **Chapter 6**, SAXS and WAXS techniques are used to systematically study additively manufactured polyimide precursors for the first time. Polyimides possess a unique phase separated morphology consisting of chain-extended polyimide crystallites due to the rigid polymer backbone. While this crystalline morphology gives polyimides their important properties, little is known about how this morphology differs between 2D polyimide films and polyimides prepared from additively manufactured precursors. In this study, additively manufactured polyimides from two structural variants are discussed: the conventional pyromellitic dianhydride/4,4'-oxydianiline (PMDA/ODA) polyimide and a more recently reported variant, PMDA/4,4'-diaminodiphenyl sulfone (PMDA/DDS). SAXS experiments were critical in understanding the formation of porosity in the additively manufactured materials that formed during post-processing,

which correspond to excess scattering at small angles. In-depth computational modelling studies helped explain these observations on the basis of differences between interaction energies between polymer strands. **Chapter 6** will help inform future research efforts to optimize the post-processing and synthetic design of new polyimides for additive manufacturing.

Chapter 7 presents the discussion of many other collaborative studies where X-ray scattering was used to characterize phase separated morphologies. These studies include semicrystalline blocky copolymers, biologically engineered plastics, and high-performance thermoplastics, among others. A variety of experimental techniques are utilized, including grazing-incidence X-ray scattering, hydrated SAXS experiments, and experiments on very small samples (ca. 2 mm). These studies further highlight the wide applicability of X-ray scattering experiments to characterize phase separated morphologies of polymeric materials.

Chapter 2. X-ray Scattering Methods and Theory

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2.1 An introduction to X-rays

2.1.1 Historical description and applications of X-rays

X-rays are a high-energy form of electromagnetic radiation discovered by German physicist and professor Wilhelm Conrad Röntgen in 1895.¹ To appreciate the value of X-rays for modern scientific experiments, it is useful to provide a historical context for their discovery and applications. Röntgen made his discovery of X-rays by experimenting in his laboratory with electrical currents in vacuum tubes. Specifically, Röntgen was working with a Crookes tube, a glass tube evacuated to low pressure. Inside the tube were two electrodes, a cathode and an anode, between which Röntgen applied a large voltage. The aim of his experiment was to determine if additional radiation was escaping the tube,¹ as previous researchers had primarily focused on what was occurring inside of the tube. To answer his scientific question, Röntgen covered the Crookes tube with black cardboard to block visible light from escaping, thus isolating visible radiation, and subsequently applied the voltage across the electrodes. While working in his dark laboratory one night, Röntgen noticed that a nearby screen coated with barium platinocyanide began to glow despite the tube being covered. This observation led Röntgen to hypothesize that

these rays, while invisible to the human eye, could escape the tube and cause the screen to fluoresce.

Six years later, Röntgen was awarded the first Nobel Prize in physics in 1901 “in recognition of the extraordinary services he has rendered by the discovery of the remarkable rays subsequently named after him.” X-rays rapidly attracted significant interest due to their applications in imaging the internal structure of objects. Results from one of the earliest experiments utilizing these rays are shown in **Figure 2.1**, where the X-ray image plate revealing the hand of Röntgen’s wife, Bertha’s is shown. From this early experiment, an astounding discovery was made. This previously unreported form of radiation produced an image where skin, ligaments and tendons appeared light, whereas Bertha’s bones and metal ring appeared dark. Röntgen named this form of radiation “X” due to the unknown nature of them, and published his results in 1896 in a paper titled “On a New Kind of Rays.”² Interestingly, Röntgen noted in his paper that the image from “lead glass is much more opaque than glass free from lead,” and that “the density of the bodies is the property whose variation mainly affects their permeability.”² More than a century later, X-rays remain at the heart of experiments to study density variations in materials, and lead continues to serve as a primary shielding material due its high absorption of X-rays.



Figure 2.1. A radiograph revealing the hand and ring of Anna Bertha Rongten, titled “Hand mit Ringen.” Image from the Countway Library, Harvard University (Onview item no. 6414).³

Early uses of X-rays were primarily focused on medical imaging applications due to the ability to capture images (i.e., radiographs) of the internal composition of a patient’s body. Even today, this use of X-rays is the most known by the public. A common misconception among first-time X-ray scattering users is that X-ray scattering experiments produce a direct “image” of a sample, akin to medical X-ray imaging. It is therefore important to make a distinction between the nature of X-ray experiments for imaging and scattering applications. Medical X-ray imaging, called radiography, produces direct images of a material by leveraging the differential absorption X-rays by matter. In other words, X-ray radiography is a spatially-resolved transmission measurement that generates a direct image of a material, where the resulting image

contrast depends on the extent of X-ray *absorption*. In contrast, X-ray scattering experiments provide indirect results in reciprocal space, based on how the X-rays are *scattered* by the material.

As X-ray use in medical imaging rapidly advanced, scientists began to utilize X-rays in experiments to study matter at the atomic scale which would eventually form the field of X-ray crystallography and X-ray scattering. While the field of crystallography had already existed prior to the discovery of X-rays, scientific investigations primarily focused on the visible symmetry and optical properties of crystals. Before 1912, there was no direct experimental method to probe the internal arrangement of atoms within crystals. According to Wim H. De Ju in “Basic X-ray Scattering for Soft Matter,” early discussions between Paul Peter Ewald and Max von Laue brought on the idea that crystals could act as a three-dimensional diffraction grating for electromagnetic radiation, similar to optical gratings.¹ The initial experiments to diffract visible light with crystals were unsuccessful due to the mismatch between optical wavelengths and the length scales of periodicity of atoms of the crystals. This initial failure led Laue to hypothesize that X-rays might be more appropriate, as he speculated that the shorter wavelength of X-rays would match the periodic dimensions within crystals. This concept, that the wavelength of electromagnetic radiation must align with the length scale of investigation, was novel at the time, and remains a central concept in choosing appropriate materials characterization technique based on the size scale of interest, as will be discussed later (Section 2.4.2).

In 1912, Max von Laue and his colleagues Walter Friedrich and Paul Kipping generated the first X-ray crystallographic image by conducting an experiment with a

copper sulfate crystal, shown in **Figure 2.2**.^{1, 4} By passing a polychromatic beam of X-rays through the crystal, diffraction “spots” were recorded on the photographic plate placed on the other side of the sample.¹ This simple experiment ultimately provided concrete evidence to Laue’s hypotheses that X-rays behave as waves and that crystals have a periodic structure that can diffract the X-rays.¹ In 1914, Max von Laue was awarded the Nobel Prize in Physics “for his discovery of the diffraction of X-rays by crystals.”

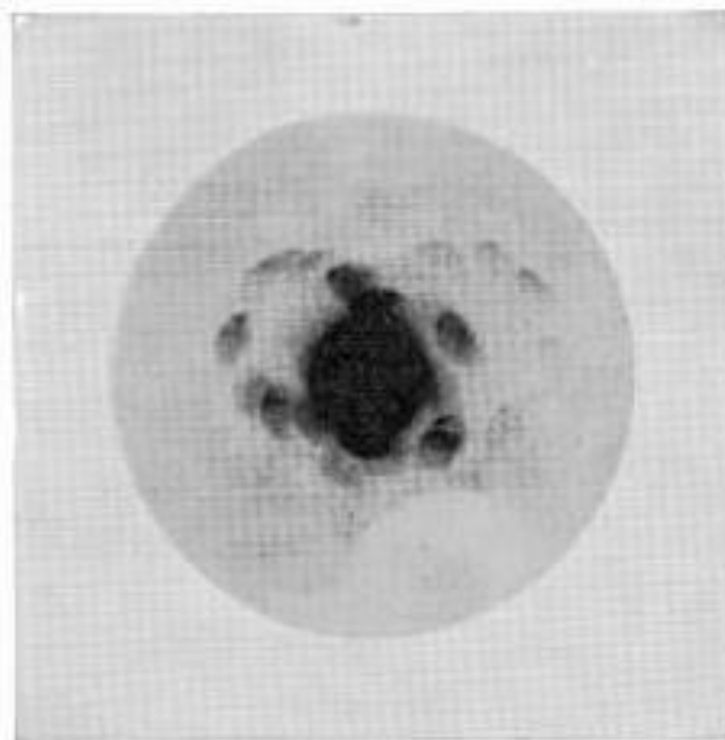


Figure 2.2. X-ray diffraction pattern of a copper sulfate crystal obtained by Max von Laue. Picture obtained from ref. 4.⁴

In 1915, Sir William Henry Bragg and his son William Lawrence Bragg shared the Nobel Prize in Physics award “for their services in the analysis of crystal structure by

means of X-rays.” Building on Laue’s findings that crystals can diffract X-rays, the Braggs developed a practical framework for interpreting X-ray diffraction patterns. Their key finding, first reported in their 1913 paper “The reflection of X-rays by crystals,”⁵ was a relationship they constructed that relates the angle that X-rays are diffracted by the crystal to the real-space dimensions within the crystal, commonly known as “Bragg’s Law” (Equation 2.1):

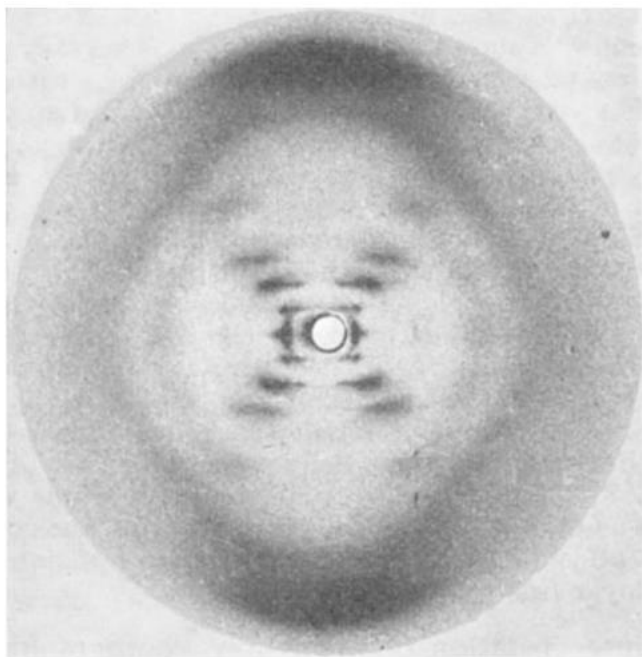
$$n\lambda = 2d\sin(\theta) \quad (2.1)$$

where n is the order, λ is the X-ray wavelength, d is the interplanar spacing, and 2θ is the angle between the incident beam and the diffraction spot (i.e., the diffraction angle). This relationship made it possible to calculate interplanar dimensions directly from diffraction patterns and will be discussed in mathematical and geometric detail in Section 2.2.3.

From Bragg’s Law expressed in Equation 1, it can be seen that the correct interpretation of the relationship between the scattering angle and the interplanar spacing requires control over and knowledge of the X-ray wavelength. This is an important concept because it directly influences the relationship between the diffraction angle and the real-space dimension resulting in the diffraction peak. Interestingly, in the Braggs’ original paper,⁵ the X-ray wavelength was not directly measured. Rather, the Braggs purposely used crystals with lattice parameters determined through other experimental techniques (goniometry and density) to back-calculate the X-ray wavelengths. By using a crystal of “rock-salt” (i.e., NaCl), which possessed a suspected cubic crystallographic structure, the Braggs designed an experiment that involved collecting the X-ray diffraction pattern as a function of the position of the crystal. As stated in their paper,

“Rays of a definite quality are reflected from a crystal when, and only when, the crystal is set at the right angle.” This was the first experiment that definitively proved that Bragg’s Law must be satisfied in order to observe diffraction and confirmed the fundamental link between the diffraction angle, the X-ray wavelength, and the real-space dimension d . In contrast to early X-ray diffraction experiments, modern X-ray instrumentation, including both lab and synchrotron sources, utilizes X-rays with wavelengths that are almost always known *a priori*.

Much of the early X-ray crystallography history is focused on studying inorganic crystals. X-ray diffraction methods were subsequently applied to macromolecules. A notable example is the investigation of the structure of sodium deoxyribose nucleate (DNA) (**Figure 2.3**) by Rosalind Franklin and Maurice Wilkins in 1953, which confirmed the double helix nature of DNA and accelerated the field of molecular biology. Other biomacromolecules, such as cellulose and natural rubber, were the focus of many of the early experiments utilizing X-rays to characterize the structure of polymers. The crystalline structure of synthetic polymers such as Nylon, polyethylene, and polyesters was also investigated, and the number of characterized polymers continued to increase with the development of polymer synthetic chemistry. This brief historical summary of X-rays experiments demonstrates the versatility of X-rays in scientific experiments for over 100 years and highlights the immense progress that has been made in the field since their discovery in 1895.



Sodium deoxyribose nucleate from calf thymus. Structure *B*

Figure 2.3. Diffraction pattern reported by Rosalind Franklin and Raymond Gosling. Reprinted with permission from Springer Nature.⁶

As described in “Basic X-ray Scattering for Soft Matter,” the important distinction between X-ray scattering and diffraction must be made. X-ray scattering and X-ray diffraction instruments share similar concepts (X-ray source, sample stage, and detector) but differ in configuration. A general schematic of a small-angle X-ray scattering experiment is shown in **Figure 2.4**. X-rays are generated at an X-ray source, and a monochromatic X-ray beam with wavelength λ encounters the sample. The heterogeneities in electron density within the material results in scattering of the X-rays at an angle, 2θ , relative to the incident beam. The scattered X-rays are collected on a 2D area detector. The magnitude of the scattering vector, q , is equal to the difference of the wavevector transfer between the transmitted and the incident beam. The scattering vector

q serves as the ruler on the detector for the reciprocal space distance that is probed through the scattering technique.

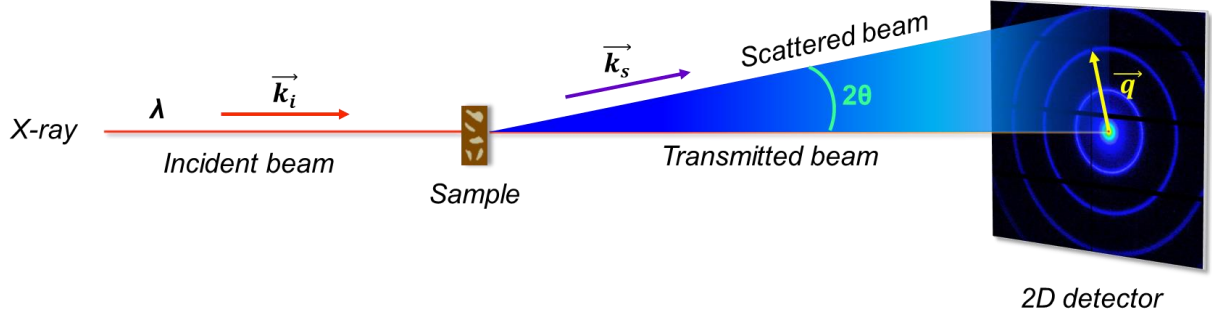


Figure 2.4. Schematic diagram showing the basic components of an X-ray scattering experiment.

The scattering vector q is defined by Equation 2.2, which shows that the scattering vector is dependent on the scattering angle, and the X-ray wavelength.

$$q = \frac{4\pi}{\lambda} \sin\left(\frac{2\theta}{2}\right) \quad (2.2)$$

For a first-order scattering feature ($n = 1$), Equations 2.1 and 2.2 can be simplified to yield Equation 2.3, which is a special case of Bragg's law that defines the relationship between the scattering vector and the real space dimension:

$$q = \frac{2\pi}{d} \quad (2.3)$$

2.1.2 Fundamental properties of X-rays

Like all forms of electromagnetic radiation, X-rays exhibit wave-particle duality. X-rays can be described as both waves and particles (photons), exhibiting behavior characteristic of both. Different models and interpretations of X-ray scattering data will leverage these two classifications. First, X-rays can be described as waves with a

wavelength that ranges from 0.01 nm to 10 nm. X-rays can also be described as photons with discrete energy pockets of energy, represented by the equation $E = h\nu$, where E is the energy of the photon energy, h is Planck's constant, equal to 6.62×10^{-34} J/Hz or 4.136×10^{-15} eV/Hz, and ν is the frequency (Hz or 1/s). The typical energy range of X-rays ranges from 0.1 to 100 keV.

2.1.3 Flux and differential scattering cross section

Before discussing scattering and diffraction phenomenon, it is also useful to define the properties of X-ray beams. The flux of scattered X-rays generally describes the “strength” of an X-ray beam. More specifically, when treating X-rays as waves, flux describes the energy that is transmitted per unit area per unit time.⁷ However, flux can also be described by treating X-rays as particles, and therefore can be defined by the number of X-ray particles/photons passing through a unit area per unit time.

In **Figure 2.5**, an example of an X-ray diffraction experiment is shown. The detector is placed at a distance from the sample. The incident X-ray beam interacts with the sample, causing scattering at an angle 2θ relative to the incident beam as a spherical wave. The solid angle Ω defines the angle over which the scattered X-rays are detected.

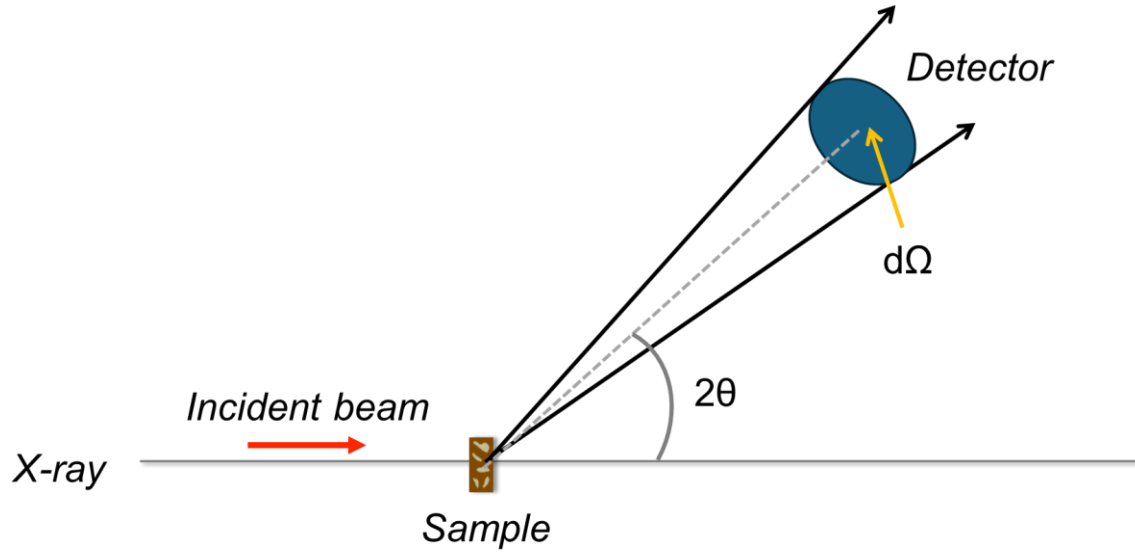


Figure 2.5. Schematic drawing of a simple scattering geometry. The scattering angle is given by 2θ and the solid angle is given by Ω . Adapted with permission from Oxford University Press.

The differential scattering cross section, also called the intensity of scattered X-rays, is defined by the following Equation:

$$\frac{d\sigma}{d\Omega} = \frac{J}{J_0} \quad (2.4)$$

where J is the flux spherical wave and J_0 is the flux incident plane wave. Understanding how the morphology of a material can be inferred from the measured scattering intensity (differential scattering cross-section) is at the heart of X-ray scattering experiments.

2.2 Interaction mechanisms

2.2.1 Scattering vs. diffraction

As described in Ryong-Joon Roe's "*Methods of X-Ray and Neutron Scattering in Polymer Science*," two phenomena occur when an X-ray interacts with matter:⁷

- 1) X-rays are scattered by electrons in the material (i.e., scattering)
- 2) The scattered waves interfere with one another (i.e., diffraction)

This naturally leads to the important distinction between the physical phenomena of scattering and diffraction, which will be made throughout the rest of this dissertation. The precise definition of scattering is the initial event that occurs as a result of the interactions between the X-rays and atoms within matter.⁷ In the secondary event, termed diffraction, the resulting X-rays that are scattered via the primary interactions constructively interfere with each other to produce an intensity of scattered X-rays at specific angular locations, giving rise to diffraction peaks collected onto the detector. Simple examples of the scattering and diffraction events are discussed below in Section 2.2.2 and Section 2.2.3, respectively.

Although the terms possess a clear distinction in formal definition, it is important to discuss the terms 'diffraction' and 'scattering' as it pertains to experiments. X-ray scattering experiments (i.e., SAXS and WAXS) correctly refer to experiments which yield diffuse scattering profiles. In contrast, X-ray diffraction experiments (i.e., WAXD) correctly refer to experiments yielding diffraction peaks, like those associated with crystalline reflections. Similarly, diffraction and scattering instrumentation are distinct. X-ray diffraction instrumentation, such as a powder X-ray diffractometer, possess a short

sample-to-detector distance and often a sample stage capable of rotating the sample which is commonly used to align the crystalline planes with the beam. In contrast, X-ray scattering instrumentation, such as the Xenocs Xeuss 3.0 SAXS/WAXS, possesses a much longer sample-to-detector distance to accommodate for the SAXS experiments, and the sample stage generally cannot be rotated to align the crystal planes with the beam. Crystalline materials characterized on a scattering instrument present a grey area, so they can be termed WAXS/WAXD experiments to reflect that a diffraction pattern was collected on a scattering instrument.

2.2.2 Classical scattering from a single electron

To understand the interactions of X-rays with matter comprised of many atoms with potentially varying elemental compositions, it is useful to first consider the mechanism of an X-ray interacting with a single free electron. The classical scattering of an X-ray is known as Thomson scattering and can be summarized as follows. As discussed previously, X-rays, like all electromagnetic radiation, can be represented as waves with an oscillating magnetic and electric field. The electric field interacts with the electrical charge of the free electron, exerting a force and resulting in acceleration of the electron. The accelerating electron radiates energy, and the resulting angular-dependent intensity is termed the Thomson differential scattering cross section. The Thomson scattering equation describes this classical scattering scenario and forms the basis for more complex scattering behavior of multi-electron systems. A derivation of this behavior is presented below.

This derivation will consider an incident X-ray that propagates along a single axis at an angular frequency ω towards a single free electron. Specifically, consider that the

incident X-ray propagates along the X-axis, where the electric field component is randomly polarized in the YZ-plane, as shown in **Figure 2.6**.⁷ Thomson scattering exclusively involves the interactions of the electron with the electric field component of the wave, therefore the magnetic component is neglected. The magnitude of the electric field of the incident wave can be defined as E_0 . Since the wave is located in the YZ-plane, the magnitude E_0 is comprised of components from both the Y and Z directions, as shown in Equation 2.5:

$$E_0^2 = E_{0y}^2 + E_{0z}^2 \quad (2.5)$$

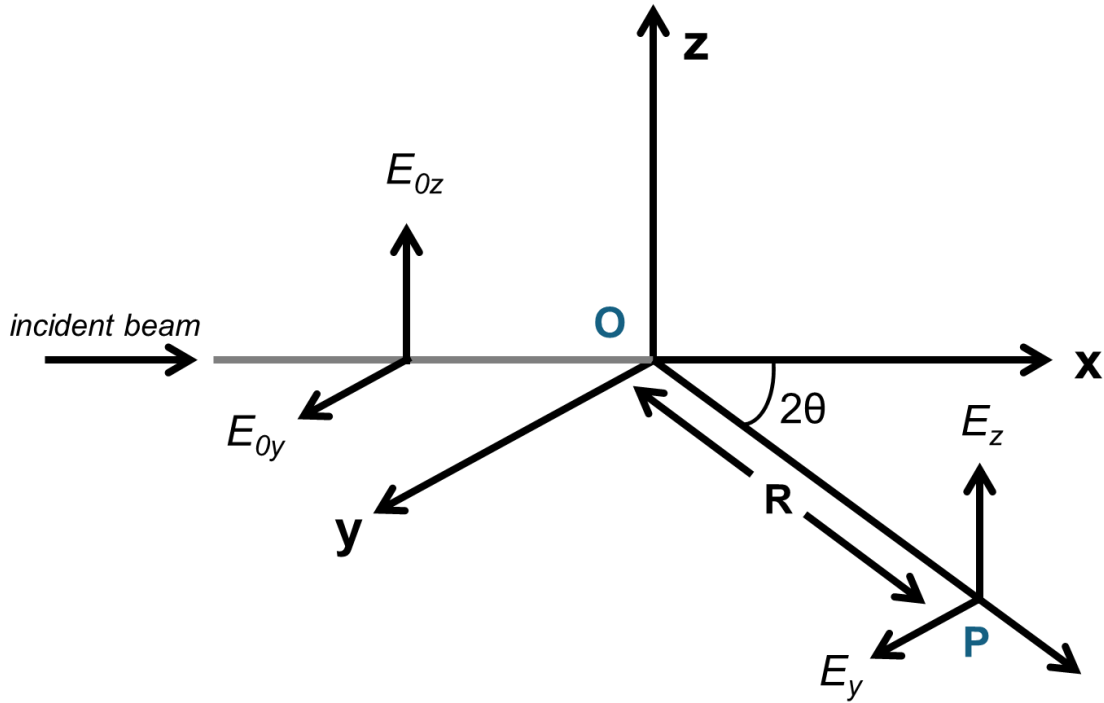


Figure 2.6. Schematic drawing showing an X-ray whose electric field component is located in the YZ-plane. A single, free electron is located at the origin (point O), and the

observation point is designated by point P. The scattering angle is denoted by 2θ . The distance between the position of the electron and the observation point P is given by R.

The oscillatory nature of the electric field component is apparent in Equation 2.6:

$$E(t) = E_0 \cos(\omega t) \quad (2.6)$$

The single, free electron, originally located at the origin (point O, **Figure 6**), experiences a force from the electromagnetic component of the incident wave. According to Newton's second law of motion ($F=ma$), the exerted force is termed the Lorentz force (Equation 2.7):

$$F = -eE_0 \cos(\omega t) \quad (2.7)$$

where F is the force, e is the magnitude of the charge of an electron, equal to 1.602×10^{-19} C, and E_0 is the magnitude of the electric field vector. The force imposed by the X-ray on the electron causes the electron to accelerate and oscillate at the same frequency as the incident X-ray, and by substituting it into Newton's second law, this acceleration as a function of time is given by Equation 2.8:

$$a(t) = -\frac{e}{m} E_0 \cos(\omega t) \quad (2.8)$$

The resulting magnitude of the electric field vector resulting from the accelerating electron now located at point P can be calculated using Equation 2.9:

$$E_y = E_{0y} \frac{e^2}{m_e c^2} \frac{\cos(\omega t)}{R} \quad (2.9)$$

where m_e is the mass of an electron, equal to 9.1×10^{-31} kg, R is the distance from the free electron at point O to the observation point P, and c is the speed of light. The Z-component of the electric field is given by Equation 2.10:

$$E_z = E_{0z} \frac{e^2}{m_e c^2} \frac{\cos(2\theta)}{R} \cos(\omega t) \quad (2.10)$$

For an unpolarized incident X-ray beam, the following relationship holds (Equation 2.11):

$$\langle E_{0y}^2 \rangle = \langle E_{0z}^2 \rangle = \frac{1}{2} E_0^2 \quad (2.11)$$

Therefore, this relationship yields the following flux at observation point P, which depends on the observation distance R and the scattering angle 2θ (Equation 2.12):

$$J_e = J_0 \left(\frac{e^2}{m_e c^2} \right)^2 \left(\frac{1}{R^2} \right) \left(\frac{1 + \cos^2(2\theta)}{2} \right) \quad (2.12)$$

Equation 1.10 reveals that the flux decreases with the inverse of the observation distance squared. Practically, this relationship is consistent with experimental observations regarding the intensity of X-rays collected via SAXS vs. WAXS experiments: SAXS experiments, with a longer sample-to-detector distance (observation distance), yield less intense raw scattering patterns per pixel compared to WAXS experiments with shorter observation distances. However, instruments such as the Xenocs Xeuss 3.0 SAXS/WAXS commonly correct for this geometric effect automatically during data processing.

The classical radius of an electron, r_e , is defined by Equation 2.13 below,

$$r_e = \frac{e^2}{m_e c^2} = 2.818 \times 10^{-15} \text{ m} \quad (2.13)$$

The Thomson differential scattering cross-section for a single electron is given by Equation 2.14:

$$\left(\frac{d\sigma}{d\Omega}\right)_e = r_e^2 \left(\frac{1 + \cos^2(2\theta)}{2}\right) \quad (2.14)$$

By integrating Equation 2.14, the total scattering cross section of an electron is represented by Equation 2.15:

$$\sigma_e = \frac{8}{3} \pi r_e^2 \quad (2.15)$$

The scattering length of an electron by an unpolarized X-ray is therefore dependent on the scattering angle 2θ and is equal to the term shown in Equation 2.16:

$$b_e(2\theta) = r_e \left(\frac{1 + \cos^2(2\theta)}{2} \right)^{\frac{1}{2}} \quad (2.16)$$

In summary, this derivation shows that the electron is the building block for X-ray scattering experiments and describes how the electric field component of the incident wave interacts with an electron. The classical electron radius r_e is defined, which will be utilized in Section 2.4.3 to calculate the scattering length density and contrast within a phase-separated material.

2.2.3 Diffraction and Bragg's Law

The primary scattering of X-rays by electrons in the system has been discussed in Section 2.2.2. In the current section, a discussion will be presented on how those scattered waves combine with one another. This phenomenon is important because, as mentioned previously, the scattering profiles observed in scattering/diffraction experiments are not simply the sum of the individual scattering of all electrons. Rather, the scattering intensity also depends on how the resulting scattered X-rays combine with one another in a process called *interference*.

Bragg's Law, which has been previously described above through a historical lens (Equation 1), defines the geometric and mathematical constraints for constructive interference of scattered X-ray waves and is derived below using the drawing in **Figure 2.7**.

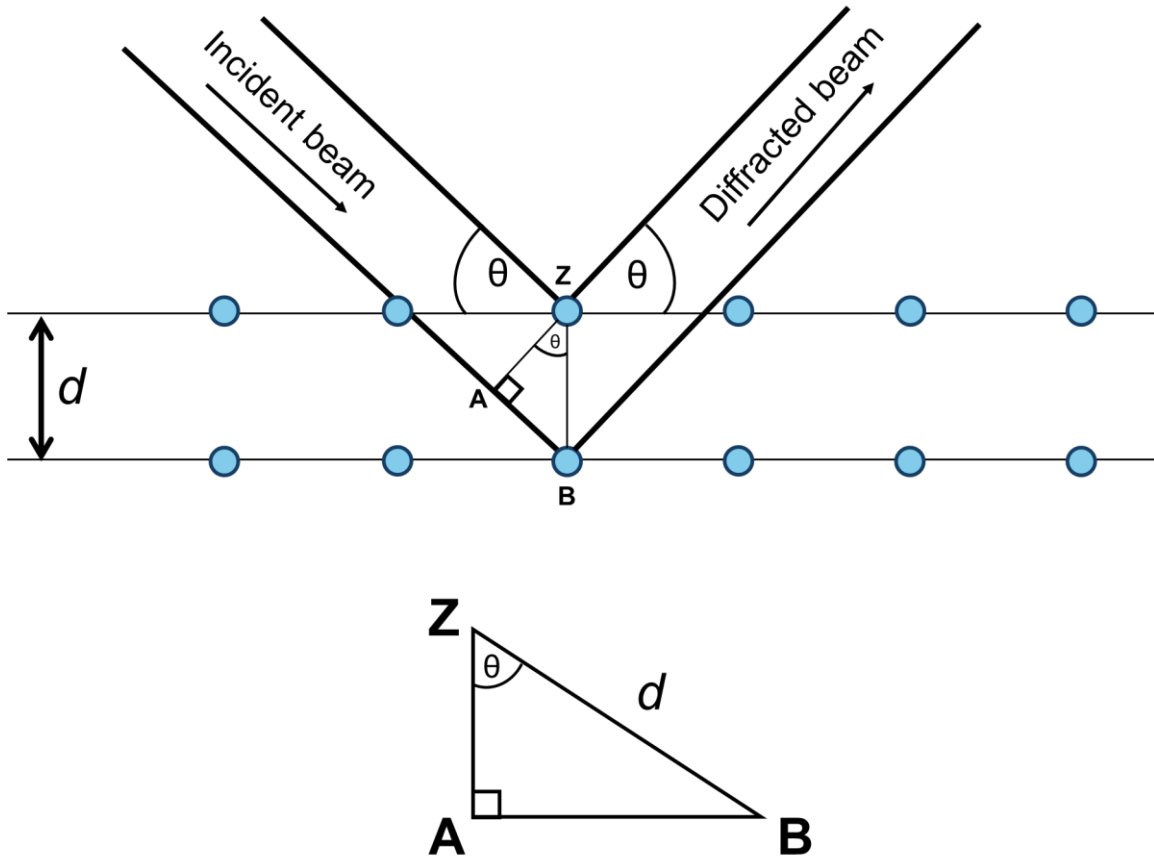


Figure 2.7. Schematic drawing of Bragg's Law. Two parallel X-ray beams contact two parallel atomic planes, such as in a crystalline lattice. In order for the X-ray beams to combine constructively, they must span an additional $n\lambda$ in distance, where n is an integer and λ is the X-ray wavelength.

Consider identical atoms located in two parallel crystal planes separated by an interplanar distance d . Two incident beams strike the crystal surface at the same incident angle, θ . In order for the two beams to add together constructively, their path difference Δ must be equal to an integer multiple n of the X-ray wavelength λ (Equation 2.17)

$$\Delta = n\lambda \quad (2.17)$$

The path difference between the two waves can be calculated by the additional distance the bottom beam must travel to add constructively with the top wave, represented by Equation 2.18:

$$\Delta = AB + AB \quad (2.18)$$

Using trigonometry, distance AB can be rewritten as:

$$AB = d \sin(\theta) \quad (2.19)$$

Therefore, Bragg's Law can be defined as Equation 2.20:

$$n\lambda = 2d\sin(\theta) \quad (2.20)$$

Bragg's Law clearly demonstrates that the X-rays scattered from two parallel planes of atoms will only combine when the diffraction angle yields a path length that is related to an integer of the X-ray wavelength.

2.3 X-ray scattering methods

2.3.1 Introduction to X-ray scattering length scales

X-ray scattering is a non-destructive material characterization technique that probes heterogeneities in electron density in materials. The size of the probed heterogeneities in X-ray scattering experiments depends on the angle of scattered X-rays being measured. Angular ranges therefore split X-ray scattering experiments into three broadly defined categories: wide-angle X-ray diffraction/scattering (WAXD/WAXS),

small-angle X-ray scattering (SAXS), and ultra-small angle X-ray scattering (USAXS). The defining boundaries of these experiments can vary and often overlap with one another. However, in general, WAXS is sensitive to features with dimensions smaller than 1 nanometer, SAXS experiments can probe dimensions up to around 100 nanometers in size, and USAXS experiments can probe dimensions of up to a micron. Therefore, performing combined USAXS/SAXS/WAXS experiments on a given material can offer hierarchical structural insights on multiple decades of dimensions (sub-nanometer to micrometer length scales). USAXS/SAXS/WAXS techniques rely on shared fundamental scattering principles which will be explored in the following sections.

2.3.2 Classifying material characterization techniques

X-ray scattering is among many materials characterization techniques that can provide information about the microstructure or morphology of a material. Shown in **Figure 2.8** are common examples of experimental techniques used to characterize polymeric materials. It is important to discuss the key features, similarities, and differences between these many techniques as their distinctions can be leveraged to select an appropriate technique for scientific investigations. As will be demonstrated later throughout this chapter, many of these techniques are complementary to one another, so users will commonly utilize several of these experimental techniques to ascertain information about their material. The material characterization techniques shown in **Figure 2.8** can be classified into different groups based on:

1. the length scale of microstructural information afforded by the technique
2. whether the technique probes bulk properties or surface properties
3. whether the technique yields information in real or reciprocal space

4. whether the technique provides spatial information directly or indirectly

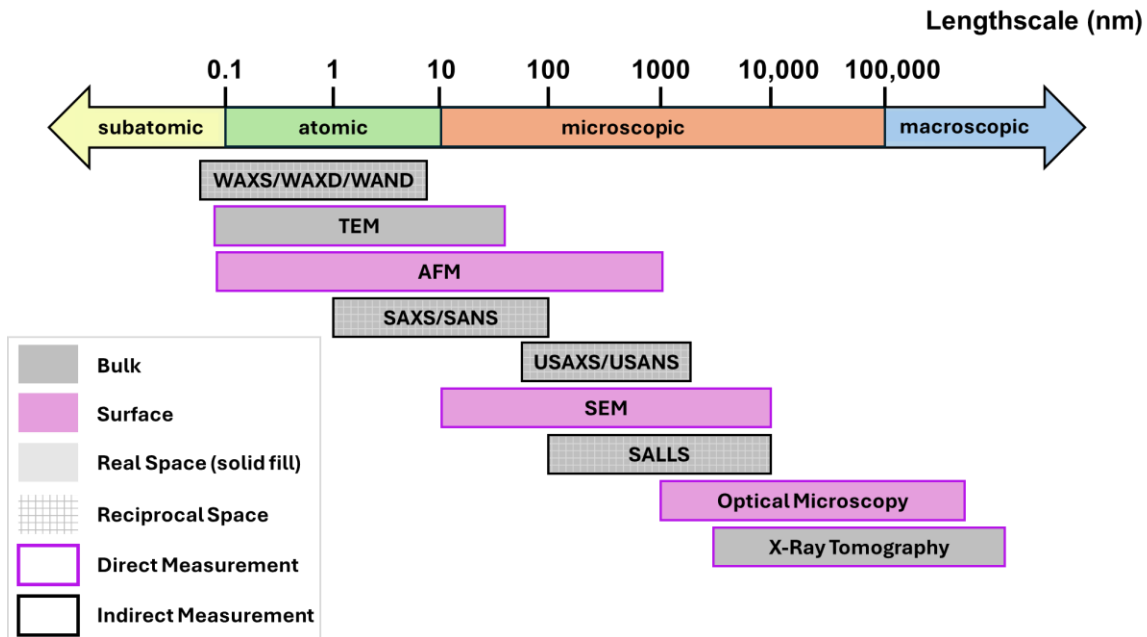


Figure 2.8. Approximate length scales that are probed with various characterization techniques, along with designations for bulk vs. surface techniques, real vs. reciprocal space techniques, and direct vs. indirect techniques.

2.3.2.1 Spatial resolution

First, many experimental techniques differ in the length scales over which they probe a material's morphology. The spatial resolutions of various materials characterization techniques are illustrated in **Figure 2.8**, and it becomes clear that materials characterization techniques can easily span many decades of length scale. The length scale of morphological information afforded by different techniques depends on the type of radiation or deformations involved in the experiment. Techniques such as AFM and WAXS/WAXD probe Angstrom-to-nanometer sized structures, whereas techniques such as optical microscopy and small-angle laser light scattering (SALLS)

probe micron-sized structures. Techniques that overlap in spatial resolution are considered complementary to one another, which can be useful as they provide an opportunity to validate the results from our technique with results from another.

With respect to the first distinction of length scale, it is important to note that morphological information on one length scale does not necessarily predict structure on a different length scale. For example, a material's morphology that appears to be homogeneous on larger length scales (e.g. featureless on the 10's of nanometer length scale via optical microscopy) may exhibit heterogeneities on smaller length scales (e.g. crystalline reflections on the nanometer length scale via WAXD). Similarly, materials that do not possess well-defined nanoscale structures (e.g., amorphous homopolymers), may possess large-scale heterogeneities (e.g. voids) that can be detected on SEM. A discussion the length scales probed with X-ray scattering experiments is given in Section 2.3.3, and further derived in Section 2.4.2 below. Throughout this dissertation, different morphological features in materials that are commonly observed will be presented and analyzed.

2.3.2.2 Surface vs. bulk

The second distinction that can be made when comparing different materials characterization techniques is whether the technique probes the surface or bulk morphology of a material. In general, bulk materials characterization techniques measure the volume-averaged dimensions, environment, motions, or response of a material. Examples of bulk characterization techniques include neutron scattering, X-ray scattering, NMR spectroscopy, dynamic mechanical analysis, differential scanning calorimetry, and X-ray tomography. SANS/WANS, SAXS/WAXS, and X-ray

tomography are examples of bulk characterization techniques that specifically probe morphology, while the others probe bulk atomic nuclei environments (NMR), bulk thermomechanical behavior (DMA), or bulk thermal transitions (DSC). In contrast, imaging techniques such as TEM, AFM, SEM, and optical microscopy in general are restricted to resolving surface-level features. Although surface-sensitive techniques such as SEM and TEM cannot directly probe the bulk morphology of a material, the internal structure of a material can be indirectly ascertained through these methods by sample preparation approaches including cryo-fracture⁸ or ultramicrotomy,⁹ both of which can be used to expose the internal surfaces for imaging.

2.3.2.3 Real vs. reciprocal

The third distinction that can be made is whether a characterization technique probes “real” space or “reciprocal” space. Real space techniques can be broadly defined as techniques that provide spatially resolved information in physical space (i.e., the Cartesian coordinate system). Real space techniques, such as TEM, AFM, SEM, and optical microscopy produce data with coordinates that directly correspond to physical locations on the sample, yielding images. In contrast, reciprocal space techniques can be defined as those which probe the sample in reciprocal, Fourier space. The concept of reciprocal space is clearly defined through Bragg’s law (presented in mathematical detail in Section 2.2.3), which demonstrates that the scattering vector q , which can be informally defined as the ruler of the dimension probed in such reciprocal space techniques, possesses units of inverse length scale (e.g., $\text{\AA}^{-1}$ or nm^{-1}). Some common examples of techniques that strictly probe reciprocal space include X-ray scattering,

neutron scattering, and electron diffraction. By using scattering models, the reciprocal space data can be interpreted into yield real-space insights.

2.3.2.4 Direct vs. indirect

The fourth and last distinction that can be made is whether a technique provides direct or indirect spatial information about the morphology of a material. Direct techniques include real-space imaging tools such as SEM and TEM that produce spatially resolved images of a material. These results can often be interpreted intuitively through visual inspection of the images. For example, spherical inclusions in a micrograph could reasonably be interpreted as corresponding to the nanoparticles added to a matrix in a nanocomposite. In contrast, indirect characterization techniques yield non-specific results which require additional modelling or information to extract quantitative information. Examples of indirect techniques include NMR spectroscopy, X-ray and neutron scattering. The nonspecific, indirect nature of X-ray scattering data can present challenges when fitting the data to obtain quantitative information. As discussed by Pauw,¹⁰ SAXS data can be mathematically interpreted in many ways that can yield dramatically disparate quantitative results. As a result, the task of quantitatively fitting the indirect data can be approached by combining knowledge about the system from complementary techniques or sources. The assumptions and factors that contribute to choosing a mathematical method to fit X-ray scattering data are discussed throughout each section of this dissertation. Understanding these distinctions of length scale, surface vs. bulk, real vs. reciprocal space, and direct vs. indirect data are essential when selecting appropriate methods for characterizing the hierarchical microstructure of phase-separated polymeric materials.

2.3.3 Comparing X-ray scattering with direct imaging techniques

2.3.3.1 Similarities

It can be useful to make a more detailed comparison of the benefits and drawbacks of X-ray scattering as it relates to imaging techniques with similar spatial resolution such as SEM, TEM, and AFM (**Figure 2.8**), as these are some of the most commonly utilized techniques in polymer science. Some key aspects of these techniques are given in **Figure 2.9**. X-ray scattering and direct imaging techniques such as SEM, TEM, and AFM share some of the same strengths, including their nanoscale resolution which allows for morphological analysis of nanometer sized structures including crystallites, nanoparticles, pores, and other features. Moreover, both X-ray scattering and direct imaging techniques can often take advantage of small sample sizes, which allows users to obtain microstructural information when material supply is limited or to selectively characterize different regions of a larger sample. Finally, SEM, TEM, and benchtop SAXS systems often require an evacuated sample chamber, so liquid or hydrated samples must be sealed in capillaries or enclosed samples holders for successful characterization under reduced pressure.

X-ray Scattering	Both	SEM/TEM/AFM
• Indirect technique • Non-destructive • Bulk, volume-averaged information • Requires modeling for quantitative analysis	• Nanoscale resolution • Structural analysis • Crystallinity information • Often requires vacuum • Can use small sample size	• Direct imaging • Surface detail • Real-space visualization • Elemental analysis (EDS) with SEM • Can be destructive

Figure 2.9. A comparison of the similarities and differences between X-ray scattering techniques and SEM/TEM/AFM imaging techniques.

2.3.3.2 X-ray scattering

While X-ray scattering is similar to imaging techniques in many ways, there are several key aspects that make it unique. As summarized in **Figure 2.9**, X-ray scattering experiments are non-destructive for most materials, as specimens for SAXS experiments can be characterized in their original form without mechanical contact, which occurs in AFM, or chemical staining/coating of the specimen, which is often required for electron microscopy experiments. The non-destructive nature of X-ray scattering experiments enables coupling of the scattering data with data from other material characterization techniques such as DSC or DMA. Additionally, the ability to characterize the sample via X-ray scattering in its native form (solid, liquid, gel, etc.) with little to no additional manipulation offers the opportunity to perform in-situ X-ray scattering experiments while changing the environment of the sample (i.e., temperature, stress, etc.). These experiments allow users to ascertain the morphological changes that are occurring within the sample during various processes such as heating, cooling, or stretching. Finally, X-ray scattering experiments have the advantage of providing volume-averaged, bulk structural information, whereas direct imaging techniques generally provide information on the surface level. This can be particularly useful when the morphology of the material can

vary throughout the sample thickness or when data needs to be correlated with bulk behavior of a material.

2.3.3.3 Direct imaging

Direct imaging techniques such as SEM, TEM, and AFM have unique attributes which make them advantageous for certain applications. As summarized in **Figure 2.9**, material characterization methods such as TEM, SEM, and AFM generate a direct image of the specimen which allows for surface-level features to be mapped in real space. In contrast, X-ray scattering techniques yield indirect and nonspecific scattering patterns in reciprocal space which require modelling through various scattering equations and frameworks to yield quantitative dimensions. While X-ray scattering experiments provide bulk, volume-averaged data, micrographs from SEM/TEM are often restricted to providing 2D images of surfaces. In order to probe the internal morphology of a material, various fracture methods are commonly employed to expose the internal surfaces for imaging.⁸ FIB-SEM (focused ion beam SEM) tomography is a notable exception to other 2D imaging techniques as it provides direct volumetric imaging of materials in 3D.¹¹ Finally, when coupled to energy-dispersive X-ray spectroscopy equipment, SEM and TEM can provide the composition of elements on the surface of a material.

2.4 Material Considerations for X-ray Scattering

2.4.1 Requirement 1. Internal structure

As demonstrated through the proportionalities in Equation 2.21, the intensity of scattered X-rays is related to the form factor, structure factor, the square of the electron density contrast. From this relationship, guidelines can be deduced that define an ideal

experimental system suitable for X-ray scattering experiments, which are summarized in **Table 2.1**. The first and most important requirement is that the sample must possess an inhomogeneous distribution of electron density. A heterogeneity can be defined as any form that exhibits a fluctuation or deviation from the average electron density. Some examples of such heterogeneities include the density fluctuations associated with preferred random coil conformations that polymer chains adopt in a solvent, the density fluctuations arising from the relatively electron dense crystalline polymer domains formed within an amorphous matrix in semicrystalline polymers, and those arising from electron-rich nanoparticles dispersed throughout an amorphous polymer matrix in nanocomposite systems. In each of these examples, the system has an unequal distribution of electron density due to a specific structure or morphology that the material possesses.

$$I(q) \propto P(q)S(q)(\Delta\rho)^2 \quad (2.21)$$

Table 2.1. Summary of the requirements for X-ray scattering to be applied to a given material system.

Requirement	Relationship
Heterogeneity/structure	$I(q) \propto P(q) S(q)$
Heterogeneity has dimension within instrument limit	$q = 2\pi/d$
Heterogeneities have contrast in electron density	$I(q) \propto (\Delta\rho)^2$

2.4.2 Requirement 2. Feature size and length scale

The second requirement for X-ray scattering applicability is that the heterogeneity must be characterized by a dimension that is within the range that the instrument is capable of probing. It has been noted that SAXS probes nanostructures approximately 1-100 nm in size and that WAXS probes nanostructures around a nm in size. However, the

precise range of real-space dimensions, d , that a SAXS/WAXS instrument can resolve is based on several factors, including the sample-to-detector distance (D) and the size of the 2D detector. Both factors contribute to determining the angular range of X-rays that can be collected on the detector area, the limits of q , and through Bragg's law, the limits of the real space dimension, d , being probed. A simple derivation of the limits of the instrumental range is presented below, which can allow users to determine an optimal sample-to-detector distance based on the expected size of the morphological features in their material.

Because most X-ray detectors have rectangular active areas, the dimensions of the 2D detector will be denoted by L_x and L_z , representing the horizontal and vertical dimensions, respectively, and assuming that in general $L_x < L_z$. The Xenocs Xeuss 3.0 SAXS/WAXS system at Virginia Tech was used to collect much of the data presented in this dissertation and is shown in **Figure 2.10**. This instrument has a minimum sample-to-detector distance D of approximately 42 mm due to the motor limits on the detector. The dimensions of the Dectris EIGER2 4M detector (**Figure 2.11**) associated with the Xenocs Xeuss 3.0 SAXS/WAXS at Virginia Tech are used in this example, assuming a copper source is utilized ($\text{Cu K}\alpha = 1.54 \text{ \AA}$).

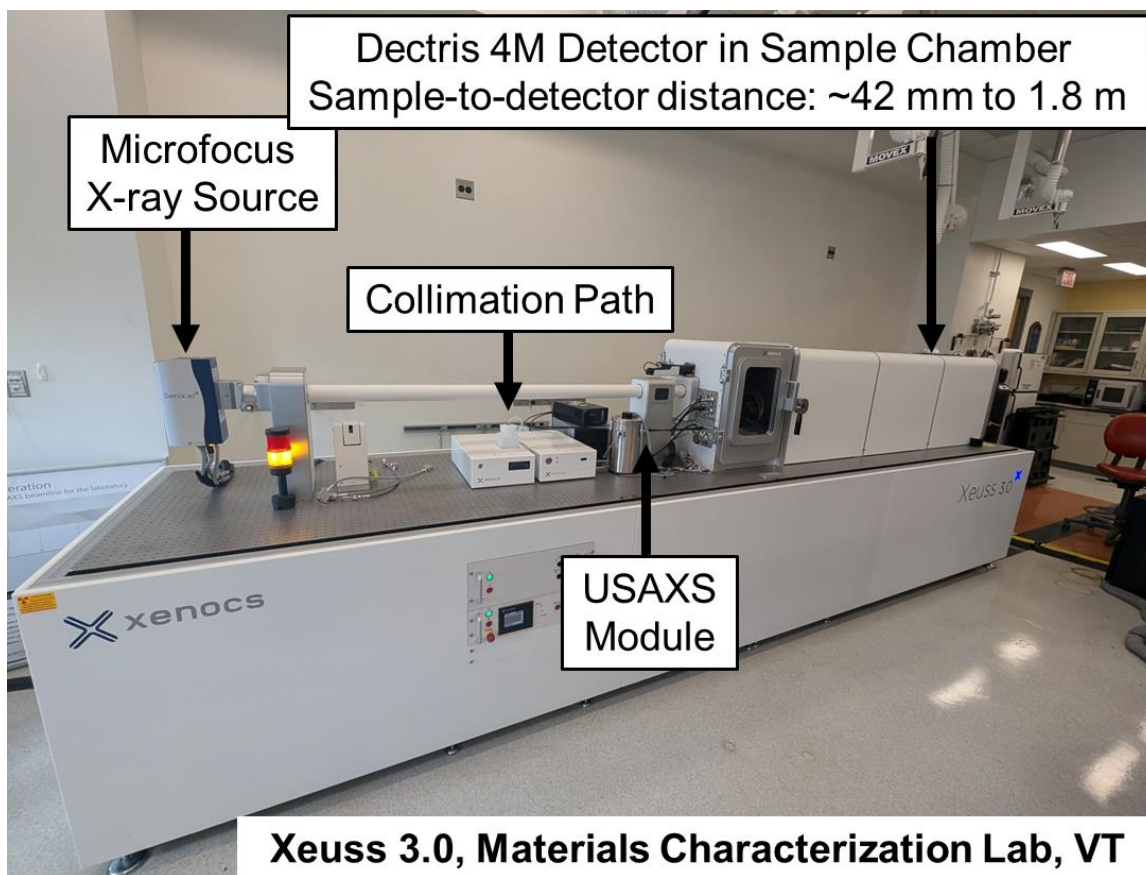


Figure 2.10. Xenocs Xeuss 3.0 SAXS/WAXS at Virginia Tech.



Figure 2.11. Dectris Eiger2 4M detector on the Xenocs Xeuss 3.0 SAXS/WAXS system. A protective plastic film covers the detector during changes in pressure, including chamber evacuation and venting.

The minimum and maximum scattering vector q , q_{min} and q_{max} , can be derived from the limits of Bragg's law shown in Equation 2.22 and Equation 2.23,

$$q_{min} = \frac{4\pi}{\lambda} \sin\theta_{min} \quad (2.22)$$

$$q_{max} = \frac{4\pi}{\lambda} \sin\theta_{max} \quad (2.23)$$

where q is the scattering vector, λ is the X-ray wavelength, and θ is $\frac{1}{2}$ of the scattering angle. For a given sample-to-detector distance D_y , the maximum scattering vector, q_{max} , is determined by the greatest scattering angle that can be collected on the 2D area detector at the corner of the detector. Therefore, the longest dimension of the detector, L_z , is the size-limiting dimension and will be used in the following derivation. A right triangle is formed by the sample-to-detector distance (D) and the radial distance from the beam center to the pixel of interest on the detector (r), as shown in **Figure 2.12**.

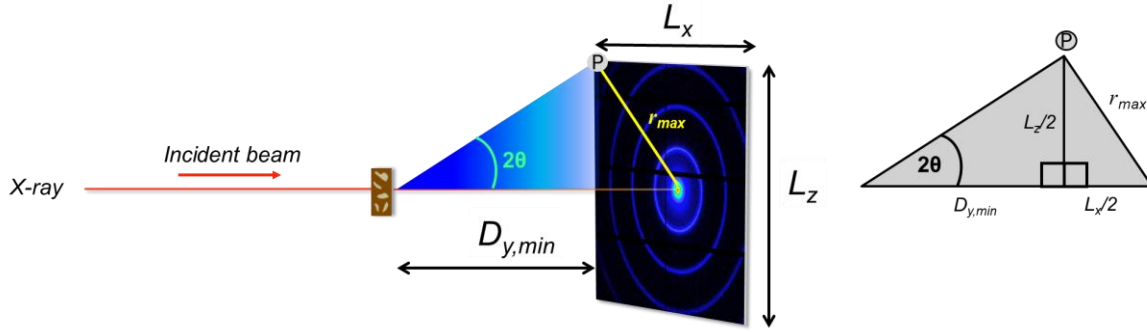


Figure 2.12. Schematic drawing showing the minimum sample-to-detector distance ($D_{y,min}$), the maximum radial length on the detector (r_{max}), and the dimensions of the detector L_x and L_z . As drawn, the vertical dimension L_z is greater than L_x .

The angle formed by the right triangle is the scattering angle, 2θ . Using basic trigonometry, Equation 2.24 follows:

$$\tan(\theta) = \frac{r}{D} \quad (2.24)$$

Equation 2.25 solves for θ :

$$\theta = \tan^{-1}\left(\frac{r}{D}\right) \quad (2.25)$$

Since the relationship between the scattering angle, 2θ , and the scattering vector, q , has already been established in Equations 2.22 and 2.23, the following substitution can be made, giving a clear relationship between r and D_y in Equation 2.26:

$$q_{max} = \frac{4\pi}{\lambda} \sin \left(\frac{1}{2} \tan^{-1} \left(\frac{r_{max}}{D_{y,min}} \right) \right) \quad (2.26)$$

The maximum q (q_{max}) occurs at the corner of the detector where the radial dimension on the detector, r , is maximized (point P, **Figure 2.12**). Therefore, $r_{max} = \sqrt{\left(\frac{L_x}{2}\right)^2 + \left(\frac{L_z}{2}\right)^2}$.

Substituting this relationship into r from Equation 2.26 yields Equation 2.27:

$$q_{max} = \frac{4\pi}{\lambda} \sin \left(\frac{1}{2} \tan^{-1} \left(\frac{\sqrt{\left(\frac{L_x}{2}\right)^2 + \left(\frac{L_z}{2}\right)^2}}{D_{y,min}} \right) \right) \quad (2.27)$$

From Equation 2.27, it becomes clear that the minimum sample-to-detector distance D_{min} as well as the size of the detector are the key experimental variables that determine the q_{max} of an X-ray scattering experiment. In order to characterize the smallest real-space dimensions possible, and therefore the largest values of q (Equation 2.23), D_y should be minimized and the detector size should be maximized. It therefore becomes understandable why large 2D area detectors and short distances between the sample and detector are desirable for WAXS experiments. The Dectris Eiger2 4M detector associated with the Xenocs Xeuss 3.0 SAXS/WAXS has an active area with dimensions $L_x = 155.1$ mm and $L_z = 162.15$ mm. Substituting the values of $D_{y,min} = 50$ mm, L_x and L_z into

Equation 2.27 yields $q_{\max} \approx 4.4 \text{ \AA}^{-1}$ ($2\theta_{\max} \approx 66^\circ$). Therefore, the smallest real-space dimension d that can be probed in this configuration is approximately $1.4 \text{ \AA}$.

Similarly, the smallest resolvable scattering vector $q_{\min}$ on the detector can be derived in order to calculate the largest real-space dimension that the configuration can resolve. The three key factors that determine the sample-to-detector distance are the sample-to-detector distance, the size of the X-ray beam, and the size of the detector pixels. The standard beam size of the Xenocs Xeuss 3.0 SAXS/WAXS system is $0.7 \text{ mm} \times 0.7 \text{ mm}$ but can be changed to high resolution ($0.4 \text{ mm} \times 0.4 \text{ mm}$) or high intensity ($1.4 \text{ mm} \times 1.4 \text{ mm}$) mode. For this example, the standard beam size will be used. The pixel size (length $\times$ width) on the detector is $75 \text{ }\mu\text{m} \times 75 \text{ }\mu\text{m}$. The minimal radial distance, $r_{\min}$, is associated with the center location of the pixel that collects the smallest angles of scattering from the sample, while simultaneously being resolved from the main beam (shown in **Figure 2.13** and **Figure 2.14**). Considering the main beam sets a dimension of 0.35 mm (half of the beam length), the center of the first pixel is located at $0.35 \text{ mm} + 37.5 \text{ }\mu\text{m}$ which is equal to $r_{\min} = 0.0003875 \text{ m}$.

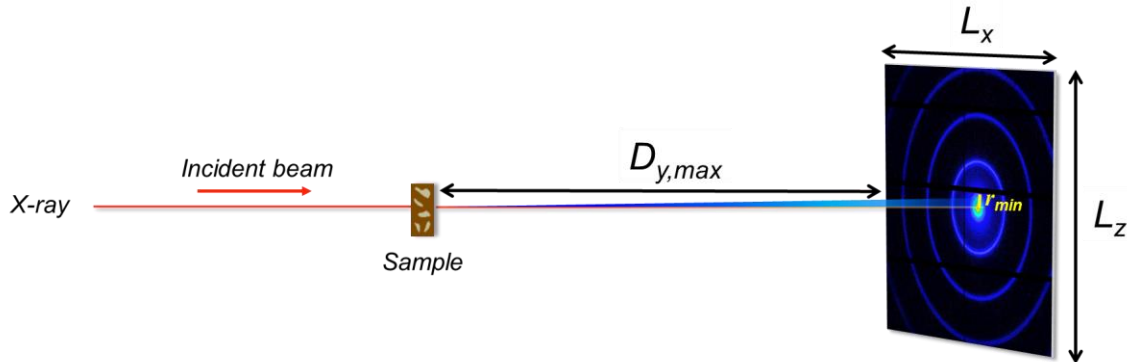


Figure 2.13. Schematic drawing showing the maximum sample-to-detector distance ($D_{y,max}$), the minimum radial length on the detector (r_{min}), located and the dimensions of the detector L_x and L_z . As drawn, the vertical dimension L_z is greater than L_x .

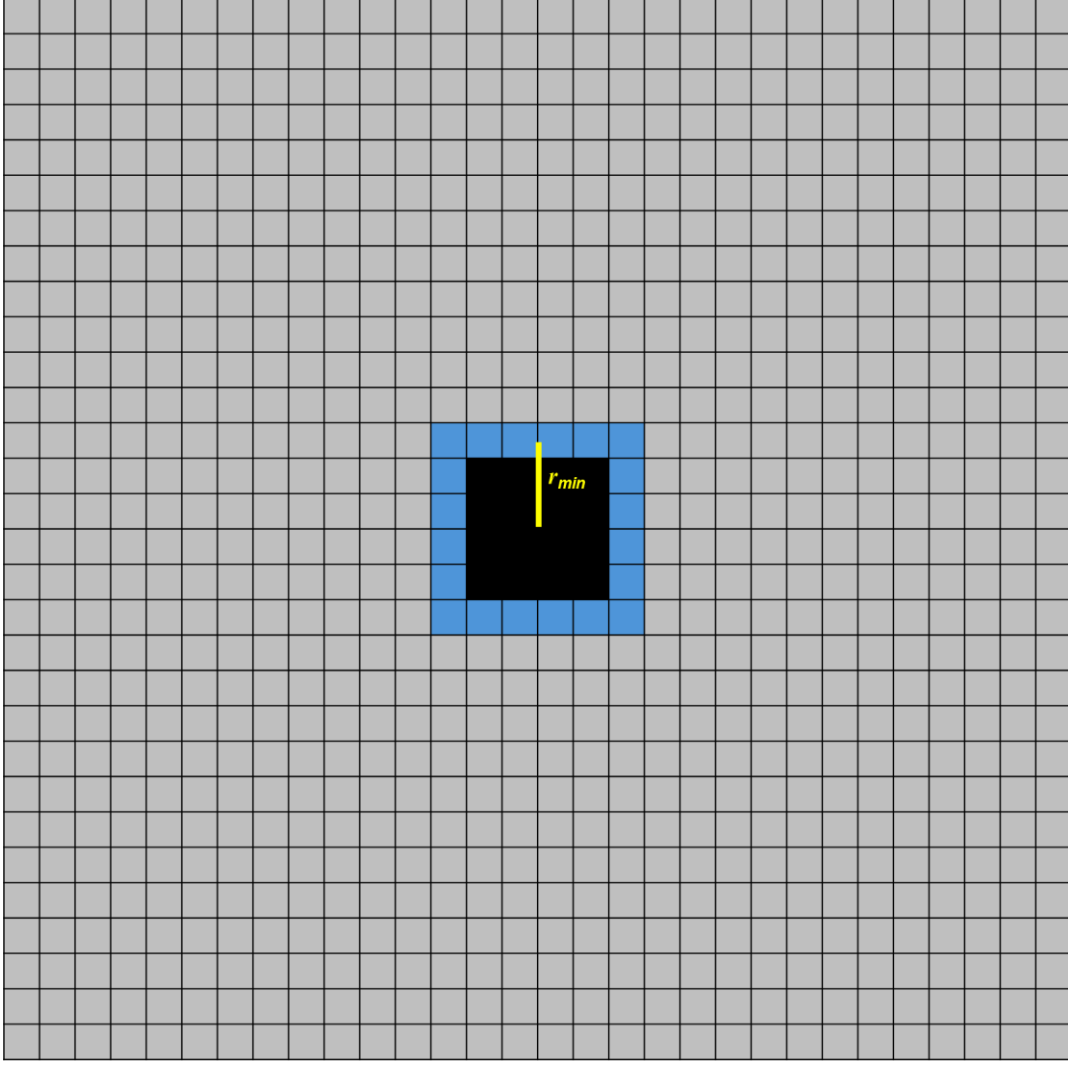


Figure 2.14. Example of detector active area (900 square pixels). The direct, transmitted beam is located in the center as black pixels. X-rays scattered at the lowest scattering angle are collected on the neighboring pixels, colored blue. The center of the first resolvable pixel from the main beam is considered to define $r_{\min}$.

$$q_{\min} = \frac{4\pi}{\lambda} \sin(\theta_{\min}) \quad (2.28)$$

$$q_{\min} = \frac{4\pi}{\lambda} \sin\left(\frac{1}{2} \tan^{-1}\left(\frac{r_{\min}}{D_{y,\max}}\right)\right) \quad (2.29)$$

The maximum sample-to-detector distance is determined by the length of the sample chamber and is 1.8 m for the Xenocs Xeuss 3.0 SAXS/WAXS system for the extended SAXS configuration. However, since SAXS experiments are most commonly performed at 0.9 m, this dimension will be used. This length is known as Substituting $\lambda = 1.54$, $r_{\min} =$ and $D_{y,\max} = 0.9$ m into Equation 2.29 yields a minimum scattering vector $q_{\min} = 0.004 \text{ \AA}^{-1}$, corresponding to the real-space dimension of $d \approx 150$ nm. In extended SAXS mode (ESAXS) on the Xenocs Xeuss 3.0 system, the detector is positioned at the limit of the sample chamber which is 1.8 m from the sample. Substituting $D_{y,\max} = 1.8$ m into Equation 2.29 and also assuming the same X-ray wavelength, pixel size, and beam size yields $q_{\min} \approx 0.002 \text{ \AA}^{-1}$ corresponding to a maximum real-space dimension of $d \approx 300$ nm.

In summary, the range of the real-space dimensions that can be probed with X-ray scattering depends on several experimental factors including the X-ray wavelength, the sample-to-detector distance, the beam size, and the pixel size. While the X-ray wavelength and the pixel size are fixed by the source and the specifications of the detector, the sample-to-detector distance and the beam size can be selected to optimize the experiments to characterize the size-scale of interest. For the Xenocs Xeuss 3.0 SAXS/WAXS, the smallest dimensions that can be probed are approximately 1.4 $\text{\AA}$ (in WAXS mode) and 300 nm (in ESAXS mode). Larger structures can be probed with ultra-small-angle X-ray scattering methods which involve the use of a Bonse-Hart module.¹²

2.4.3 Requirement 3. Electron density contrast

The third requirement a material system must meet for applicability to X-ray scattering experiments is contrast in electron density between the scattering entities (i.e., the heterogeneities must possess different electron densities). Even if a sample exhibits a

morphological feature (Requirement 1) on the appropriate size-scale that can be probed by the instrument (Requirement 2), if the heterogeneities do not possess different electron densities, then X-ray scattering experiments will not provide fruitful data.

An excellent example of such a system is syndiotactic polystyrene (sPS), a stereoisomer of polystyrene in which the aromatic units perfectly alternate in their spatial orientation along the polymer backbone. sPS is known to phase-separate into a semicrystalline morphology due to the spatial regularity of the phenyl rings which allows for organized chain packing to occur. The presence of sPS crystallites has been confirmed through differential scanning calorimetry (DSC) experiments, which confirm a heterogeneity/structure in the material (meeting requirement 1).¹³ Additionally, real-space transmission electron microscopy (TEM) imaging experiments conducted by Lopez and coworkers have revealed lamellar sPS crystallites with thicknesses ranging from ~7-14 nanometers.¹⁴ This dimension is within the range that SAXS is capable of probing (meeting requirement 2). However, no feature is observed in the SAXS region of sPS.¹³ This observation is explained by the density of the amorphous region being too close to the densities of the crystalline regions (requirement 3 is not met).¹³ As stated by Barnes and coworkers, this material does not “exhibit any sort of peak that is the usual signature of lamellar microstructure in semicrystalline polymers.” It is not that the structure did not exist; Rather, the structure was not observed because there was not sufficient contrast in electron density between the phases.

The intensity of scattered X-rays is proportional to the square of the electron density contrast, as demonstrated by Equation 2.21. Quantitatively, the scattering length density of a material can be calculated from Equation 2.30:

$$SLD = \frac{\sum_{i=1}^n b_i}{V_m} \quad (2.30)$$

where b_i is the bound coherent scattering length of atom i , and V_m is the molecular volume of the material. The X-ray scattering length density (SLD) for a multi-atom system thus considers the scattering length of all atoms and normalizes for the molecular volume, and therefore has units of $(\text{length})^{-2}$. From this relationship, it becomes clear why SLD is represented in units of inverse length scale squared (e.g., $\text{\AA}^{-2}$), as it is equivalent to the scattering length per unit volume ($\text{\AA}/\text{\AA}^3 = \text{\AA}^{-2}$).

For X-rays, the bound coherent scattering length, b_i , is related to the number of electrons in the system, through Equation 2.31,

$$b_i = Z_i r_e \quad (2.31)$$

where Z is the atomic number of atom i within the molecular volume V_m , and r_e is the classical electron radius, equal to $r_e = 2.817 \times 10^{-15}$ m. For neutron scattering, the bound coherent scattering length, b_i , is used to describe how a nucleus scatters neutrons coherently, and the values can be found in tables.¹⁵ Unlike X-ray scattering, the neutron SLD depends on the isotopic composition of the sample. More detailed information on the neutron scattering length density is presented by Sears.¹⁵

It can therefore be seen that the SLD of any material can be determined when the atomic composition of a material, along with its molecular volume. If the molecular volume is not readily known, it can be calculated from the following equation:

$$V_m = \frac{MW}{\rho N_a} \quad (2.32)$$

where MW is the molar mass (and the molar mass of the repeating unit for a polymer) in g/mol, ρ is the mass density of the material in g/cm³, and N_a is Avogadro's number in mol⁻¹. Therefore, in order for the X-ray SLD to be calculated for a polymer, the chemical formula of the repeating unit, the molecular weight of the repeating unit, and the mass density of the polymer must be known.

The electron density contrast is equal to the following Equation,

$$\Delta SLD = SLD_1 - SLD_2 \quad (2.33)$$

From Equation 2.30, it can be seen that the X-ray SLD of a material ultimately depends on the electron density of the material, and that the SLD differences dictate the contrast that contributes to the scattering intensity. Therefore, if a user does not observe a scattering feature when one is suspected, it would be advisable to calculate the contrast in scattering length density to determine if that is the source of unobservable scattering intensity.

2.5 Corrections/Calibrations

2.5.1 q Calibrations

The most important calibrations that must be executed when performing X-ray scattering experiments are the q -space calibrations. These calibrations enable quantitative

q-space to be mapped onto the qualitative 2D detector image. Without calibration, the 2D detector images collected from X-ray scattering experiments cannot provide the user with any quantitative information on the length scale of the heterogeneities that are giving rise to the sample scattering.

Materials with well-defined and isotropic scattering patterns are commonly used to perform these calibrations due to their predictable intrinsic values. The calibration process involves two steps. First, a scattering pattern of the calibrant is collected at the same sample-to-detector distance used for the sample measurements. Second, the positions (in q space) of the scattering peaks are compared to well-known values documented for that material in the literature. The experimentally measured peak positions of the standard will only match the literature value for that standard at a specific sample-to-detector distance. When the measured values match the literature values for the peak positions, the instrument is considered calibrated for that particular configuration (i.e., sample-to-detector distance). The scattering pattern of the standards must be collected at the time of each experiment due to small fluctuations that could occur in the position of the detector.

Silver behenate (AgBeh) is commonly used to calibrate the q -range for SAXS and MAXS experiments.¹⁶⁻¹⁷ The diffraction pattern of AgBeh was first reported in 1993 by Huang and co-workers and proposed as a potential standard for low-angle diffraction experiments.¹⁶ AgBeh crystallizes into a triclinic unit cell, shown in **Figure 2.15 a,b**. The interlayer spacing is 5.8 nm along the c -axis, yielding strong diffraction peaks associated with the 001, 002, etc. family of planes (**Figure 2.15b**). From the 2D diffraction pattern

shown in **Figure 15c** and the 1D reduced pattern in **Figure 15d**, it is clear why AgBeh is used as a SAXS q standard; The peaks are intense, symmetrical, and regularly spaced.

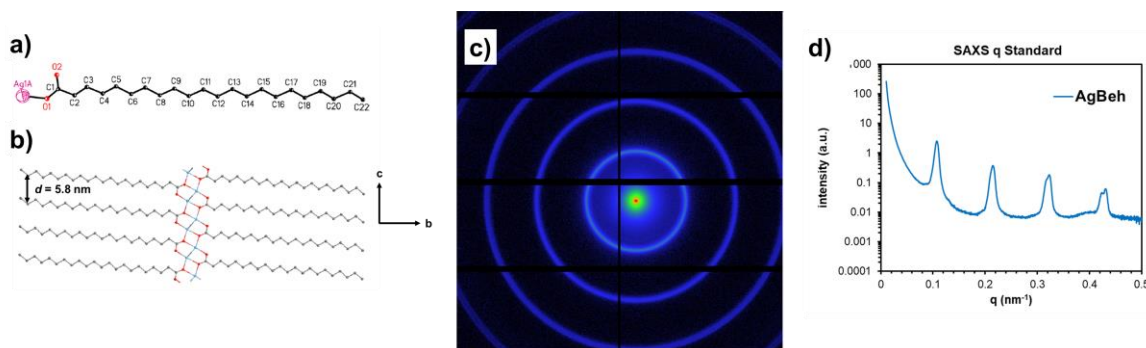


Figure 2.15. **a)** Atoms labeled in a single fatty acid chain of silver behenate. Reprinted with permission from the International Union of Crystallography.¹⁶ **b)** The crystalline structure of several fatty acid chains of silver behenate. Each fatty acid chain is separated by ca. 5.8 nm.¹⁶ **c)** The 2D scattering pattern of AgBeh collected on the Xenocs Xeuss 3.0 SAXS/WAXS. **d)** The diffraction pattern of silver behenate as characterized by the Xenocs Xeuss 3.0 SAXS/WAXS utilizing Cu K_{α} radiation ($\lambda = 1.54$ Å) associated with the 00 l crystalline planes (001, 002, etc.).

Similarly, lanthanum hexaboride (LaB₆) is commonly used as a standard material for calibrating the WAXS regime due to its strong and regular diffraction pattern at wide angles.¹⁸ LaB₆ crystallizes into the body-centered cubic space group $Pm-3m$, where the boron atoms are located in the center of the unit cells and lanthanum atoms are located at the corners of the unit cells (**Figure 2.16a**). Similar to the SAXS standard silver behenate, lanthanum hexaboride also produces a strong scattering pattern consisting of intense and isotropic rings (**Figure 2.16b**). The peak positions associated with the crystalline planes are documented in the NIST certification of LaB₆ as a standard reference material for powder diffraction experiments (**Figure 2.16c**).¹⁹ Together, the overlap in scattering regions of the SAXS and WAXS profiles can be observed (**Figure 2.17**).

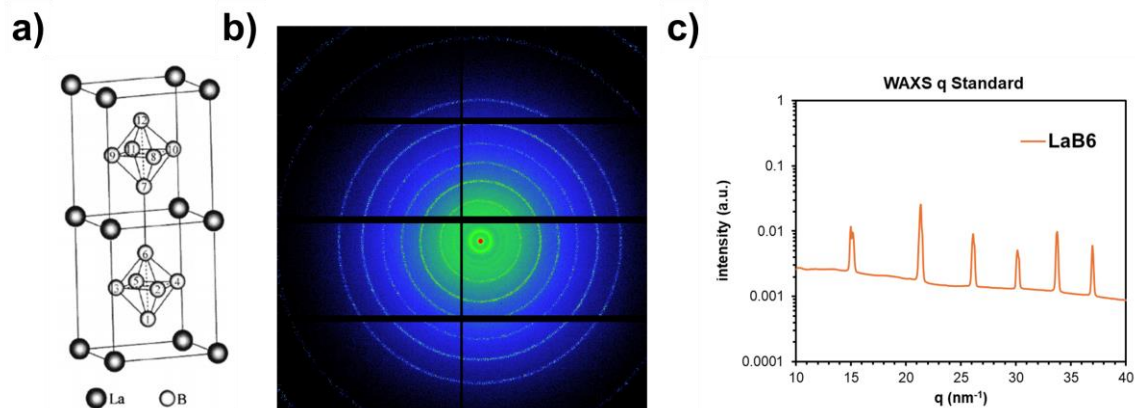


Figure 2.16. **a)** Crystal structure of lanthanum hexaboride (LaB₆) revealing two unit cells. Reprinted with permission from American Physical Society.¹⁸ **b)** The 2D scattering pattern of LaB₆ collected on the Xenocs Xeuss 3.0 SAXS/WAXS. **c)** The diffraction pattern of LaB₆ as characterized by the Xenocs Xeuss 3.0 SAXS/WAXS utilizing Cu K_α radiation ($\lambda = 1.54 \text{ \AA}$).

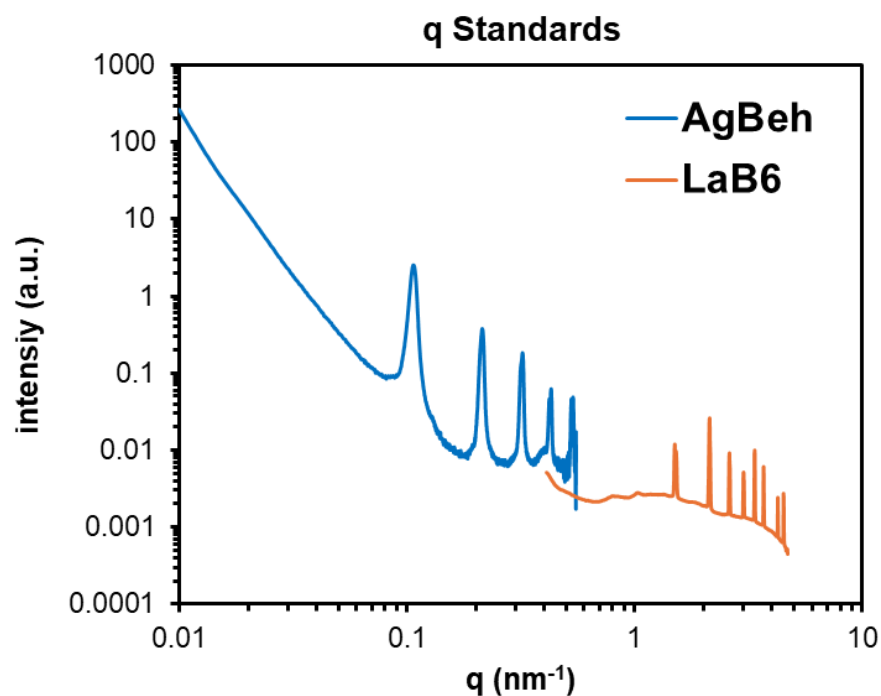


Figure 2.17. Scattering patterns of AgBeh and LaB₆, collected in a SAXS configuration and a WAXS configuration, respectively. While there is some overlap in q -space between the two configurations, MAXS experiments are commonly used to offer additional

overlap between different configurations, and is similar to SAXS, is commonly calibrated with AgBeh.

2.5.2 Absolute Intensity Calibrations

Throughout this work, most of the X-ray scattering data presented will be plotted on an absolute intensity scale, presented in absolute units of scattering intensity. Scaling X-ray scattering data to absolute intensity units is powerful because it represents the specimen-specific scattering in absolute terms. Due to this, absolute intensity units allow new information about the scattering entities: not only can information be gleaned from the q -value but also the intensity of scattered X-rays. An advantageous outcome of this calibration is that converting the intensity into absolute units allows for direct comparisons to be made between scattering data collected from different instruments (i.e., data collected on a lab-based system and on a synchrotron-based system). As will be discussed below, only a few simple corrections are required to obtain scattering data into absolute intensity units. As noted by BR Pauw in his 2013 work titled “Corrigendum: Everything SAXS: small-angle scattering pattern collection and correction,” he argues that this correction “can be a great boon to the value of the data,” and therefore lists it in his table of key corrections that should be made.¹⁰ The advantages of absolute intensity units are worth taking time to correct the data, and should therefore be conducted whenever possible.

In an X-ray scattering experiment, the scattered X-rays are collected onto a detector such as a 2D area detector. As described earlier, in the absence of a sample in the beam path, the intensity of X-rays produced by the main beam is described as the X-ray flux. High flux sources include synchrotron radiation sources, whereas relatively low flux sources can be found in lab-based X-ray scattering instruments.

Simply defined, absolute scattering intensity represents the differential scattering cross-section per unit volume, yielding units of cm^{-1} . The differential scattering cross section has been previously described in Equation 2.4. Scaling to absolute units can be accomplished using several different methods as described by Roe.⁷ A commonly utilized method involves a secondary standard material with a known absolute scattering intensity. Glassy carbon is a common standard for absolute intensity corrections and has been used for several decades.²⁰ This method was used to scale the data collected on the Xenocs Xeuss 3.0 SAXS/WAXS system presented throughout this work.

2.6 Conclusions

A historical explanation of X-ray and their scattering methods has been discussed, which highlights the immense strides that have been made in instrumental design for modern SAXS/WAXS instruments over the past two centuries. Ultimately, these advancements have increased the accessibility of SAXS/WAXS experiments which has allowed for a more detailed understanding of the morphology of materials at the nanoscale by a wider and more diverse population of scientists. A theoretical basis for the scattering of X-rays has been presented, beginning with the simplest case of scattering by a free electron, followed by a discussion on the interference of scattered X-ray waves. Having established these fundamental principles, the practical aspects X-ray scattering methods are compared with other materials' characterization techniques, which can be useful as scientists contemplate the suitability of X-ray scattering and other techniques for their scientific investigations. From these principles, a framework was developed that clearly defines which aspects of materials must be considered in order to thoughtfully plan for X-ray scattering experiments. Finally, some practical aspects regarding the

proper treatment of X-ray scattering data are explained. These fundamental concepts form the basis for the remainder of the work that will be discussed throughout this dissertation.

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Chapter 3. Morphological Origins of Small Angle X-ray Scattering in Ionomers

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3.1 Introduction

Ionomers are formally defined by the IUPAC as “polymers composed of macromolecules in which a small but significant proportion of the constitutional units has ionic or ionizable groups, or both.”¹ In this low ion content regime, ionomers are insoluble in polar solvents, and the bulk properties like storage modulus, glass transition temperature, and viscosity are controlled by ionic interactions that induce phase separation between the matrix and ionic groups.² In contrast, the IUPAC defines polyelectrolytes as “polymers composed of macromolecules in which a substantial portion of the constitutional units contains ionic or ionizable groups, or both.”¹ Synthesizing ionomers conventionally involves two steps: 1) preparing a pre-ionic copolymer and 2) neutralizing the pre-ionic groups with a base to install the corresponding counterion.

Ionomers are fascinating because incorporating a few ionic groups onto a hydrophobic polymer can dramatically influence its physical, mechanical, dynamic, and optical properties. For example, polymerizing a small number of methacrylic acid units with ethylene and subsequently neutralizing the acid transforms polyethylene into a transparent, impact-resistant coating for golf balls known as Surlyn® (Dupont).³ Ionomers are utilized in many applications that leverage properties from the hydrophobic polymer

and the ionic groups, including compatibilizers for polymer blends,⁴ energy storage⁵ and transport⁶ materials, and adhesives.⁷ Undoubtedly, the remarkable physical properties of ionomers have structural underpinnings, so researchers have collectively devoted immense effort over more than half a century to elucidate the origins of ionomer morphologies, with X-ray scattering being a key tool. The aim of this literature review is to summarize the current understanding of morphologies of random, amorphous ionomers, with a focus on the treatment of the scattering at very small angles, an arguably understudied region of ionomer scattering patterns. The long-term goal of this body of work is to use new insights from X-ray scattering to construct fundamental structure-property relationships that will ultimately guide the design of future high-performance materials.

3.2 Experimental observations of ionomers

The solid-state physical properties of ionomers are governed by associative electrostatic interactions that form distinct ionic domains, owing to the immiscibility of a small number of ionic groups in a predominantly hydrophobic matrix.⁸ The morphologies of the phase-separated material are hierarchical, so the characterization method used to probe the structure is chosen based on the size scale of interest.⁹ At the smallest length scales (1-10 Å), there is a strong driving force for ion-counterion association into “ion pairs.” When association *between* ion pairs is favorable, several ion pairs coalesce to form higher-order aggregates, generally termed “ionic aggregates.”¹⁰ Numerous X-ray absorption spectroscopy, electron spin resonance, and nuclear magnetic resonance experiments have been used to probe the local environment of the cations, providing information about the sub-nanometer length scale of these aggregates.⁹

Small angle X-ray scattering (SAXS) provides structural information on length scales ranging from 1-100 nm and is extensively used to characterize the spatial arrangement of ionic aggregates. SAXS is based on the principle that periodic differences in electron density cause X-rays to scatter at an angle that is related to the distance between the scattering centers.¹¹ This is shown in Equations 3.1 and 3.2,

$$q = \frac{4\pi}{\lambda} \sin\theta \quad (3.1)$$

$$q = \frac{2\pi}{d} n \quad (3.2)$$

where q is the wavevector transfer, θ is half the scattering angle, λ is the X-ray wavelength, d is the “real space” distance, and n is the order of reflection. SAXS is often utilized to characterize ionomer morphology because ionomers display a peak between 0.5-3 nm⁻¹ in plots of $I(q)$ vs. q (**Figure 3.1a**), where $I(q)$ is the azimuthally integrated scattered intensity.⁸ Origins of this feature, generally termed the “ionomer peak,”¹² were the subject of great debate for several decades. Additionally, SAXS patterns of ionomers exhibit increased scattered intensity at low angles close to the main beam, known as the “small angle” or “low q ” upturn, though much less attention has been given to this feature.

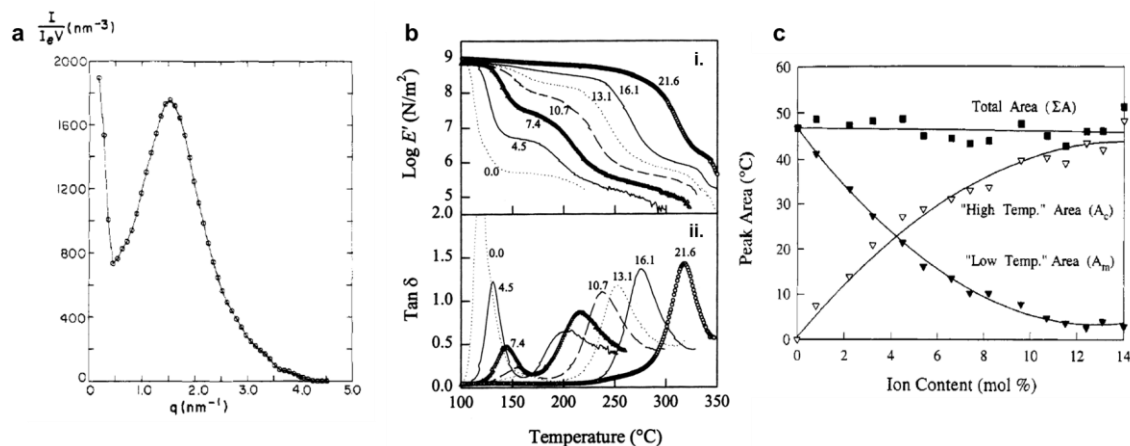


Figure 3.1. a) SAXS $I(q)$ vs. q data of Zn^{2+} -neutralized sulfonated atactic polystyrene (SaPS). Reprinted with permission from American Chemical Society.¹³ b) i. $\log E'$ and ii. $\tan \delta$ plots for poly(styrene-co- Na^+ methacrylate) from DMA. c) Areas under the two $\tan \delta$ peaks as a function of temperature. Reprinted with permission from American Chemical Society.¹⁴

On a larger size scale, ionomers display unique bulk thermomechanical behavior.¹⁴

As shown in dynamic mechanical analysis (DMA) data in **Figure 3.1b**, the glass transition temperature (T_g) of the matrix at low temperatures, shown as a peak in $\tan \delta$, increases slightly with ion content, which is expected as the ionic aggregates act as multifunctional crosslinks.¹⁴ However, as the ion content is increased, a second transition appears at higher temperatures and dominates at high ion contents (**Figure 3.1c**). The origins and explanations of these experimental observations were highly disputed for many decades, and the main theories attempting to unite the unexpected features will be covered in the next section.

3.3 Morphological models of random ionomers

In 1970, Eisenberg constructed one of the first models to describe the phase-separated morphologies of ionomers.¹⁰ It is well known that association between ions takes place in media of low dielectric constant.¹⁵ In ionomers, this driving force favors the

formation of ion pairs between the polymer-bound anion and the counteranion. Eisenberg proposed that the same driving force could cause ion pairs to associate into higher-order aggregates known as “multiplets” that consist of multiple ion pairs.¹⁰ Because ion pairs are anchored to polymer chains, the number of ion pairs within a multiplet, and therefore the size of the multiplet, is limited by the available surface area for the chains to occupy. Considering these steric factors, multiplets were postulated to be small (~ 10 Å in diameter) and spherical. At sufficiently high ion content, electrostatic interactions between multiplets were thought to favor the formation of a phase-separated “cluster” region that is rich in ionic material. Although the theoretical model did seem to explain the apparent two-phase mechanical behavior, it did not attempt to resolve the SAXS feature.

In another model by Marx and coworkers in 1973, the SAXS peak was thought to arise from interference between small ionic aggregates that exist as points on a paracrystalline lattice, where the lattice exhibits a moderate degree of order.¹⁶ Disorder in the lattice was believed to account for the single, broad peak seen in SAXS. The model did not allow for the formation of larger-scale agglomerates or clusters and was unable to describe two-phase behavior observed with DMA.

In 1983, Yarusso and Cooper developed a modified hard-sphere model that also assigned the SAXS peak to interference between small, spherical ionic aggregates, but the aggregates were proposed to display liquid-like order. The quantitative model fit the ionomer SAXS peak of sulfonated atactic polystyrene (SaPS) ionomers with great accuracy, and the size and shape of these aggregates were later verified with high-angle annular dark-field transmission electron microscopy images (**Figure 3.2b**).¹⁷ In this model, ionic aggregates are approximated as hard spheres with a core radius R_1 (**Figure 3.2a**).

Because polymer chains emanate from the ionic core, the radius of closest approach between aggregates R_2 must be greater than the radius of the aggregate ($R_2 > R_1$). The parameters R_1 and R_2 were found to be independent of ion content and neutralization levels, indicating that the size of the aggregates remained constant, but that their number density increased with increasing ion content. Although the model provided an excellent quantitative framework to fit the main SAXS peak, it failed to fit the small angle upturn and made no attempt to reconcile the mechanical behavior. Later, a similar model by Kinning and Thomas was developed that more effectively accounted for multi-body correlations and is now the standard model to fit ionomer SAXS patterns but again does not integrate the upturn.¹³

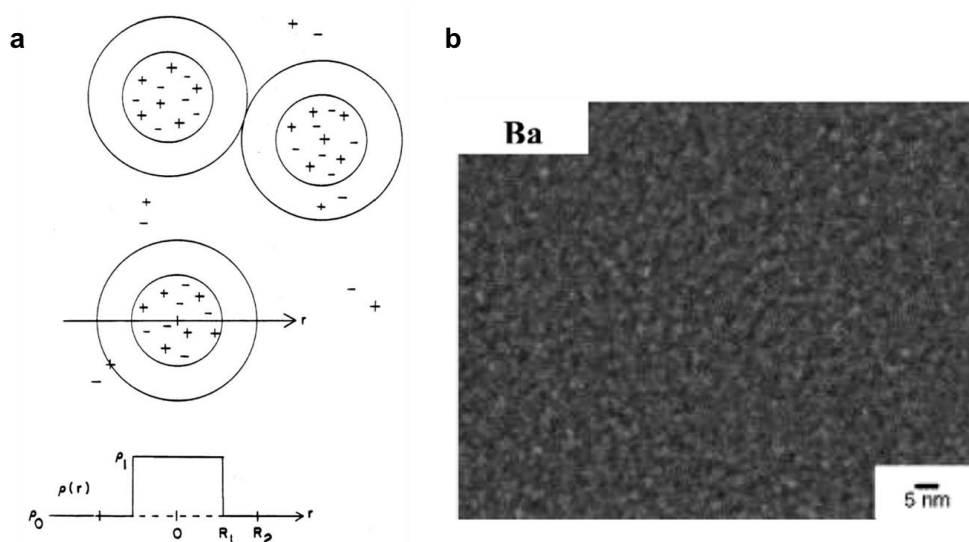


Figure 3.2. **a)** Schematic representation of the hard-sphere model, where R_1 is the ionic aggregate radius, R_2 is the hard-sphere radius, and ρ is electron density. Reprinted with permission from American Chemical Society.¹⁸ **b)** HAADF-STEM images of SaPS ionomers revealing monodisperse, spherical ionic aggregates. Reprinted with permission from American Chemical Society.¹⁷

In 1990, Eisenberg, Hird, and Moore published a new multiplet-cluster model (EHM model) that settled the presence of both the ionomer peak observed in SAXS and

the two-phase behavior seen in DMA,¹² and is the accepted framework for ionomer morphology.³ The EHM model defines a multiplet as it had been previously described by Eisenberg:¹⁰ an aggregate of ion pairs containing only ionic material (**Figure 3.3**). The SAXS peak is assigned to the *intermultiplet* spacing. For multiplets to form, the electrostatic forces between ion pairs must overcome the opposing elastic forces of the polymer chains. Ion pairs within the multiplet act as multifunctional crosslinks, anchoring the polymer chains, so the chains close to the multiplet have significantly less mobility than the chains in the bulk material. The layer of polymer chains around the multiplet is identified as the region of restricted mobility (RRM) and the thickness of the region is thought to be on the order of the persistence length of the bulk polymer chain.¹² It should be noted that the RRM need not be related to the thickness of the “shell” ($R_2 - R_1$) in the Yarusso-Cooper model.¹⁸

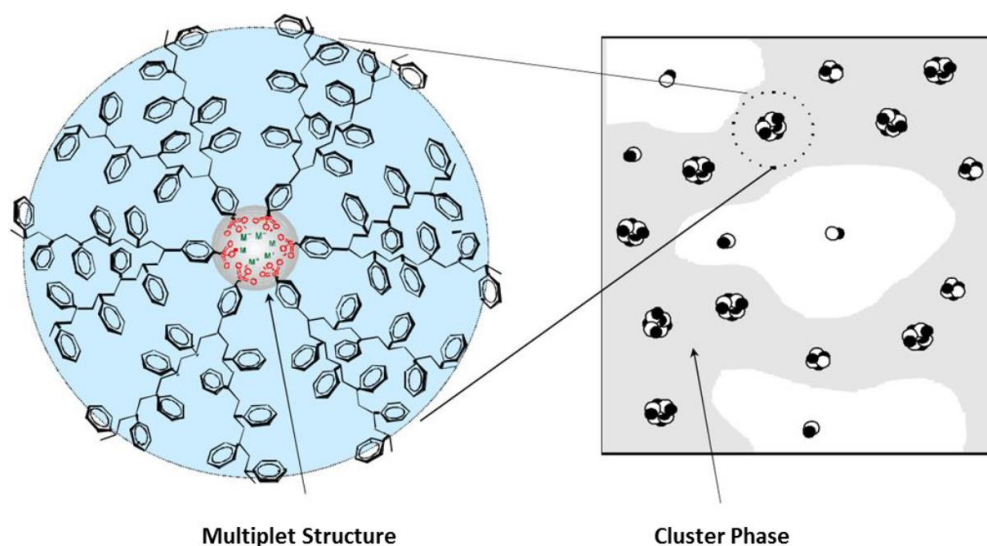


Figure 3.3. Schematic representation of a multiplet with the RRM (blue), as well as the contiguous cluster phase (shaded) that forms when the RRM overlap. Reprinted with permission from American Chemical Society.¹²

Due to the small size of the multiplets, the RRM surrounding an individual multiplet is too small to have its own T_g , so it cannot explain the large volume fraction of the second apparent phase seen by DMA (**Figure 3.1c**). Instead, the EHM model proposes that intermultiplet distances decrease with increasing ion content, causing the RRM of separate multiplets to overlap and form a contiguous “cluster” phase (**Figure 3.3**). Therefore, the low and high-temperature transitions in DMA are attributed to the unclustered and clustered material, respectively. The multiplets are thought to stay in tact during cluster formation, but do not exhibit strong multiplet-multiplet attraction. As such, the cluster phase is formed from the overlapping RRM, a conclusion that is consistent with the hard-sphere model, and not by agglomeration of multiple aggregates.¹⁸

While the EHM model does not place restrictions on the number of ion pairs or multiplets within a cluster, most ionic material is thought to exist in the cluster phase, whereas the regions between clusters are thought to consist primarily of nonionic polymer chains. The exact size of the cluster necessary to show two-phase behavior is not known, but based on block copolymer studies,¹⁹ the domain size must be at least 5-10 nm to be detected by DMA. A quantitative description of the size of the cluster phase is absent from the literature.

3.4 Debate over the origins of the small angle upturn

As demonstrated by the historical models above, the key feature of SAXS data used to describe ionomer morphology for many decades was the ionomer peak, which corresponded to the most prevalent spacing between multiplets. The universal upturn in scattered intensity at low q (**Figure 3.1a**) was disregarded in many early models. Given the

context, this dismissal was merited for several reasons. At the time, scattering instruments suffered from high background at low q because of additional scattering and smearing effects from the collimation system, as well as scattering from the beamstop. As such, Yarusso and Cooper first dismissed the upturn as merely an artifact from the instrument or data manipulation processes.¹⁸ Another reason this feature was justifiably ignored was that the small angle limit of SAXS instruments (around $q \sim 0.01 \text{ \AA}^{-1}$) shrouded any additional features that might be present at lower angles. Additional scattering intensity at low q suggests the presence of long-range correlations, so others posed voids or larger-scale impurities as explanations of the upturn.²⁰ Because ionomers are typically neutralized with inorganic salts, many believed the impurities could be particles of precipitated neutralization reagent.²⁰ However, an upturn in intensity had also been observed in pure polymers and acid-form ionomers that did not show an ionomer peak, contradicting this claim.¹⁶ Clearly, the origins of excess scattering of ionomers at very small angles were highly uncertain which limited integration of the upturn into early morphological models.

Regarding the small angle upturn, the initial question researchers sought to answer was whether the ionic material was a major contributor.²¹ A simple way to probe this question is to compare the scattering profiles of a neutralized ionomer to the pure polymer or acidic precursor. By assuming that any voids, non-ionic impurities, and thermal density fluctuations in the parent polymer are also in the ionomer, the difference between the ionomer and precursor profiles should yield the net scattering intensity of the ion content. This method is uncommon because the morphologies of the acidic and ionic form must be identical to make any real comparison, but at the time served as a rough approximation of the relative scattering contributions. In 1989, Wu and coworkers compared the scattering

profiles of Zn^{2+} and Na^+ -neutralized SaPS to the sulfonic acid form, shown in **Figure 3.4a**.²¹

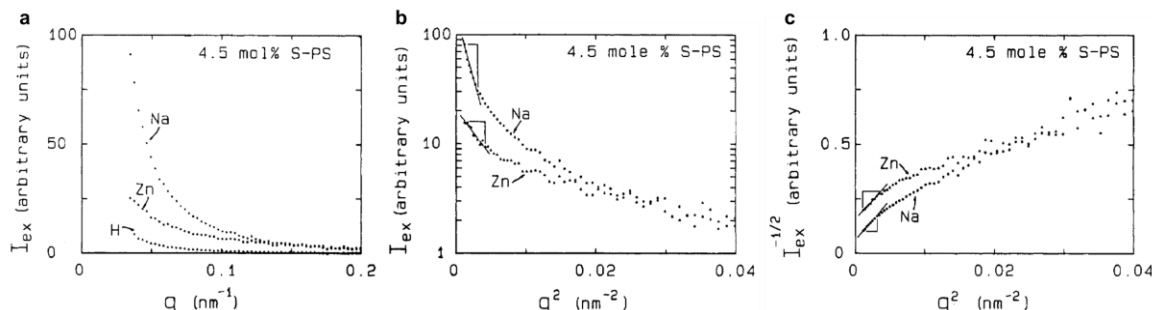


Figure 3.4. a) SAXS profile of 4.5 mol% SaPS with H^+ , Zn^{2+} , and Na^+ counterions. b) Guinier plot, where I_{ex} is the net scattering intensity of the ionomer using PS as the background. c) Debye-Bueche plot. Reprinted with permission from American Chemical Society.²¹

The small angle upturn was more intense in the neutralized ionomers compared to the acidic precursor, suggesting that the ionic material was a source of scattering. Interestingly, the upturn was more intense for the Na^+ -neutralized ionomer compared to the Zn^{2+} -neutralized ionomer. This observation is not consistent with behavior of the ionomer peak that generally increases in intensity with increasing atomic number of the counterion. Thus, the intensity of the upturn does not generally scale with electron density contrast, suggesting that another physical phenomenon may be a factor, such as the relative amounts of each phase. The authors estimated the size of the inhomogeneity by fitting the initial slope of the net intensity upturn using the Guinier approximation, which describes scattering from particulate systems as

$$I(q) = I(0)\exp\left(-\frac{R_g^2 q^2}{3}\right) \quad (3.3)$$

where $I(0)$ is the zero-angle scattering and R_g is the radius of gyration of the inhomogeneity (**Figure 3.4b**). The fits gave R_g values of 39 nm and 30 nm for the Na^+ and Zn^{2+} forms,

respectively, though the authors had little confidence in these values given the limited measurable data at low q . The authors also attempted to fit the upturn using the Debye-Bueche model, which is generally used to describe systems with random distributions of inhomogeneities in electron density by Equation 3.4,

$$I(q) = \frac{I(0)}{(1 + q^2\zeta^2)^2} \quad (3.4)$$

where ζ is the correlation length of the inhomogeneity (**Figure 3.4c**). Correlation lengths for the Na^+ and Zn^{2+} -form ionomers were determined to be 23 and 15 nm, respectively. Ultimately, the authors postulated from this comparative data that long-range spatial arrangement of isolated ion pairs was a plausible explanation of the upturn.

3.5 Anomalous X-ray scattering experiments

Advancements in instrument design and synchrotron radiation sources allowed for new experiments such as anomalous small angle X-ray scattering (ASAXS) to directly probe scattering from individual components of a sample. Simply, ASAXS is an element-specific contrast variation technique based on the concept that the scattering intensity of a particular element decreases when the energy of the incident beam is near the element's absorption edge because some of the X-rays are absorbed.²² The X-ray scattering factor of an atom as a function of incident energy is represented by

$$f = f_0 + f'(E) + if''(E) \quad (3.5)$$

where the energy-independent scattering is represented by f_0 (related to the atomic number), and the energy-dependent anomalous terms are represented by f' and f'' . In a typical experiment, two X-ray scattering patterns are collected using an incident beam with

two different energies: one far from the absorption edge, where f_0 dominates, and one close to the edge, where anomalous contributions appear. Subtracting these two scattering patterns yields a “difference pattern” that shows the scattering contribution from the element of interest.

In 1988, Ding and coworkers first reported using ASAXS to study an ionomer.²³ The authors irradiated Zn^{2+} -SaPS with X-ray energies 5 and 100 eV below the Ni K edge. Both the upturn and the ionomer peak were present in the difference pattern, providing additional evidence that the upturn was due to the neutralizing counterion. The Debye-Bueche two-phase model provided a correlation distance of approximately 100 nm which was assigned as the length scale of isolated ions in the matrix.

It is important to consider that an inhomogeneous distribution of cationic species could have many different physical bases. For example, possible scattering pairs involving the neutralizing cation that could give rise to this scattering are ionic aggregates/nonionic polymer, precipitated salts of the neutralizing base/polymer, and the bulk sample/voids. In 1990, Register and Cooper conducted a more thorough ASAXS study to narrow down the possible explanations.²⁰ The researchers prepared a series of SaPS ionomers neutralized with varying amounts of Ni^{2+} , and measured the scattering intensity using incoming X-rays both near and far from the Ni^{2+} K-edge. If the upturn was due to precipitated salts, then its intensity should increase with neutralization levels above 100 mol% where excess reagent would likely precipitate. However, the intensity of the upturn decreased with neutralization degree, even past stoichiometric equivalence, so the authors concluded that the upturn could not be due to precipitated neutralization reagent. In investigating voids as the possible cause, the authors hypothesized that because the sample-void scattering was

dominated by the contrast of the hydrocarbon matrix, the anomalous effects of Ni should be negligible. The authors compared the single-energy patterns to the difference pattern and found that they superposed identically, ruling out voids as a source of the upturn intensity. The study concluded that the ionic material/non-ionic material scattering pair was the source of the inhomogeneity, but again the authors could not specify the “form” of the ionic material (lone ion pairs, aggregates, etc.). The authors attempted to model the upturn with Debye-Bueche but failed, likely because the measurable portion of the slope was not large enough to yield a linear relationship.

3.6 Ultra-small angle X-ray scattering (USAXS) experiments

As mentioned by Register,²⁰ a challenge in fitting the upturn was the limited range of measurable angles using Kratky collimation systems. The development of the Bonse-Hart system allowed for a straightforward way to collect ultra-small angle X-ray scattering (USAXS) corresponding to structural dimensions on the order of several microns.²⁴ The Bonse-Hart apparatus utilizes Si crystals in an incident beam monochromator to precisely control the size and position of the incoming beam, as well as a detection path analyzer to reduce the scattering background to measure scattering at ultra-small angles.

In 1992, Chu and coworkers made use of a Bonse-Hart system in the first example of measuring USAXS of an ionomer.²⁵ The timing of this paper is noteworthy in that it was published soon after the EHM model in 1990.¹² Because of this, Chu and coworkers were the first to propose that the upturn could be due to the spatial arrangement of the cluster phase. In this case, the correlation length could represent the size of the overlapped region of restricted mobility of ion-rich domains.

The presence of a small angle upturn does not require the existence of a distinct cluster phase. This point is clearly seen in telechelic ionomers, polymers containing ions only at the chain ends, that display a small angle upturn but also do not form a distinct cluster phase.²⁶ A more general explanation posed by Moore and coworkers is that an inhomogeneous distribution of multiplets in the sample could give rise to excess intensity at low q .²⁷ In clustered materials, the inhomogeneous distribution of multiplets could represent the clustered/unclustered regions, whereas in unclustered materials, it could simply represent larger spatial heterogeneities between the multiplets.

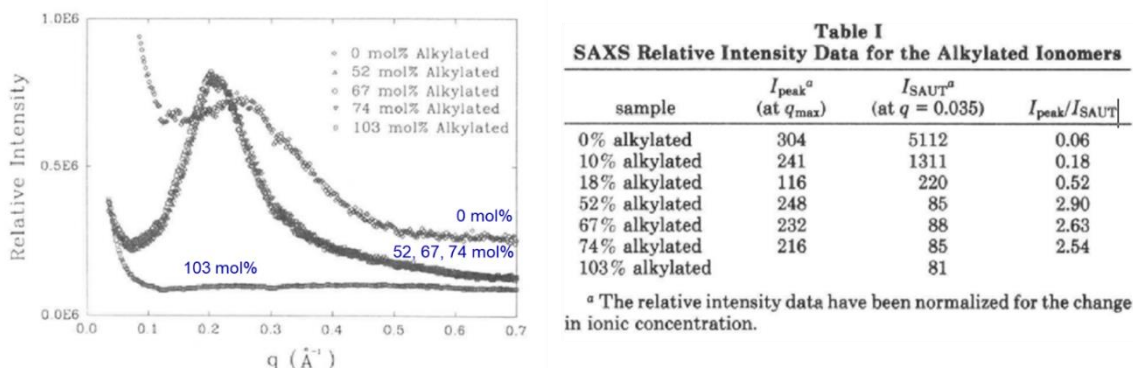


Figure 3.5. SAXS data for SaPS ionomers with varying degrees of alkylation. Labels added in blue for clarity. Adapted with permission from American Chemical Society.²⁸

In a study by Moore and coworkers, a series of polystyrene-methacrylic acid ionomers was functionalized with varying amounts of a plasticizing alkyl side chain to understand how plasticization influences the morphology as seen by SAXS.²⁷ As seen in **Figure 3.5**, the intensity of the upturn relative to the ionomer peak appears to decrease as the degree of alkylation is increased (**Figure 3.5**). Second, the onset of the upturn appears to shift to lower q with increasing degree of alkylation. The authors posed that the alkyl side chains, which lower the T_g of the polymer, facilitate the inclusion of lone ion pairs within multiplets since the elastic forces of the polymer chains are weakened, compared to the electrostatic interactions that favor multiplet formation. Therefore, as the degree of

alkylation is increased, a greater number of multiplets can arrange to form larger cluster domains. These larger cluster domains would scatter at lower angles which would cause an apparent decrease in intensity of the upturn at a particular location in the SAXS region (**Figure 3.5**). This data seems to provide evidence that the large-scale spatial arrangement of ions is not only influenced by ion content, but that the mobility of the polymer chains seems to play a role. The authors were not able to estimate the sizes of these domains due to the low q limit of SAXS.

In 1993, Li, Peiffer, and Chu conducted additional experiments on Na^+ , Zn^{2+} , and Rb^+ -neutralized SaPS ionomers using the Bonse-Hart apparatus and reported the merged USAXS/SAXS curves (**Figure 3.6**).²⁹ The authors stated that the curves over this broader q range were featureless, i.e., only power law slopes were observed. However, a slope change does appear to be present in the data at $\log q \sim 0.3$ and is well-removed from the ionic peak. It is unclear whether this is a true feature or an artifact of merging or background subtraction processes. The authors compared samples at different annealing and measurement temperatures and concluded that since the slope did not change shape, the upturn was due to the inherent chemical composition of the samples. However, these conclusions should be taken with prudence due to the quality of the data.

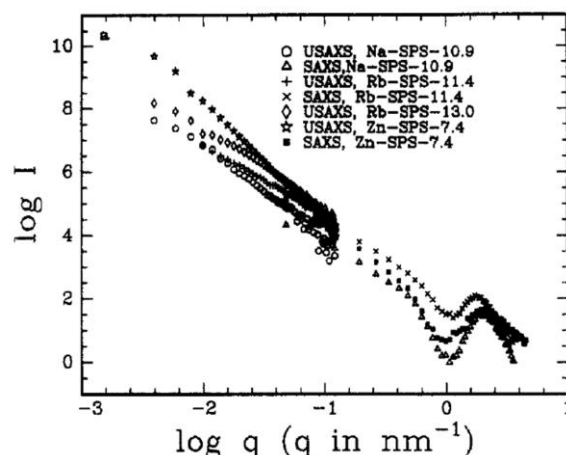


Figure 3.6. Merged USAXS/SAXS curves of SaPS ionomers. Reprinted with permission American Chemical Society.²⁹

Recently in the Moore Group, Fahs analyzed USAXS from sulfonated syndiotactic polystyrene (SsPS) ionomers with random and blocky microstructures.³⁰ Sulfonating in the heterogeneous gel-state is thought to preferentially functionalize the solvent-swollen amorphous chains, leaving long runs of pristine, unfunctionalized sPS units in what is known as a “blocky” microstructure.³¹ Fahs analyzed USAXS of random and blocky SsPS ionomers with varying ion content and observed a strong scattering feature of random ionomers in the USAXS region (**Figure 3.7a**). Interestingly, this peak was not present in the blocky ionomers at the same ion content (**Figure 3.7b**), which suggests that long-range order in ionomers depends on the microstructure at similar ion contents. Fahs attributed this feature to scattering from the cluster phase and modeled it as a set of polydisperse spheres. The peak shifts to higher q with increasing ion content, with mean radii ranging from 20 to 38 nm. If this feature truly emanates from correlations between the cluster and unclustered phase, then it agrees with the EHM model, which predicts that the intercluster spacing should decrease as the number of multiplets is increased. Another noteworthy observation is that the “ionomer peak,” clearly seen as a peak in the SAXS region of

random ionomers, has a different form in the blocky ionomers. In fact, the traditional Kinning-Thomas hard-sphere model with liquid-like order could not accurately describe the scattering profile, obfuscating information regarding the shape of the multiplets. In this study, no concrete structure-property relationships could be identified given the limited experimental techniques and variables explored.

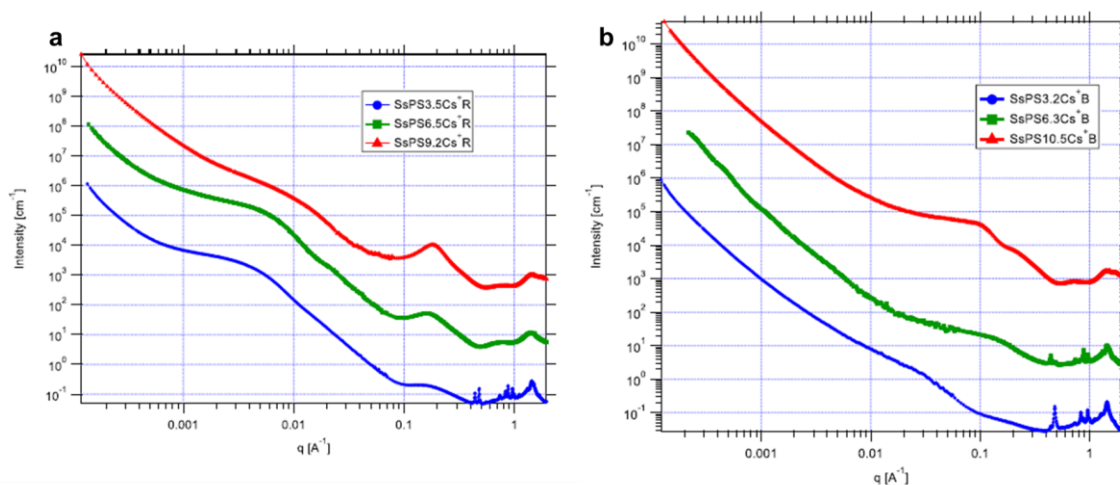


Figure 3.7. USAXS/SAXS/WAXS of **a)** random SsPS and **b)** blocky SsPS. Adapted with permission from Fahs, Virginia Tech, 2020.³⁰

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Chapter 4. X-ray Scattering as an Effective Tool for Characterization Liquid Metal Composite Morphology

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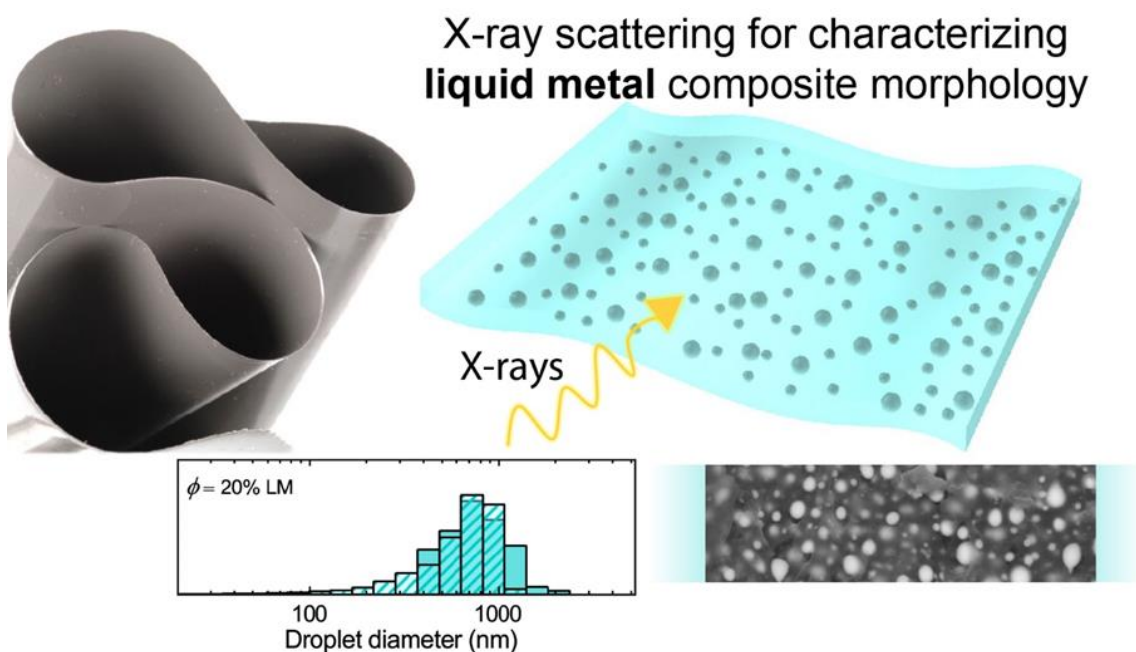
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TOC Image: X-ray scattering and scanning electron microscopy imaging techniques are used to characterize the droplet size distributions of a liquid metal filler in liquid metal/PDMS composites.



4.1 Abstract

Quantitative analysis of particle size and size distribution is crucial in establishing structure–property relationships of composite materials. An emerging soft composite architecture involves dispersing droplets of liquid metal throughout an elastomer, enabling synergistic properties of metals and soft polymers. The structure of these materials is typically characterized through real-space microscopy and image analysis; however, these techniques rely on magnified images that may not represent the global-averaged size and distribution of the droplets. In this study, we utilize ultra-small angle X-ray scattering (USAXS) as a reciprocal-space characterization technique that yields global-averaged dimensions of eutectic gallium indium (EGaIn) alloy soft composites. The Unified fit and Monte Carlo scattering methods are applied to determine the particle size and size distributions of the liquid metal droplets in the composites and are shown to be in excellent agreement with results from real-space image analysis. Additionally, all methods indicate that the droplets increase in size as they are introduced into composites, suggesting that the droplets agglomerate or possibly coalesce during dispersion. This work demonstrates the viability of X-ray scattering to elucidate structural information about liquid metal droplets for material development for applications in soft robotics, soft electronics, and multifunctional materials.

4.2 Introduction

Soft, stretchable materials with unique combinations of thermal and electrical functionalities have the potential to play a pivotal role in diverse fields ranging from soft robotics to deformable electronics.¹⁻³ These fields have seen tremendous growth in materials research and development in the past decade. In particular, soft, conformal

material systems based on low melting point metal alloys have garnered attention as solid–liquid composite systems. These metals include room temperature liquids such as gallium, eutectic gallium indium (EGaIn) and Galinstan (GaInSn), as well as Field’s metal that melts at 62°C.⁴⁻⁷ The gallium-based liquid metal alloys are attractive due to their low toxicity and viscosity, high thermal and electrical conductivity, and a surface oxide which rapidly forms a nanometer thick shell on droplets.⁸ Liquid metal materials and their composites have enabled unprecedented combinations of high thermal conductivity,⁹⁻¹¹ electrical conductivity,¹² and self-healing abilities in soft elastomers, as can be seen in **Figure 4.1**.¹³⁻¹⁴ To increase their adaptation in industry and to promote further development at the academic level, methods to tune the material properties and expand characterization techniques to elucidate the governing morphological features are being explored.

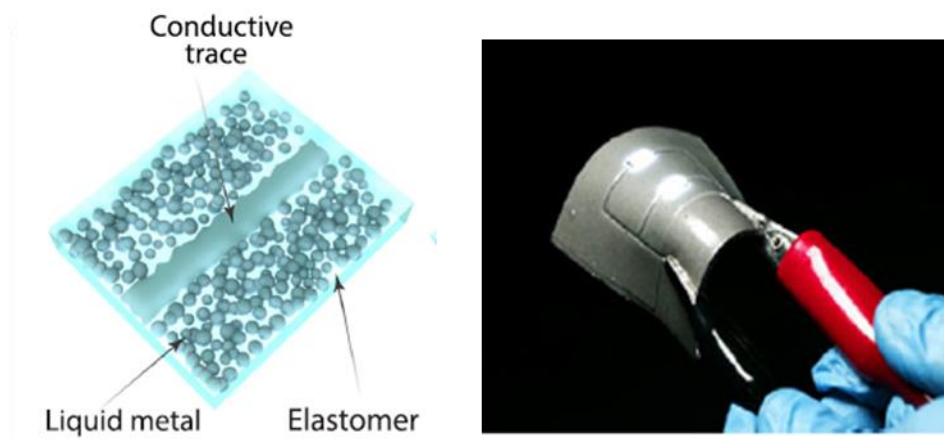


Figure 4.1. A representation of a liquid metal composite where conductive traces are formed through percolated networks of liquid metal, along with a photograph displaying the simultaneous flexibility and electrical conductivity of these materials.¹⁴

Soft composite systems have traditionally utilized rigid phase inclusions to enhance the functionality of the polymer matrix, including solid metal, ceramic, or carbon-based fillers. However, these rigid inclusions often result in undesirable changes to the bulk

mechanical behavior, such as reduced extensibility and increased stiffness, owing to the interfacial incompatibilities and the compliance mismatch that arises from the different mechanical properties of the rigid filler and the soft matrix.¹⁵⁻¹⁷ These tradeoffs in mechanical and functional properties are common features of rigid phase inclusion based polymer composites. Composites with liquid phase fillers can overcome this compliance mismatch for high stretchability and multifunctionality that is generally uncommon in polymer composites. As such, liquid filler composites are promising in applications of soft robotics, soft electronics, and reconfigurable matter that are pushing towards unconventional combinations of functional properties with soft and highly deformable mechanical responses. To this end, liquid metal-based soft composites have been developed, where the liquid metal droplets are dispersed in an elastomer matrix. In the composites, the droplets are dispersed in the liquid polymer phase through mixing or sonication and rapidly form an oxide shell during processing, which can help aid in dispersion without the need for surfactants or emulsifying agents.¹⁸⁻²⁰ The composites are then cured, resulting in a solid elastomer phase which encapsulates the dispersed liquid metal droplets. With liquid phase inclusions, the composite architecture must be designed to achieve desirable properties. For example, in liquid metal based soft composites, different droplet features can affect the ultimate material behavior, including the droplet shape, size, loading, and size distribution.²¹⁻²³ Therefore, characterization of droplet dimensions is critical to the design and development of soft composite materials.

In conventional composites, solid filler particle dimensions are often prescribed prior to composite fabrication; however, in liquid filler composites, liquid inclusions can change size and shape during material processing.²⁴ Thus, in order to determine liquid

droplet structures, post-fabrication analysis is required. Present techniques utilize imaging, either through optical or electron microscopy, and often image analysis to determine number-averaged size distributions of the inclusions.²⁵⁻²⁹ While these procedures are widely accepted, they are time-intensive and are only capable of analyzing a limited number of inclusions that are visible within a particular field of view. A technique for determining bulk, volume averaged size distributions is currently lacking. Thus, an alternative droplet characterization technique that can be effectively applied to reliably analyze the composite morphology is essential.

As an alternative to microscopy analysis of composite materials, X-ray scattering has been extensively used to characterize the shape, size, and interfaces of fillers in a wide variety of matrix materials.³⁰⁻³¹ Due to the reciprocal relationship between dimension and scattering angle, wide angle X-ray scattering (WAXS) provides structural information on the atomic scale (ca. 1 nm), small angle X-ray scattering (SAXS) characterizes structures on the order of 1–100 nm, and ultra-small angle X-ray scattering (USAXS) characterizes structures up to several microns in size. Thus, by measuring scattered X-rays over a broad angular range, information spanning several decades of length scales can be acquired. Most reports of X-ray scattering of composites consist of solid particles embedded in a solid matrix, such as silica-reinforced rubber (**Figure 4.2**).³²⁻³⁴

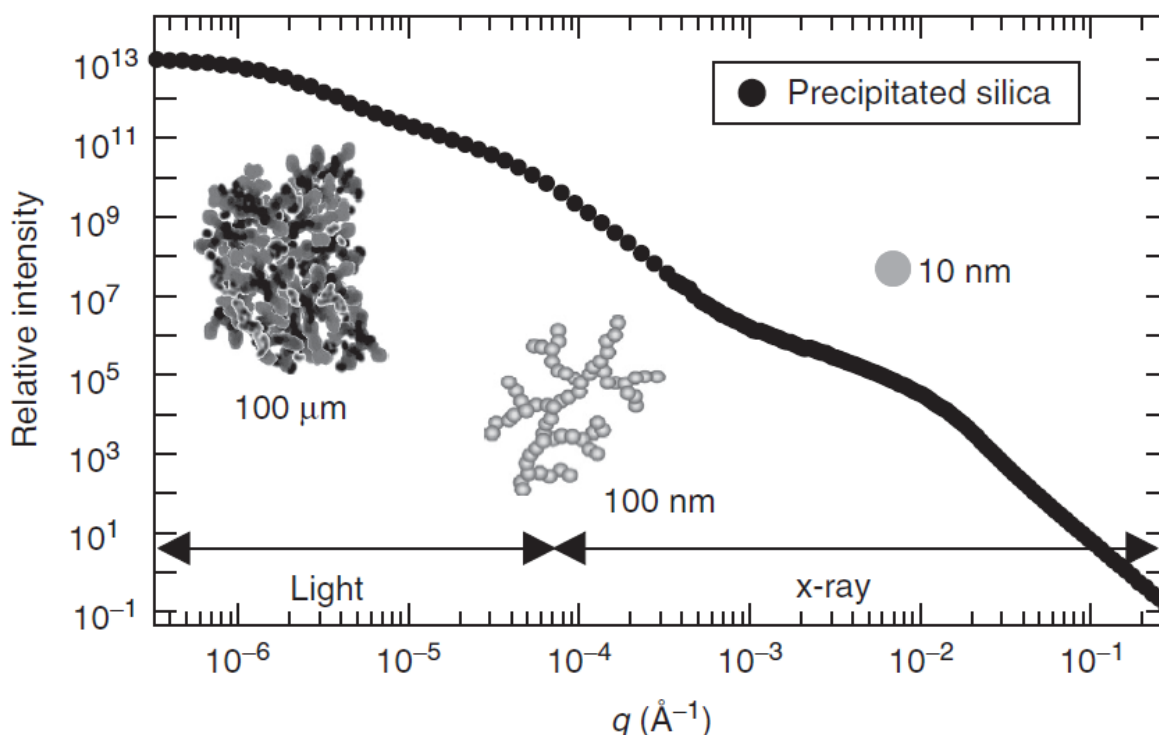


Figure 4.2. Hierarchical morphology of silica/rubber composites, a type of solid/solid composite system. SAXS, USAXS, and SALLS experiments capture the primary particle, the aggregate, and the agglomerate morphology. Reprinted with permission from Springer Nature.³⁵

In contrast, examples of scattering by liquid metal (LM) fillers are sparse. Wide angle X-ray diffraction has been used to probe the composition of multi-phase LM materials,^{17, 36-37} while SAXS has been used to confirm the presence of Ga particles in GaInSn³⁸ and to study orientation effects in an LM-embedded fiber.³⁹ A systematic morphological study of LM composites using X-ray scattering, particularly at length scales greater than 100 nm, is absent.

In this study, we report a systematic investigation of liquid metal soft composites using microscopy and X-ray scattering techniques. The purpose of this research was to demonstrate that X-ray scattering can be used as a complementary characterization tool to provide information about the droplet sizes and size distributions in liquid filler polymer

composites. To study the effects of filler loading, soft composites were prepared with nanodroplets (ca. 300 nm in diameter) of EGaIn LM dispersed as a filler in a poly(dimethylsiloxane) (PDMS) elastomer matrix at different volume loadings ($\Phi = 0.1\%$ to $\Phi = 20\%$ LM) (**Figure 4.3 a,b**). The local, real-space morphologies of the composites were analyzed using optical and scanning electron microscopy (SEM) (**Figure 4.3 c,d**) and compared to the global morphologies of the composites from analysis of USAXS. Through this work, X-ray scattering is shown to be a facile route to obtaining global-averaged droplet size distributions and informing how materials processing can influence the droplet sizes. One outcome of this analysis is that as LM droplets prepared in solution are dispersed into elastomeric composites, we find increasing droplet sizes, suggesting that the droplets are agglomerating or possibly coalescing in the composites. Given the myriad of materials based on liquid metal, the broader impact of this work is to accelerate the development of soft, functional composites through the establishment of structure–property–processing relationships in liquid metal-based materials.

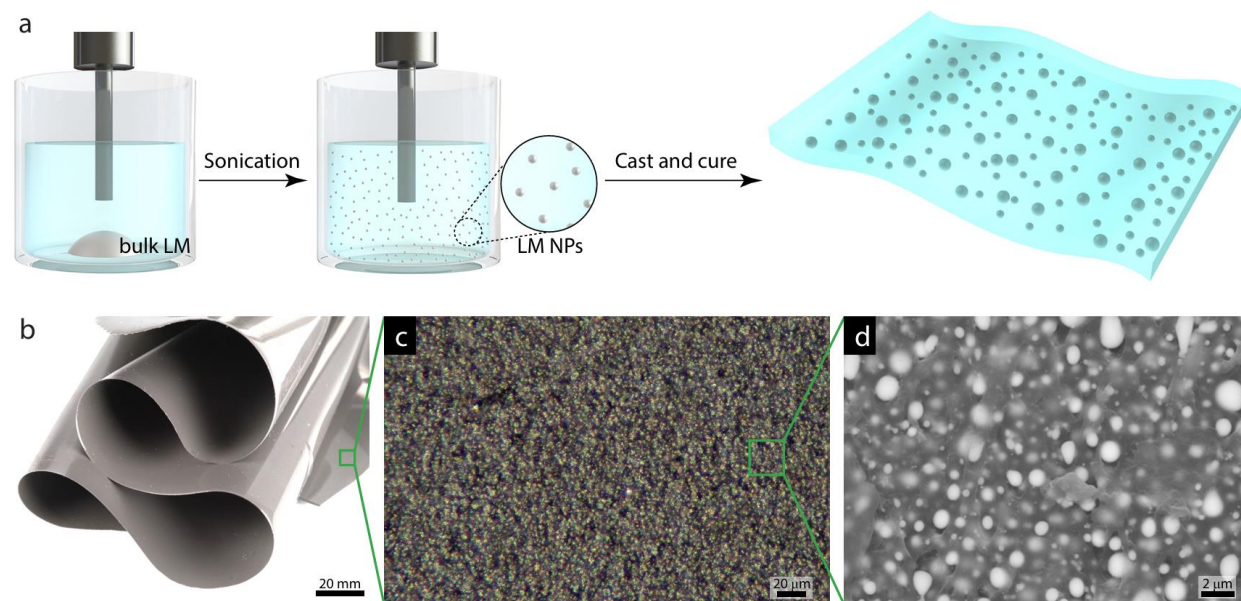


Figure 4.3. Liquid metal soft composites. **a)** Schematics showing the fabrication of LM nanodroplets using probe sonication. **b)** Photograph showing the flexibility of LM composites. **c)** Optical micrograph and **d)** SEM image of a composite showing general LM composite morphology.

4.3 Experimental Section

4.3.1 LM droplet and composite fabrication

Bulk LM was prepared by mixing Ga:In at a 3:1 ratio by mass, forming the eutectic alloy EGaIn. The pristine LM droplets were prepared by sonicating ca. 200 mg of bulk LM in 5 mL toluene solvent using a QSonica Q700 tip sonicator for 80 min at an amplitude of 30%. The LM/PDMS composites were fabricated by dispersing the LM droplets in a two-component silicone elastomer (Dow® Corning Sylgard 184). The silicone prepolymer was prepared by combining parts the base and curing agent at a 10:1 ratio by mass, respectively, in a planetary centrifugal mixer (FlackTek Speedmixer). The toluene was decanted from the droplet dispersion prior to transferring the droplets to the prepolymer mixture. For higher LM loadings ($\Phi = 10, 20\%$), multiple batches of sonicated droplets were combined to achieve the desired mass and then, toluene was decanted. The prepolymer/LM droplet

mixture was mixed again for ca. 20 min under vacuum to create an emulsion and to remove any residual toluene. The final mass of the mixture was measured and compared to the amount of LM droplets and prepolymer added to ensure complete toluene removal before casting. The final mixture was cast on a glass slide with a Universal applicator (ZUA 2000; Zehntner Testing Instruments), creating a composite film approximately 70 μm thick. The films were cured in a convection oven at 80°C for 12 hours. All fabrication procedures were carried out at ambient conditions.

4.3.2 Optical microscopy

The optical micrograph of the composite film was obtained using a Zeiss Axio Zoom v16 stereo microscope.

4.3.3 Scanning electron microscopy

To characterize the morphology of the droplets prior to loading them into the PDMS matrix, a sample of the pristine droplets was prepared. The LM droplet sample was prepared by pipetting the LM droplet/toluene dispersion onto an adhesive carbon tape attached to an SEM standard pin stub and allowing it to dry overnight at room temperature to allow for toluene evaporation. To prepare the composite films for SEM analysis, the composite films were sandwiched between two layers of PDMS to create a thicker sample and allow for easier handling during the subsequent sample preparation steps. To accomplish this, a 500 μm layer of PDMS was first cast on a glass slide using the ZUA 2000 Universal applicator and cured at 80°C for 2 hours. Next, the cured composite film was placed on the PDMS layer. Next, a second 500 μm layer of PDMS was cast on top and cured at 80°C for another 2 hours. The sandwiched composite film was frozen in liquid nitrogen to crystallize the LM droplets and a razor blade was used to cut the sandwiched

sample, exposing the interior of the LM composite. The sample cross-section was then attached to an adhesive carbon tape on the SEM standard pin stub and sputter coated with a Pt–Pd layer of ~10 nm thickness prior to SEM analysis. The micrographs were obtained on a FEI Quanta 600 FEG-SEM in back-scattered electron (BSE) mode at a spot size of 4 and an accelerating voltage of 20 kV. The BSE mode was ultimately chosen for the analysis due to the enhanced contrast between the matrix and the droplets and a greater penetration depth into the sample compared to the secondary electron mode, as will be discussed later. The droplet sizes in the SEM micrographs were analyzed using Fiji image analysis software. Details about the method used to analyze these images are discussed in Section 4.4.1.

4.3.4 X-ray scattering characterization

The pristine LM droplets were prepared for X-ray scattering analysis by pipetting the LM droplet emulsion in toluene onto a polyimide substrate and allowing the toluene to evaporate at room temperature overnight. The LM droplet/polyimide sample was then mounted onto a solid sample plate for analysis. The composites were analyzed by mounting the as-prepared LM composite films onto a solid sample plate.

Ultra-small-angle X-ray scattering (USAXS) measurements were conducted at beam line 9-ID-C at the Advanced Photon Source at Argonne National Laboratory (Lemont, Illinois).⁴⁰⁻⁴¹ The USAXS/SAXS instrument was configured with an X-ray energy of 21 keV ($\lambda = 0.5895 \text{ \AA}$), an X-ray photon flux $5 \times 10^{12} \text{ mm}^{-2} \text{ s}^{-1}$, and a combined q range of $1 \times 10^{-3} \text{ nm}^{-1}$ to 1 nm^{-1} . As discussed previously in this dissertation, the scattering vector, q , is defined by Equation 4.1:

$$q = \frac{4\pi}{\lambda} \sin(\theta) \quad (4.1)$$

where q is the scattering vector, λ is the wavelength and θ is 1/2 of the scattering angle). The Irena program was used to reduce the 2D USAXS detector profiles into 1D datasets (intensity vs. scattering vector, q) and to remove the effects of collimation-dependent instrumental smearing to generate desmeared USAXS scattering profiles.⁴² The observed scattering features of the desmeared USAXS profiles were analyzed using the Unified fit by Beaucage,⁴³ and the maximum entropy size distribution method^{43,44} described in the Irena tool suite.⁴² The open-source McSAS software package developed by Breßler and coworkers was used to obtain Monte Carlo droplet size distributions from the desmeared USAXS data.⁴⁵

Wide angle X-ray scattering experiments were performed to confirm the presence of the amorphous composite components using a Xenocs Xeuss 3.0 SAXS/WAXS, equipped with a GeniX 3D Cu HFVLF microfocus X-ray source with a wavelength of 0.154 nm (Cu K $_{\alpha}$). The sample-to-detector distance was 55 mm for WAXS, and the q -range was calibrated using a lanthanum hexaboride standard. The 2D WAXS patterns were obtained using a Dectris EIGER 4M detector and reduced to 1D intensity vs. q profiles using the XSACT software provided by Xenocs. The scattering length densities (SLD) of PDMS and EGaIn were calculated using the NIST Scattering Length Density Calculator found online.

4.4 Results and discussion

4.4.1 SEM image analysis

The SEM micrographs of the pristine LM droplets and the LM composites were analyzed to characterize the real space morphology and to determine the droplet dimensions. An example SEM micrograph collected in secondary electron mode is shown in **Figure 4.4**. The LM droplets and aggregates appear as rough features embedded underneath the PDMS matrix. The secondary electron data collection mode produced images with less contrast between the droplets and the matrix compared to the backscattered electron mode, as well as a lower penetration depth, so was not chosen for further data collection.

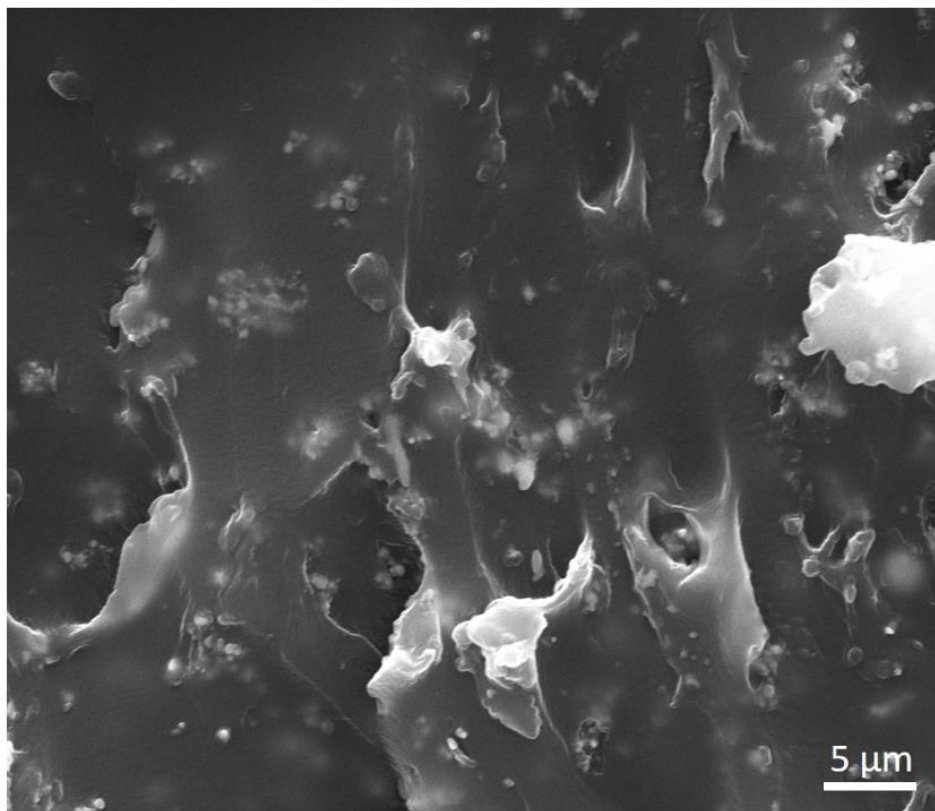


Figure 4.4. SEM image of the liquid metal composite ($\Phi = 2\%$) in the secondary electron (SE) mode.

The general analysis sequence of the backscattered electron mode SEM images is shown in **Figure 4.5** with the SEM micrographs for the pristine LM droplets in **Figure 4.5a** and $\Phi = 20\%$ LM composite in **Figure 4.5b**, with the remaining compositions discussed below. Using the image analysis tools in the Fiji software, the SEM images were first adjusted for brightness and contrast and converted into a binary format, as shown in **Figure 4.5 c,d**. The bright regions in **Figure 4.5 c,d** are associated with the LM droplets, and the dark regions represent the background or PDMS matrix for the pristine droplets and composites, respectively. Next, the connected particles were separated, which involved careful observation of the pre- and post-processed images to guarantee correct boundaries.

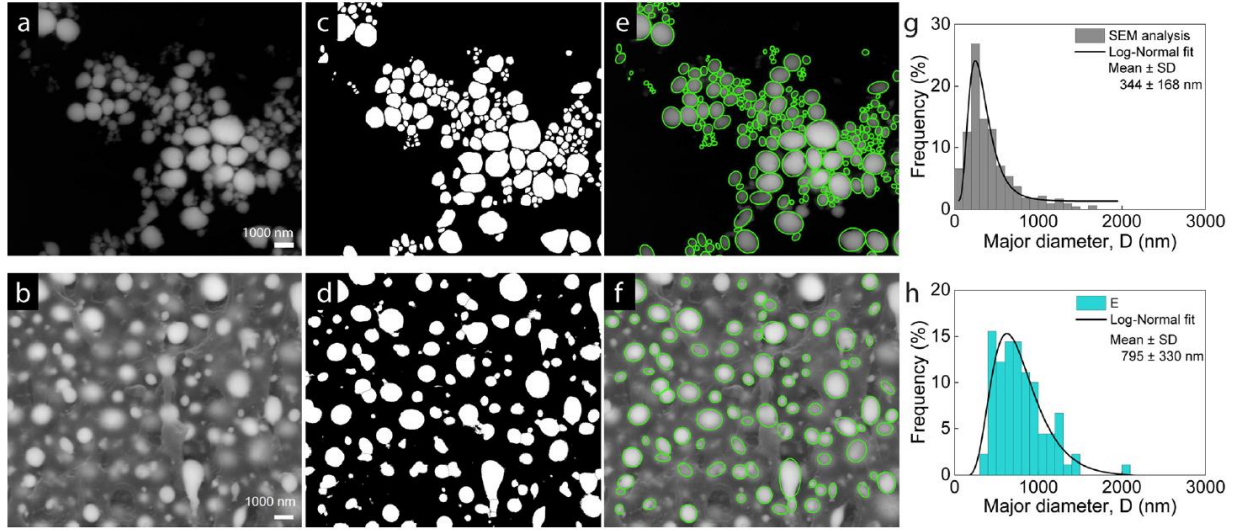


Figure 4.5. Image analysis sequence applied to SEM micrographs collected in backscattered electron mode of **a)** LM droplets fabricated through the sonication technique. **b)** $\Phi = 20\%$ LM composites made by dispersing the droplets in PDMS. **c,d)** Binary masks generated from the SEM images in **a)** and **b)**. **e)** and **f)** Ellipse fit to the bright droplet areas in **c)** and **d)** and overlaid on the actual image, **g,h)** major diameter of the ellipses in **e)** and **f)** are plotted to obtain histograms and mean size using a log-normal fit.

The resulting isolated bright regions shown in **Figure 4.5 c,d)** were considered individual droplets, and their areas were calculated by generating the best fit ellipse for the respective area. The ellipse fits were overlaid on the original micrograph as green outlines and can be seen to represent the particles well (**Figure 4.5 e,f)**. This analysis sequence was performed for all compositions of composites, and the remaining LM composite SEM images are shown in **Figure 4.6**.

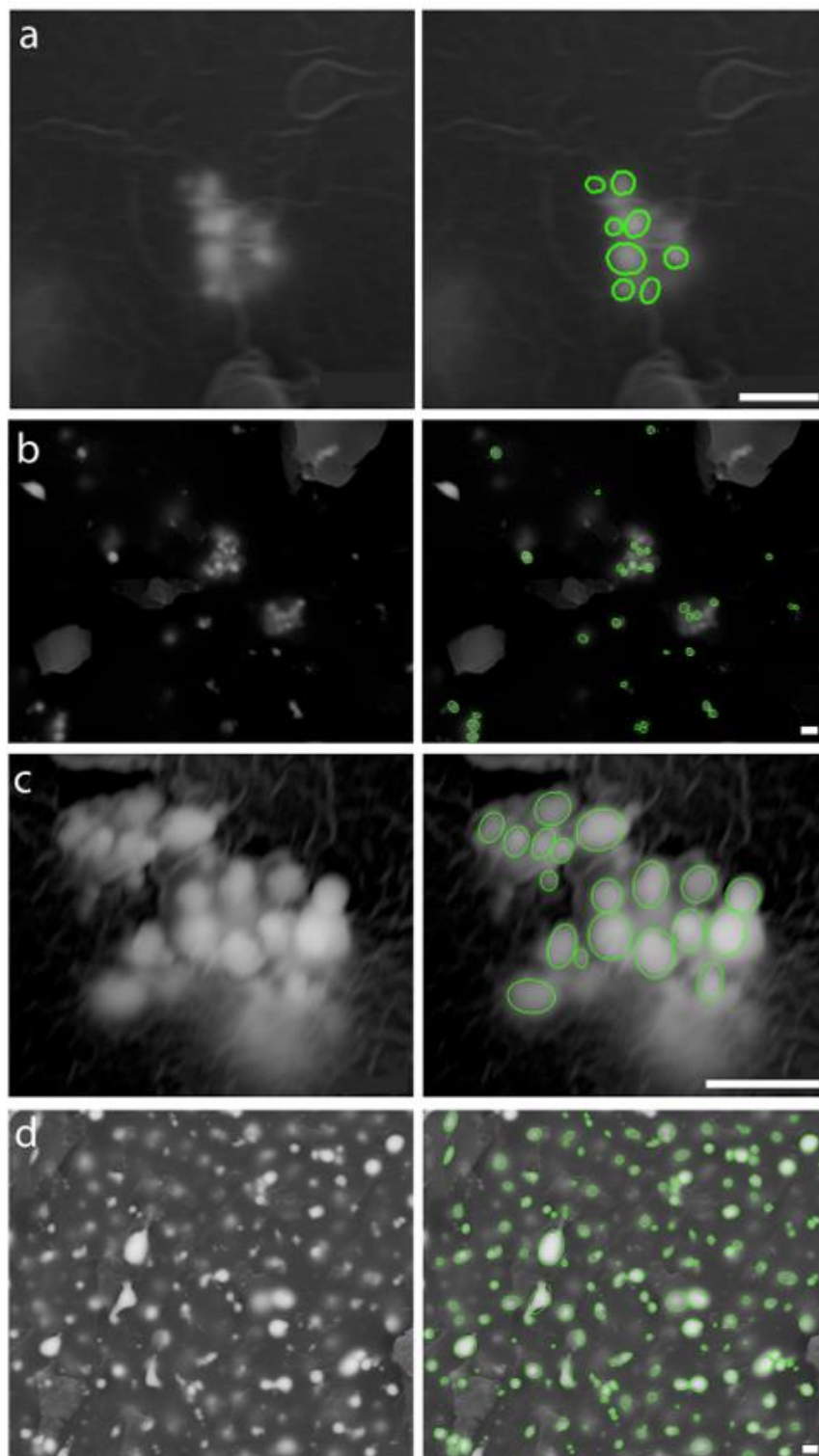


Figure 4.6. Ellipse fits as green outlines on the analyzed LM droplets for the composites with **a)** $\Phi = 0.1\%$ **b)** $\Phi = 1\%$ **c)** $\Phi = 2\%$ **d)** $\Phi = 10\%$. Scale bars represent 1000 nm (1 μm).

In each processed image, the major and minor axes of the fit ellipses were obtained, and the droplet size was represented by the major axis of the ellipse. The size distributions from image analysis are shown as the frequency % droplets analyzed vs. major diameter (D). To demonstrate this process, representative droplet size distributions in the pristine LM droplets and $\Phi = 20\%$ LM composite are shown in **Figure 4.5 g,h**, and the remainder of the compositions are presented and discussed below. A log-normal fit was performed on the plotted size distribution histograms, yielding a mean diameter of 344 ± 168 nm for the pristine LM droplets and 795 ± 330 nm for the $\Phi = 20\%$ LM composite. These initial results suggest that the initial measured LM droplet size of 300 nm increases to approximately 800 nm as the droplets are incorporated as a filler into the PDMS matrix.

To ascertain why the measured droplets were larger in the composites compared to the precursor droplet dispersion, an experiment was conducted to determine at what step during the fabrication procedure the droplets increase in size. This scientific question was tested by comparing the sizes of the pristine, sonicated droplets to the same batch of droplets in a 20% LM composite after shear mixing. The initial droplet diameter after sonication in toluene was 302 ± 202 nm and increased to 468 ± 306 nm upon shear-mixing in PDMS in a Flacktek speedmixer at 800 rpm for 15 min. The SEM image analysis is presented in **Figure 4.7**. From this experiment, it was concluded that the shear forces involved in mixing the LM droplets into the uncured matrix were likely responsible for the droplet size increase, by either aggregation or coalescence of smaller particles.

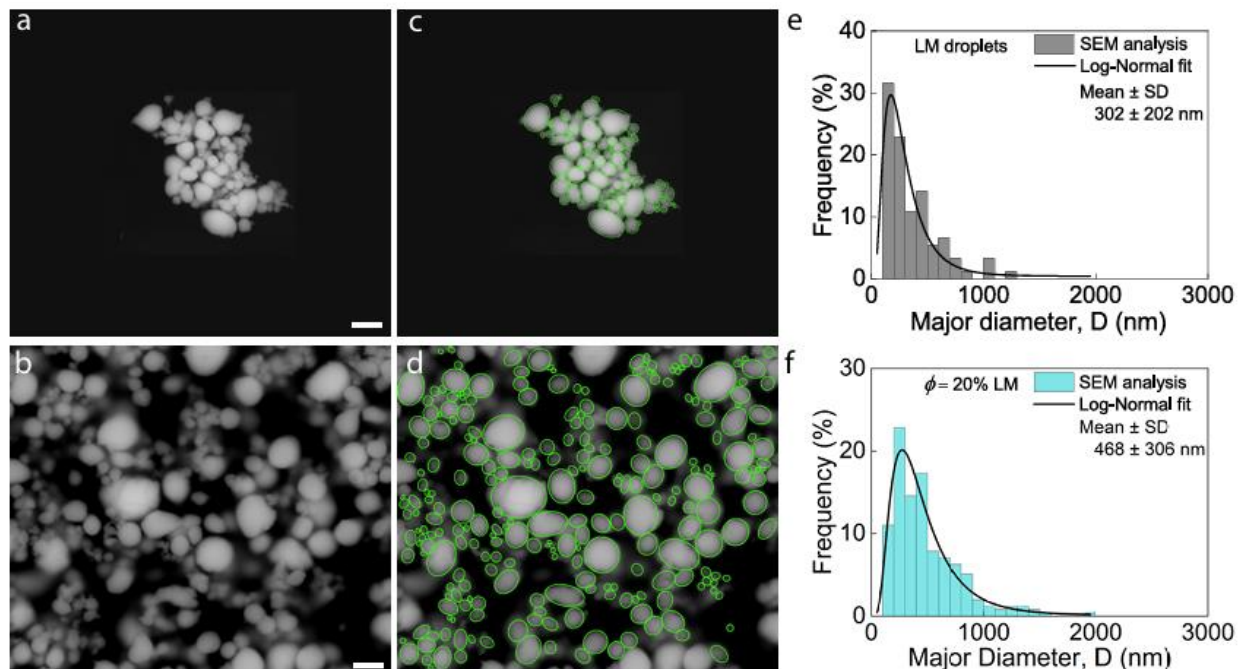


Figure 4.7. SEM image of **a)** LM droplets fabricated through the sonication technique. **b)** $\Phi = 20\%$ LM composite made by dispersing the droplets in PDMS by shear mixing at 800 rpm in a Flacktek speedmixer for 15 min. **c,d)** Ellipse fits the LM droplets in **a)** and **b)** and overlaid on the actual image. **e,f)** Major diameter of the ellipses in **c)** and **d)** are plotted to obtain distribution histograms and mean size using a log-normal fit. Scale bars represent 1000 nm (1 μm).

4.4.2 X-ray scattering analysis

Based on the size scale of the particles determined from SEM analysis and as noted in the introduction, it was hypothesized that these materials would display size-dependent scattering features in X-ray scattering experiments. The morphological characterization of the LM droplets and composites over a wide range of length scales was performed using USAXS/WAXS.

4.4.2.1 WAXS Analysis

First, the small-scale scattering features of the materials were characterized by wide-angle X-ray scattering (WAXS). The WAXS profiles of the pristine PDMS and LM

composites are shown in **Figure 4.8**. In the WAXS profiles are features that arise from the LM phase and the amorphous PDMS matrix. All samples exhibit features due to the PDMS matrix: a strong maximum at $q = 8.5 \text{ nm}^{-1}$, attributed to interchain spatial correlations, along with a shoulder around $q = 15 \text{ nm}^{-1}$, assigned to intrachain spatial correlations.⁴⁶ WAXS profiles of the composites display two broad features originating from the interatomic distances in EGaIn, with a maximum at $q = 25 \text{ nm}^{-1}$ and a shoulder at $q = 32 \text{ nm}^{-1}$, consistent with prior analysis of LM-containing materials.¹⁷ As expected, the intensity of these interferences increases with liquid metal content. The absence of sharp reflections confirms that EGaIn remains in the liquid state within the composite.⁴⁷

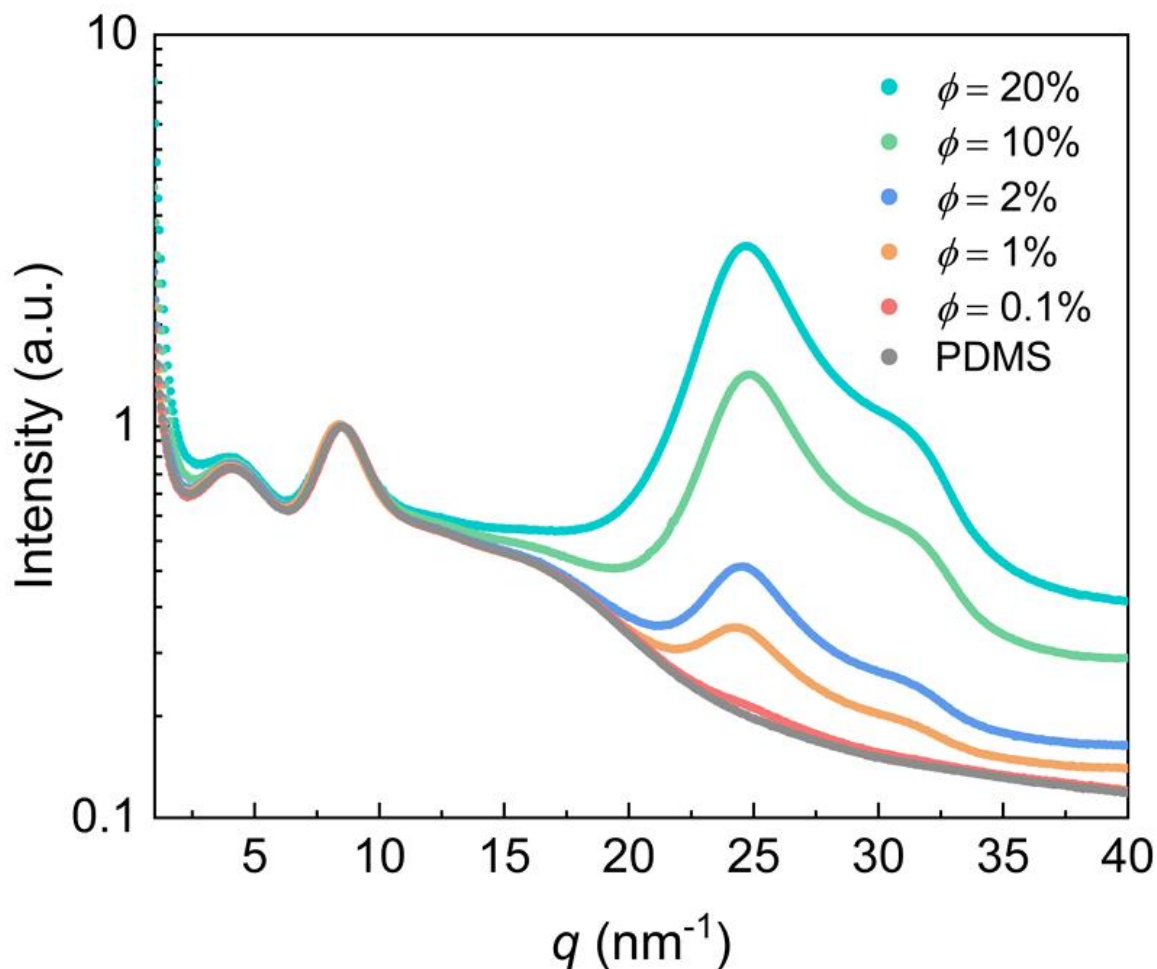


Figure 4.8. WAXS profiles of pristine PDMS elastomer and LM composites with $\Phi = 0.1, 1, 2, 10, 20\%$. The data are normalized by the matrix feature at $q = 8.5 \text{ nm}^{-1}$.

4.4.2.2 USAXS Analysis

Desmeared USAXS profiles (intensity vs. scattering vector, q) of the LM droplets and composites at various LM loadings ($\Phi = 0.1, 1, 2, 10, 20\%$) are shown in **Figure 4.9**. This data compares the effects of droplet processing and filler loading on the X-ray scattering features of these materials. The unfilled PDMS matrix is not shown for comparison because the featureless weak scattering in the USAXS region is essentially identical to the background. Given the high contrast in electron density between EGaIn

($\text{SLD}_{\text{X-ray}} = 4.5 \times 10^{-5} \text{ \AA}^{-2}$) and PDMS ($\text{SLD}_{\text{X-ray}} = 8.8 \times 10^{-6} \text{ \AA}^{-2}$), the pristine LM droplets and composites show intense scattering, indicating structure on the nanometer to micron length scale (**Figure 4.9**).

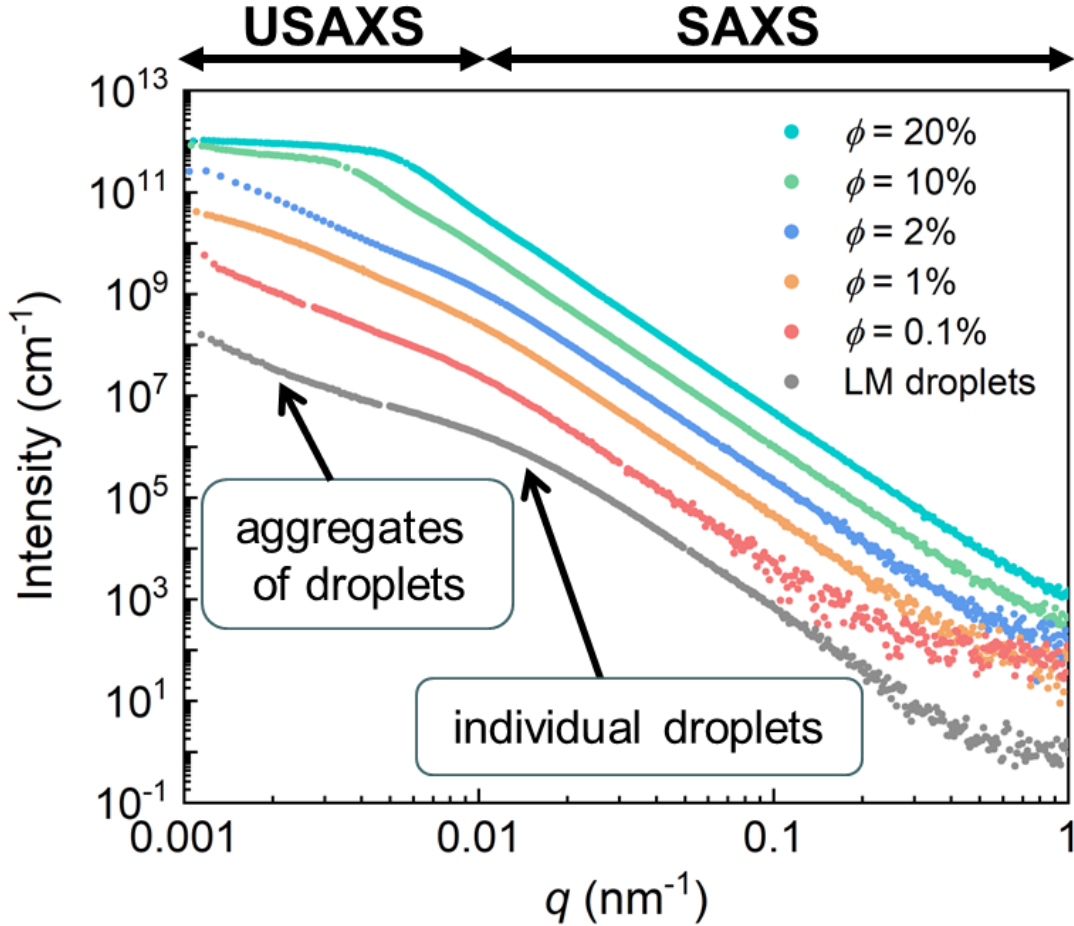


Figure 4.9. Desmeared USAXS profiles of the LM droplets and composites at various LM loadings ($\Phi = 0.1, 1, 2, 10, 20\%$). The LM droplet profile is on the original scale, and all other profiles are vertically offset for clarity.

Because the scattering intensity depends not only on the form factor (size and shape) of the scattering entities, but also on the structure factor (spatial distribution of particles), it is important to identify the concentration regimes where the structure factor becomes significant.⁴⁸ Concentration effects were studied by using the method described

by McGlasson,⁴⁸ and the concentration series was plotted as I/Φ vs. q (**Figure 4.10**). The curves superimpose at intermediate q ($0.01 \text{ nm}^{-1} < q < 0.1 \text{ nm}^{-1}$), consistent with composites with scattering from the same structure (EGaIn droplets). However, the scattering curves of the $\Phi = 10$ and 20% LM composites show significantly reduced scattering intensity at low q ($0.001 \text{ nm}^{-1} < q < 0.003 \text{ nm}^{-1}$) due to overlap of droplet/aggregate features consistent with a semidilute regime.⁴⁸ As will be discussed later, due to the presence of interdroplet interactions in all of the composites, it is likely that the dilute regime is below $\Phi = 0.1\%$, so all samples reside in the semidilute regime. In order to quantify characteristic dimensions from these data, the scattering profiles were quantitatively analyzed using a modified Unified fit approach and a Monte Carlo model.

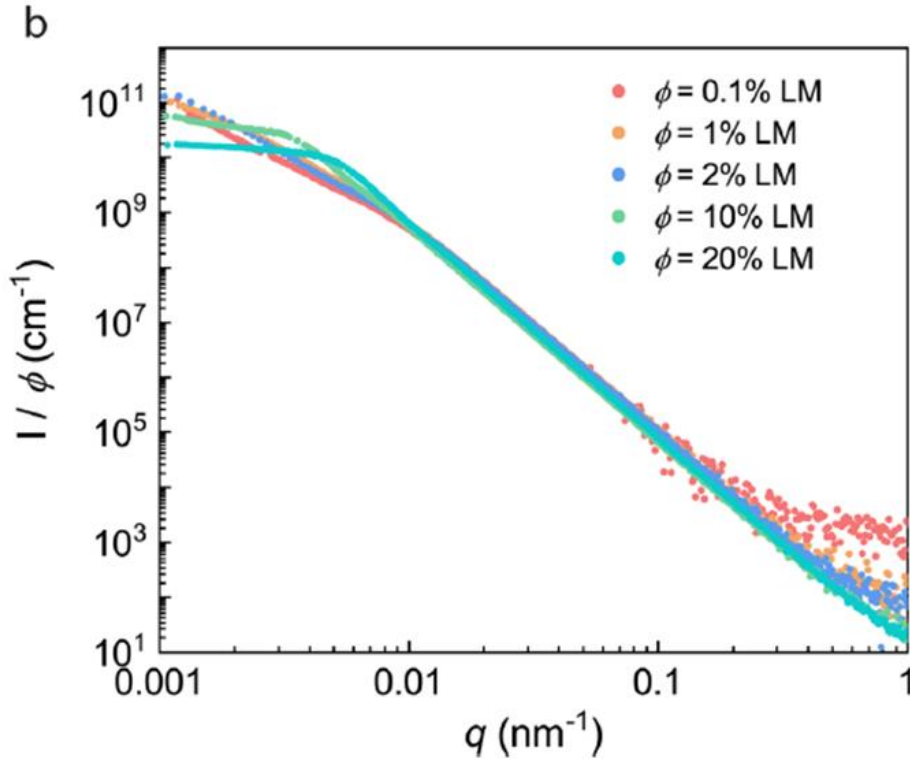


Figure 4.10. Reduced scattering curves normalized for the volume loading Φ of the liquid metal filler.

4.4.3.1 Unified fit analysis

The Unified fit approach developed by Gregory Beaucage has been used extensively to quantitatively analyze scattering profiles from heterogeneous systems having hierarchical structure.^{43, 49-50} In this model, the knee-like features (e.g., the slope change occurring around $q = 0.01 \text{ nm}^{-1}$ in the LM droplets profile (**Figure 4.9**) are interpreted as corresponding to the Guinier regime, defined by Equation 4.2 as:

$$I(q) = I_0 e^{\left(\frac{-q^2 R_g^2}{3}\right)} \quad (4.2)$$

where the radius of gyration, R_g , describes the shape-independent size of the scattering object, and I_0 is the zero-angle scattering.⁴³ Distinct power law regimes that appear as linear regions in the log/log plot are also modelled using the Unified approach. This region, known as the Porod regime, probes length scales smaller than that of the corresponding scattering entity for that level, such as the surface of the particle, and is given by Equation 4.3 as:

$$I(q) = I_0 + Bq^{-P} \quad (4.3)$$

where B is the power law prefactor, I_0 is the zero-angle scattering, and P is the power law exponent.

The value of the power law exponent P can provide information regarding the surfaces and interfaces between the particle and matrix in composites.⁴³ For structures characterized by a sharp and smooth interface between the particle and matrix, Porod's law will be satisfied and the power law regime will scale as q^{-4} ($P = 4$).⁵¹ However, particles with rough surfaces give rise to power law scaling relationships that are characteristic of the dimensionality of the interface. For example, power law scaling exponents between 3

$< P < 4$ are characteristic of surface fractals with dimension $d_s = 6 - P$,⁵² and exponents between $2 < P < 3$ are characteristic of mass fractals where particles are arranged in a self-similar fashion with a mass fractal dimension of $d_f = P$.^{49,52}

The Unified fit approach by Beaucage combines contributions from Guinier and Porod regimes into a single level, i , consisting of a knee and a power law regime in the Unified equation:^{43, 53}

$$I_i(q) = G_i e^{\left(\frac{-q^2 R_{g,i}^2}{3}\right)} + e^{\left(\frac{-q^2 R_{g,co,i}^2}{3}\right)} B_i \left\{ \frac{\text{erf}\left(\frac{kqR_{g,i}}{\sqrt{6}}\right)^3}{q} \right\}^{P_i} \quad (4.4)$$

where k is a constant related to the power law decay,^{49,52} G_i is the Guinier prefactor for scatterer i , $R_{g,i}$ is the radius of gyration of the scatterer, B_i is the power law prefactor, erf is the error function, P_i is the power law exponent, and $R_{g,co,i}$ is the high- q cutoff equal to $R_{g,i-1}$. In general, level 1 is understood to correspond to scattering from the smaller structures (i.e., the primary particles for nanocomposites), whereas level 2 is understood to correspond to a larger structure, such as the aggregates or agglomerates in nanocomposite systems.

4.4.2.3.1 Mass fractal aggregate analysis via the Unified equation

The $\Phi = 0.1, 1$, and 2% LM composites display two structural levels of scattering (**Figure 4.9**). As a representative example, the $\Phi = 2\%$ LM composite scattering profile modelled using two structural levels of the Unified equation is shown in **Figure 4.11**. Structural level 1 consists of a knee-like region (i.e., the Guinier regime) which is related

to the size of the primary LM droplets. The radius of gyration associated with scattering from level 1 ($q > 0.008 \text{ nm}^{-1}$) was determined as $R_{g,1} = 220 \pm 2 \text{ nm}$.

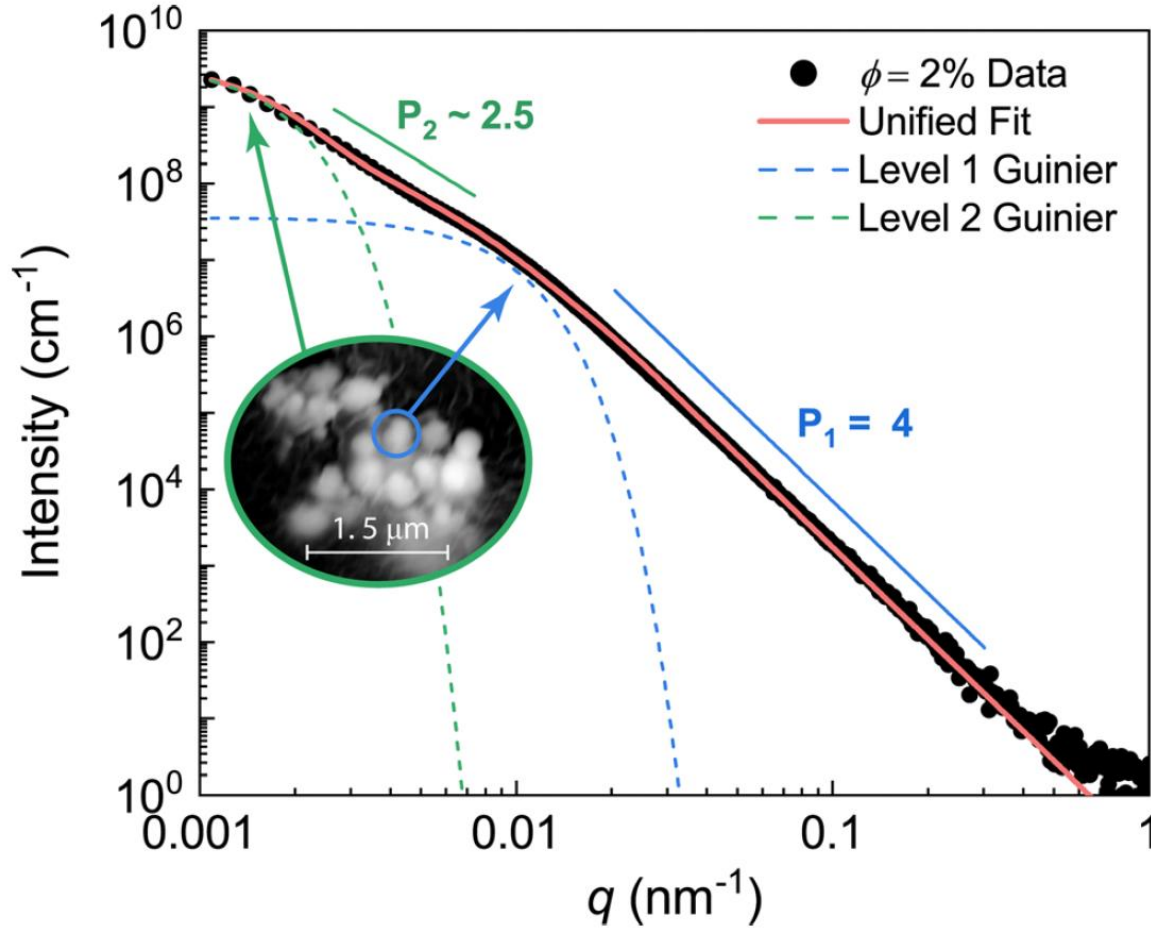


Figure 4.11. Two-level Unified fit of $f = 2\%$ LM composite. Structural level 1 represents scattering from the primary droplets, and structural level 2 represents scattering from the mass-fractal LM aggregates. The fit parameters can be found in Table 1 (level 1) and Table 2 (level 2).

Based on the SEM images (**Figure 4.6**), the droplets were reasonably assumed to be approximately spherical. The radius of gyration from the Guinier region of the Unified fit can be related to the diameter of a spherical particle, D , through Equation 4.5:⁵¹

$$D = 2 \times \frac{R_g}{\sqrt{\frac{3}{5}}} \quad (4.5)$$

The diameter of the corresponding spherical droplet for the $\Phi = 2\%$ composite was determined as 570 ± 5 nm. While this size is larger than the mean size determined from image analysis (422 ± 200 nm), it is well known that analysis of the Guinier region tends to overestimate the mean particle size in polydisperse systems, as large particles dominate the scattering volume.⁵⁴⁻⁵⁵ The level 1 power law exponent P_1 for the LM droplets was 4, suggesting a smooth gallium oxide interface at the surface of the spherical LM droplets.⁵¹ A smooth droplet surface is consistent with the SEM images of the droplets (**Figure 4.6**). The level 1 parameters obtained from analysis on the samples are tabulated in Table 4.1 and the additional fits are shown in **Figure 4.12**.

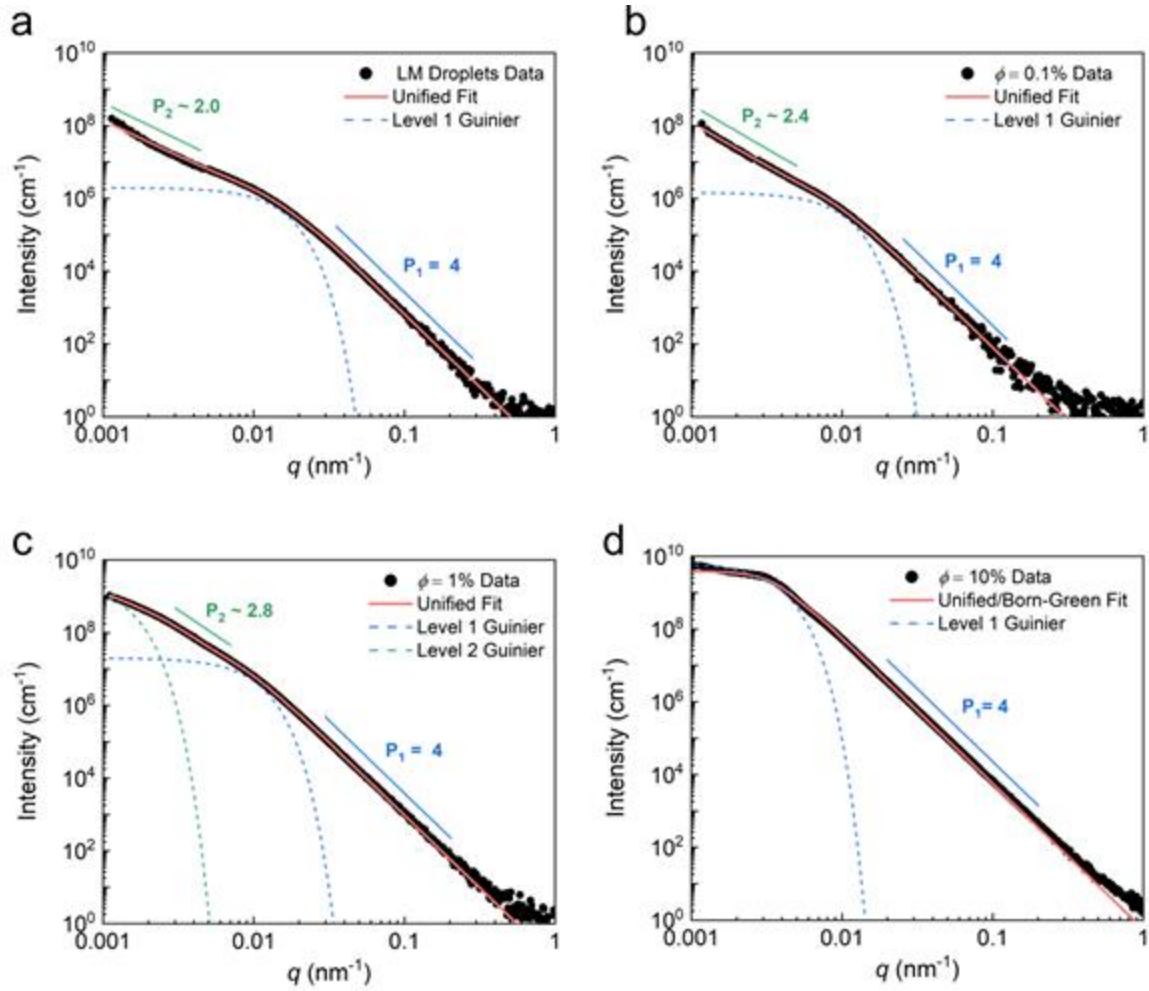


Figure 4.12. Experimental data and Unified model fit for the liquid metal droplets and composites at various liquid metal loadings ($\Phi = 0.1, 1, 10\%$).

Table 4.1. Level 1 Unified fit parameters of Equation 4.4 for the LM droplets and $\Phi = 0.1, 1$, and 2% composites. Level 1 structural parameters relate to the primary droplet size.

Sample ID	$G_1 \times 10^9$ (cm^{-1})	$R_{g,1}$ (nm)	D_1 (nm)	$B_1 \times 10^{-4}$ ($\text{cm}^{-1} \text{\AA}^{-P_1}$)	P_1
LM Droplets	2.0 ± 0.05	140 ± 2	360 ± 5	6.6 ± 0.01	4
0.1% LM	1.5 ± 0.2	210 ± 7	540 ± 20	0.81 ± 0.004	4
1.0% LM	20 ± 2	210 ± 5	540 ± 13	9.6 ± 0.05	4
2.0% LM	36 ± 1	220 ± 2	570 ± 5	18 ± 0.03	4

At lower q ($0.001 \text{ nm}^{-1} \leq 0.007 \text{ nm}^{-1}$), structural level 2 consists of a Guinier and power law region arising from scattering from larger aggregates of primary droplets (**Figure 4.11**). This level was similarly fit using the Unified equation (Equation 4.4), and the resulting fit parameters are shown in Table 4.2. The level 2 power law exponent, P_2 , ranged from 2.4 to 2.8 in the $\Phi = 0.1$, 1, and 2% composites, which is consistent with mass fractal aggregates comprised of mass-fractal particles arranged in a self-similar fashion.^{49,52} For the $\Phi = 2\%$ composite, the level 2 Guinier region was used to determine the radius of gyration of the mass-fractal aggregates as $R_g \approx 1.2 \text{ }\mu\text{m}$. This aggregate size is in good agreement with the aggregates observed via SEM, as shown in the inset of **Figure 4.11**. Additionally, the degree of aggregation (the number of primary droplets per aggregate) was calculated from the fit parameters according to previously reported methods⁵⁶⁻⁵⁷ as approximately 100 droplets per aggregate. This is consistent with the number of droplets observed in the aggregates via SEM analysis and will be the focus of future studies related to the aggregation of droplets in LM composites.

Table 4.2. Level 2 Unified fit parameters of Equation 4.4 for the LM droplets and $\Phi = 0.1$, 1, and 2% composites. Level 2 structural parameters relate to the mass fractal aggregates of droplets. Because the LM droplets and the $\Phi = 0.1\%$ scattering curves did not display a level 2 Guinier knee, only the power law region was fit.

Sample ID	$G_2 \times 10^9 \text{ (cm}^{-1}\text{)}$	$R_{g,2} \text{ (nm)}$	$B_2 \times 10^{-4} \text{ (cm}^{-1} \text{ \AA}^{-P_1}\text{)}$	P_2
LM Droplets	--	--	1.3 ± 0.5	2.0 ± 0.01
0.1% LM	--	--	0.030 ± 0.01	2.4 ± 0.04
1.0% LM	2.5 ± 0.1	1500 ± 60	0.023 ± 0.01	2.8 ± 0.04
2.0% LM	3.9 ± 0.1	1200 ± 10	0.28 ± 0.08	2.5 ± 0.03

The $\Phi = 1\%$ composite also displays a second Guinier and power law region at low q arising from scattering from the mass fractal (**Figure 4.12c**). The approximate size of the aggregates, $R_{g,2}$, is 1.5 μm . This is again consistent with the SEM images that display

aggregates of primary droplets approximately 1–2 mm in size (**Figure 4.6b**). Although the $\Phi = 0.1\%$ LM composite displays a second level of power law scattering (**Figure 4.12b**), a second Guinier knee corresponding to the mass fractal aggregates is not observed. A reasonable explanation for the absence of this feature despite the presence of aggregates in the SEM images (**Figure 4.6a**) is that the $\Phi = 0.1\%$ composite is just entering the semidilute regime, where only a small fraction of particles exists as aggregates with minimal contribution in the USAXS region.

4.4.2.3.2 Correlation analysis via Unified/Born-Green equation

At higher volume loadings of liquid metal ($\Phi = 10, 20\%$), the stronger spatial correlations between particles can be effectively modelled using the Born–Green modification of the Unified function.⁵⁸ The Born–Green closure of the Ornstein–Zernike equation modifies the scattering pattern through the structure factor shown in Equation 4.6:

$$S(q) = \frac{1}{(1 + p \times \theta(q, \eta))} \quad (4.6)$$

where $S(q)$ is the structure factor, p is the packing factor, proportional to the ratio of the occupied to available volume, and $\theta(q, \eta)$ is the spherical amplitude function (Equation 4.7):

$$\theta(q, \eta) = \frac{3[\sin(q\eta) - q\eta \cos(q\eta)]}{(q\eta)^3} \quad (4.7)$$

where η is the correlation distance. $S(q)$ is multiplied by $I_i(q)$ to include structure factor contributions to the specified level in the Unified equation.

The scattering data of the $\Phi = 10\%$ and 20% LM composites were modelled using the Unified/Born–Green approach due to the distinct peak/knee observed near $q = 0.005 \text{ nm}^{-1}$ (**Figure 4.9**). An example fit to the $\Phi = 20\%$ data utilizing the Unified/Born–Green

approach is shown in **Figure 11**. The Guinier region was used to quantify the size of the primary droplets as $D = 1.1 \pm 0.2$ μm . Additionally, the correlation length shown as the interdroplet distance in the inset of **Figure 4.13** was determined as 940 ± 20 nm. The Unified parameters for the $\Phi = 10$ and 20% composites are tabulated in Table 4.3. The packing factor, which ranges from 0 for uncorrelated systems to 5.92 for closely packed spheres,⁴³ was determined as $p = 0.62 \pm 0.06$ and 0.98 ± 0.09 for the $\Phi = 10$ and 20% composites, respectively. The slight increase in packing factor with increasing volume fraction is expected, and the relatively low packing factors are consistent with semidilute compositions.

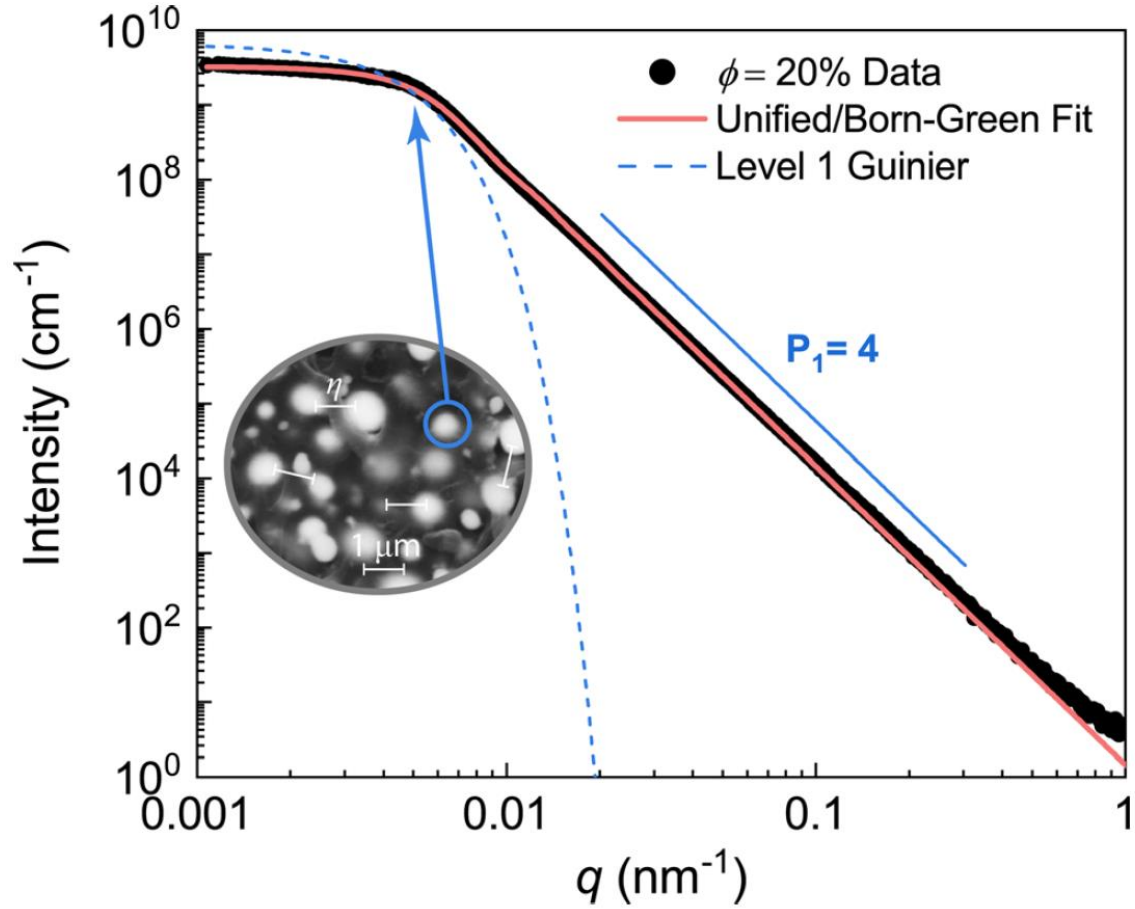


Figure 4.13. Unified fit of $\Phi = 20\%$ LM composite. The single structural level represents scattering from the primary droplets. The correlation length calculated from the Unified/Born-Green equation is on the order of 1 mm. The fit parameters can be found in Table 4.3.

Table 4.3. Unified/Born-Green fit parameters of Equations 4.4, 4.6 and 4.7 for the $\Phi = 10$ and 20% composites.

	10% LM Composite	20% LM Composite
$G_1 \times 10^9 \text{ (cm}^{-1}\text{)}$	6.5 ± 0.2	6.5 ± 0.3
$R_{g,1} \text{ (nm)}$	580 ± 10	430 ± 8
$D_1 \text{ (nm)}$	1500 ± 30	1100 ± 20
$B_1 \times 10^{-4} \text{ (cm}^{-1} \text{Å}^{-P_1}\text{)}$	0.57 ± 0.001	0.57 ± 0.003
P_1	4	4
$\eta \text{ (nm)}$	1500 ± 30	940 ± 20
Packing factor, p	0.62 ± 0.06	0.62 ± 0.09

4.4.4 Particle size distribution methods

In addition to the mean particle size, the distribution of particle sizes has been shown to impact the bulk properties of nanocomposites,⁵⁹ and the presence of both large and small droplets is apparent in the SEM images (**Figure 4.6**). To elucidate the distribution of droplet sizes present in the composites from the X-ray scattering profiles, several scattering analytical methods were applied and compared.

4.4.4.2 Unified fit size distributions

Using the Unified particle size distribution method established by Beaucage,⁶⁰ the droplet size distributions were obtained from the level 1 parameters of the Unified fit (Tables 4.1 and 4.3). This method assumes a log-normal distribution of polydisperse spheres and requires a scaling relationship that follows Porod's law ($P = 4$). The volume-weighted log-normal size distributions obtained from the Unified fit are shown as the solid black curves in **Figure 4.14** for each sample. The shifting peaks of the size distributions clearly reveal that the average droplet size increases as the filler is incorporated into the composite (from pristine LM droplets to the composites) and as the filler volume loading is increased from $\Phi = 0.1\%$ to 20%. This finding is consistent with the droplet size increase observed in the SEM image analysis.

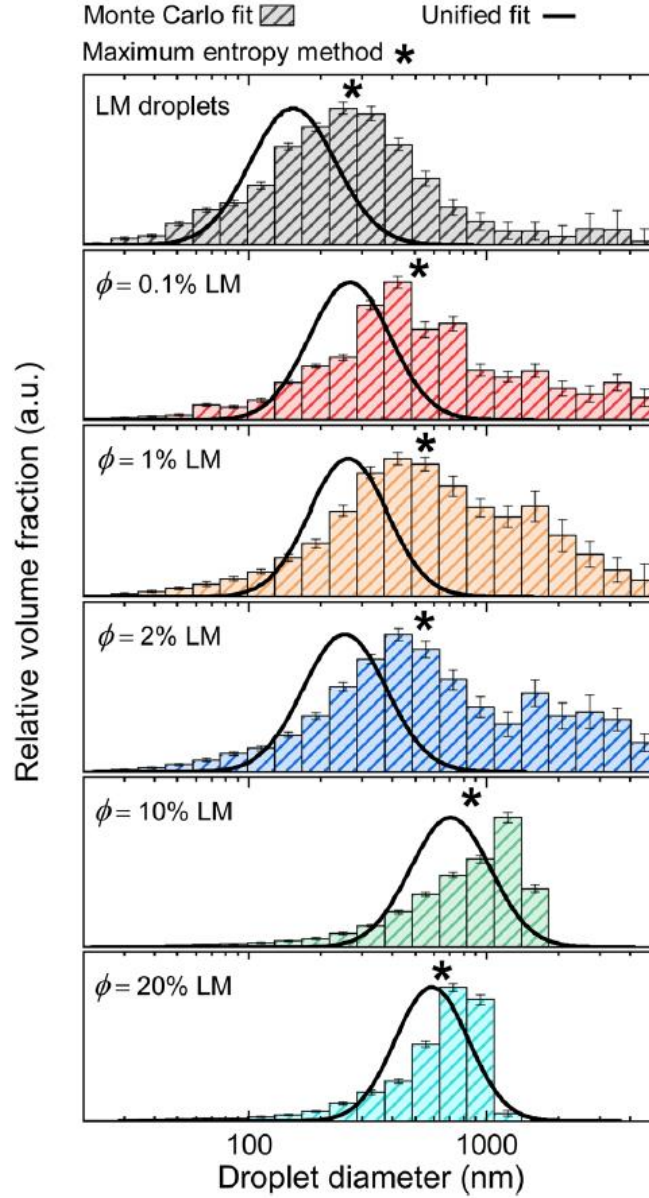


Figure 4.14. Volume-weighted size distributions from the Unified fit distribution method (solid black curves) and the Monte Carlo method (histogram bars). The droplet size determined from the maximum entropy method is shown as the asterisk (*).

4.4.4.2 Arbitrary side distributions

A reverse Monte Carlo (MC) approach initially developed by Pedersen⁵⁸⁶¹ and later modified by Pauw⁶² was also employed to obtain arbitrary size distributions from the X-ray scattering data, as opposed to log-normal size distributions given by the Unified fit.

The MC method has been shown to agree with results from classical model fitting and is capable of fitting arbitrary size distributions with excellent reproducibility and validity.⁶²⁻
⁶⁵ The method consists of an iterative rejection–acceptance procedure in which the size of one sphere in a set of spheres is changed, at random, until a solution to the weighted sum of the geometric form factors converges to the data (**Figure 4.15**).⁶²

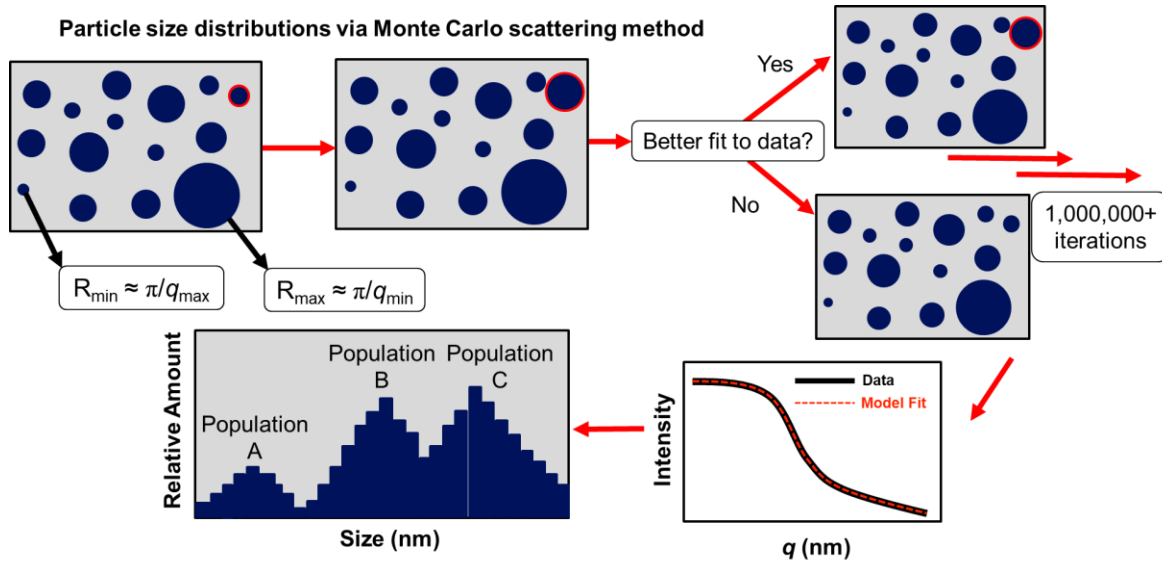


Figure 4.15. Monte Carlo size distribution method sequence.

This model assumes scattering from smooth and sharp interfaces ($P = 4$) and was used without structure factor. Although the model is typically applied to dilute systems, it was used to model these samples which are in the semidilute regime, to compare to the Unified method. The initial estimation of the scattering intensity profile is calculated using Equation 2.7:⁵¹

$$I_{MC}(q) = b + A \sum_{k=1}^{n_s} |F_{sph,k}(qR_k)|^2 \left(\frac{4}{3}\pi\right)^2 R_k^{(6-p_c)} \quad (4.8)$$

where I_{MC} is the calculated scattered intensity, b is a background term, A is a scaling factor, $F_{sph,k}$ is the spherical form factor,⁵¹ R_k is the radius for sphere k , n_s is the number of

scattering particles contributing to the calculation, and p_c is a volume-weighting correction that increases the speed of the model calculations.⁶² As recommended by Pauw et al.,⁶² the limits of the sphere radii were chosen as $R_{min} \approx \pi/q_{max}$ and $R_{max} \approx p/q_{min}$. After the initial estimation of the scattering profile, the method employs an optimization cycle that changes the size of a randomly selected sphere, and accepts the size of that sphere if the calculated scattering intensity more closely matches the experimental data than the previous size. Convergence to the experimental data results in a set of spheres whose sizes can be represented in a histogram to visualize the size distribution.

The volume-weighted MC droplet size distributions for the LM droplets and composites are shown in **Figure 4.14** as the striped histogram bars. For both the LM droplets and the composites, the histograms reveal a broad distribution of droplet sizes. For the $\Phi = 1$ and 2% composites, an additional population of larger features appears, which is related to the intensity upturn at low q (**Figure 4.9**). The histograms for the $\Phi = 10$ and 20% LM composites reveal an asymmetric distribution with a limiting size of $D \approx 1500$ nm. The primary droplet diameter from the Monte Carlo method was chosen as the mode of the histograms (i.e., the most prevalent droplet size corresponding to the height of the histogram distribution) and is discussed below. In agreement with the Unified size distribution, the MC method also reveals that the droplet sizes increase as the volume fraction of the filler is increased. The slight weighting of the Monte Carlo distributions towards larger droplet sizes can be attributed to the fact that the Unified method models a single level of the scattering profile, whereas the MC method models the full scattering profile. The MC model fits are shown in **Figure 4.16**.

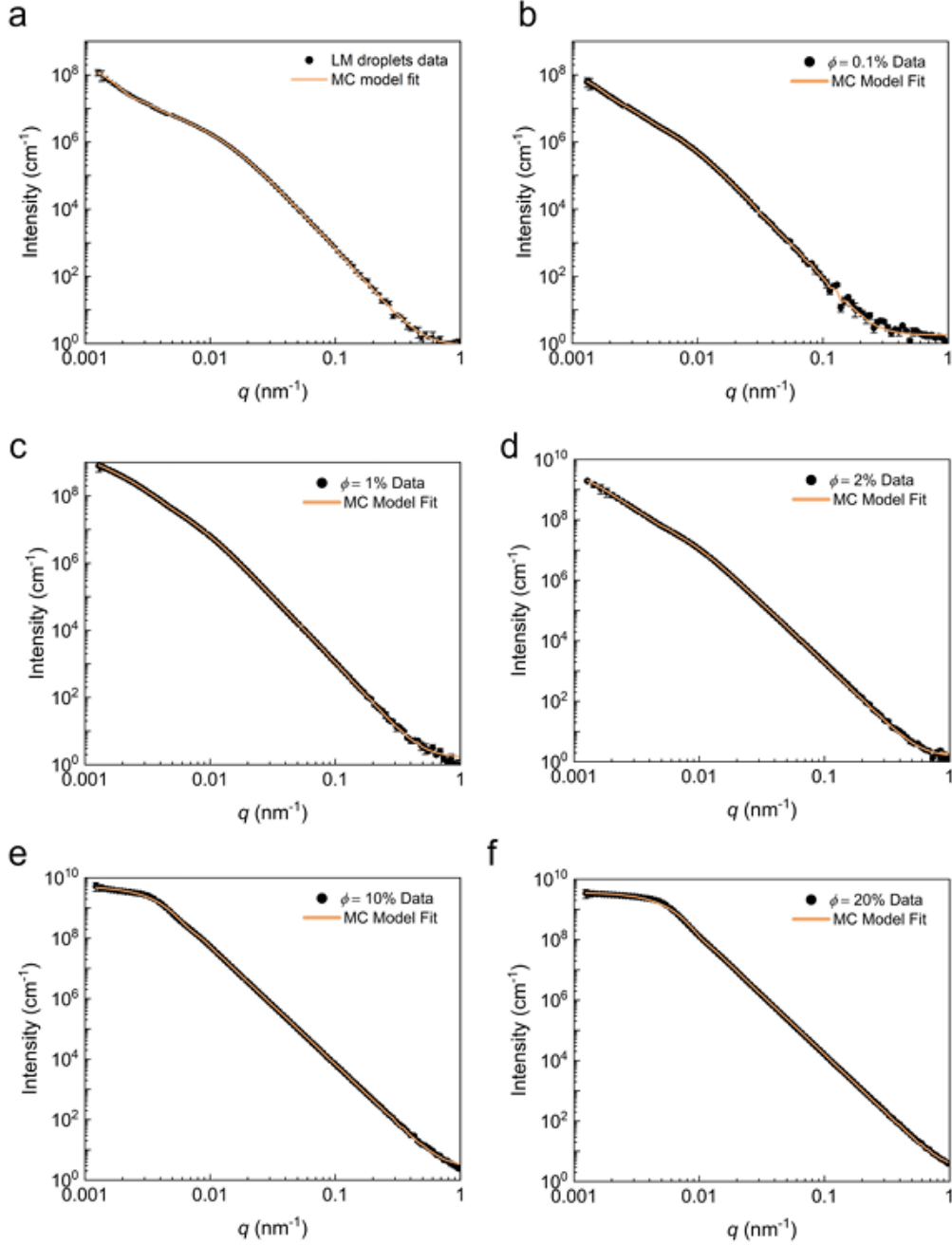


Figure 4.16. Experimental data and Monte Carlo model fit for the liquid metal droplets and composites at various liquid metal loadings ($\Phi = 0.1, 1, 2, 10, 20\%$).

The maximum entropy method, another robust method for determining arbitrary size distributions of dilute scatterers,^{44, 66-67} was also used to determine the droplet size distribution, yielding the fits shown in **Figure 4.17** and the particle size distributions shown

in **Figure 4.18**. The median droplet size from these distributions is denoted by an asterisk (*) in **Figure 4.14** to allow for comparison with the other methods. Again, the maximum entropy method reveals reasonable agreement between the particle size distribution methods.

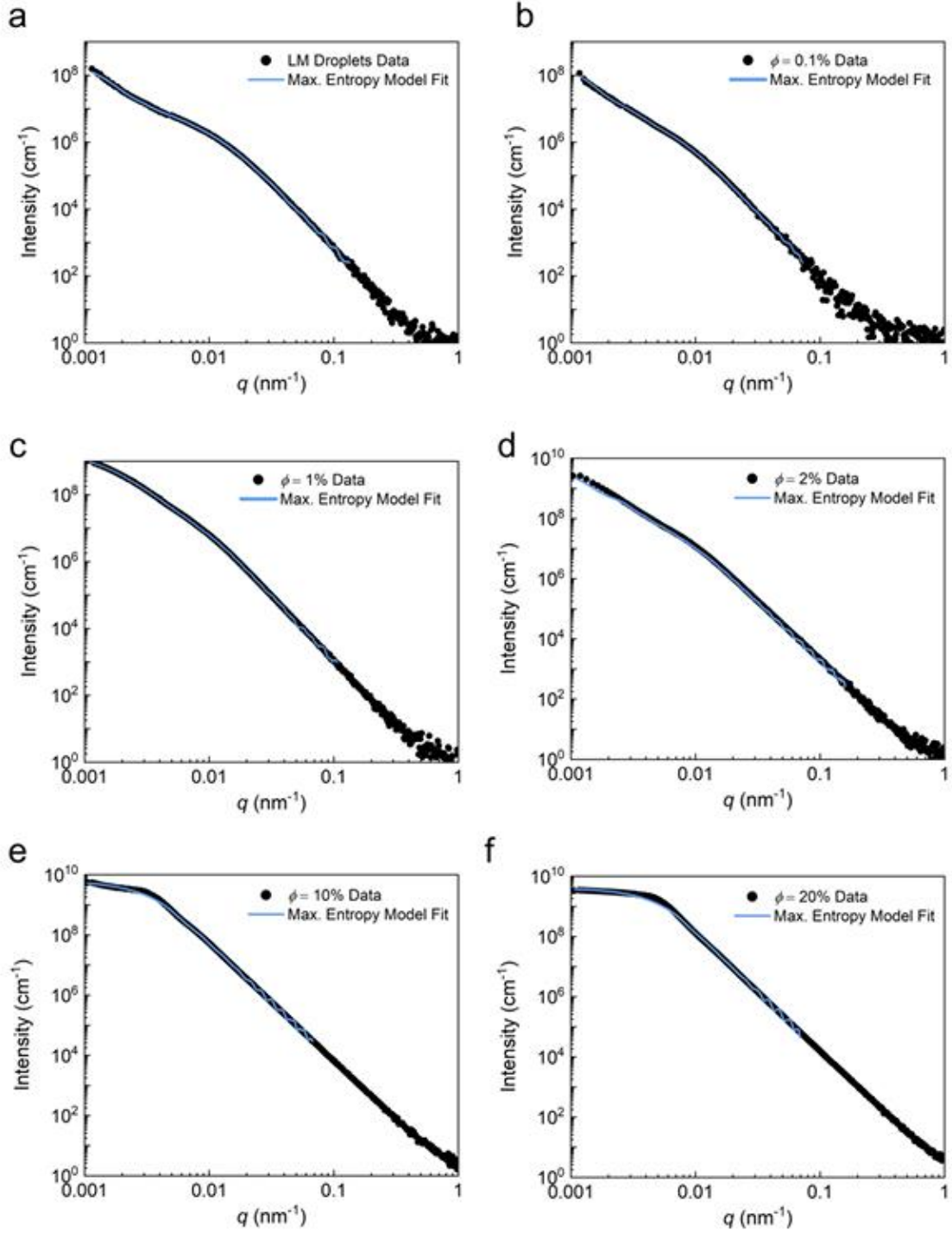


Figure 4.17. Experimental data and Maximum entropy model fit for the liquid metal droplets and composites at various liquid metal loadings ($\Phi = 0.1, 1, 2, 10, 20\%$).

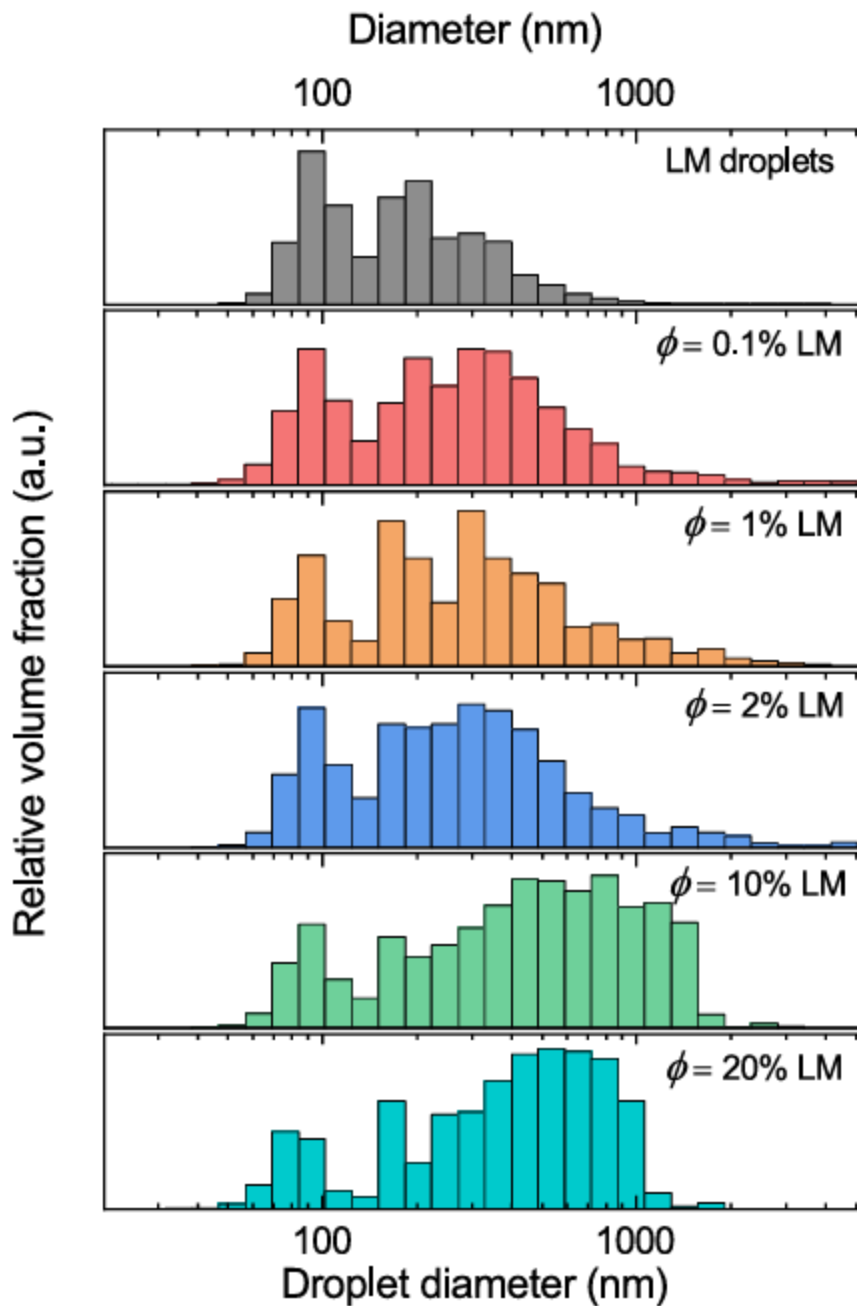


Figure 4.18. Volume-weighted size distributions of the LM droplets and composites at various LM loadings based on the maximum entropy fits. In each of the size distributions, an additional population of small scatterers centered around $D = 95$ nm appears. The origin of this population is likely a minor collection of relatively small LM droplets. The broad distribution of larger scatterers likely originates from a combination of primary particles and aggregates; however further experiments would be required to decouple particle and aggregate contributions.

4.4.5 Comparison of SEM and X-ray scattering methods

The mode of the droplet sizes obtained from the Monte Carlo method is compared to the sizes obtained from SEM image analysis in **Figure 4.19**. This analysis of the prevalent droplet sizes demonstrates strong agreement between the different characterization methods. A comparison of the particle size distributions obtained from SEM image analysis and the Monte Carlo analysis of the scattering data is visualized in **Figure 4.20a**, where the size distributions from both SEM and Monte Carlo scattering analyses are plotted together, alongside representative SEM images for the corresponding specimen (**Figure 4.20b**). One notable observation is that the results from the Monte Carlo analysis show the presence of scatterers larger than the individual droplets observed in SEM analysis. This observation can be attributed to the mass fractal aggregates that form through agglomeration of primary droplets. Again, this is seen in the SEM images of the low volume loading composites ($\Phi = 0.1, 1, \text{ and } 2\%$) that show distinct agglomeration (**Figure 4.20b**). From the comparison in **Figure 4.19 and 4.20**, it is clear that X-ray scattering is capable of detecting the structures of LM composites across many length scales and revealing size distributions that would require many SEM images to elucidate. While the structure-free Monte Carlo method is typically applied for dilute systems, it showed excellent agreement with the Unified model and maximum entropy size distribution methods. The small discrepancies between SEM image analysis and X-ray scattering techniques can be understood by microscopy being a surface technique, providing only a local two-dimensional description of the morphology, whereas scattering is a bulk measurement technique providing more information as it relates to the bulk of the sample.

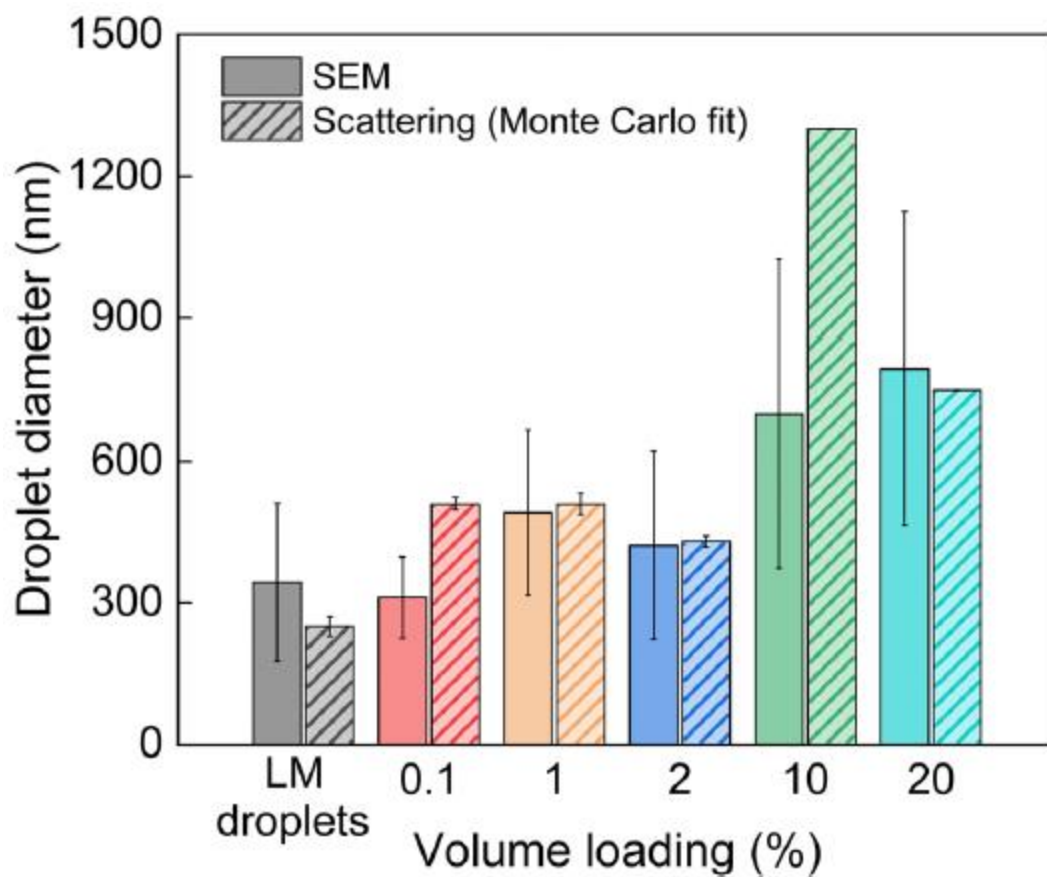


Figure 4.19. Droplet sizes for the pristine LM droplets and when dispersed as a filler in PDMS at different volume loadings, as determined from the image analysis on SEM micrographs and Monte Carlo fits on the X-ray scattering data. The values from the Monte Carlo fit correspond to the particle size in the greatest frequency (i.e., the mode).

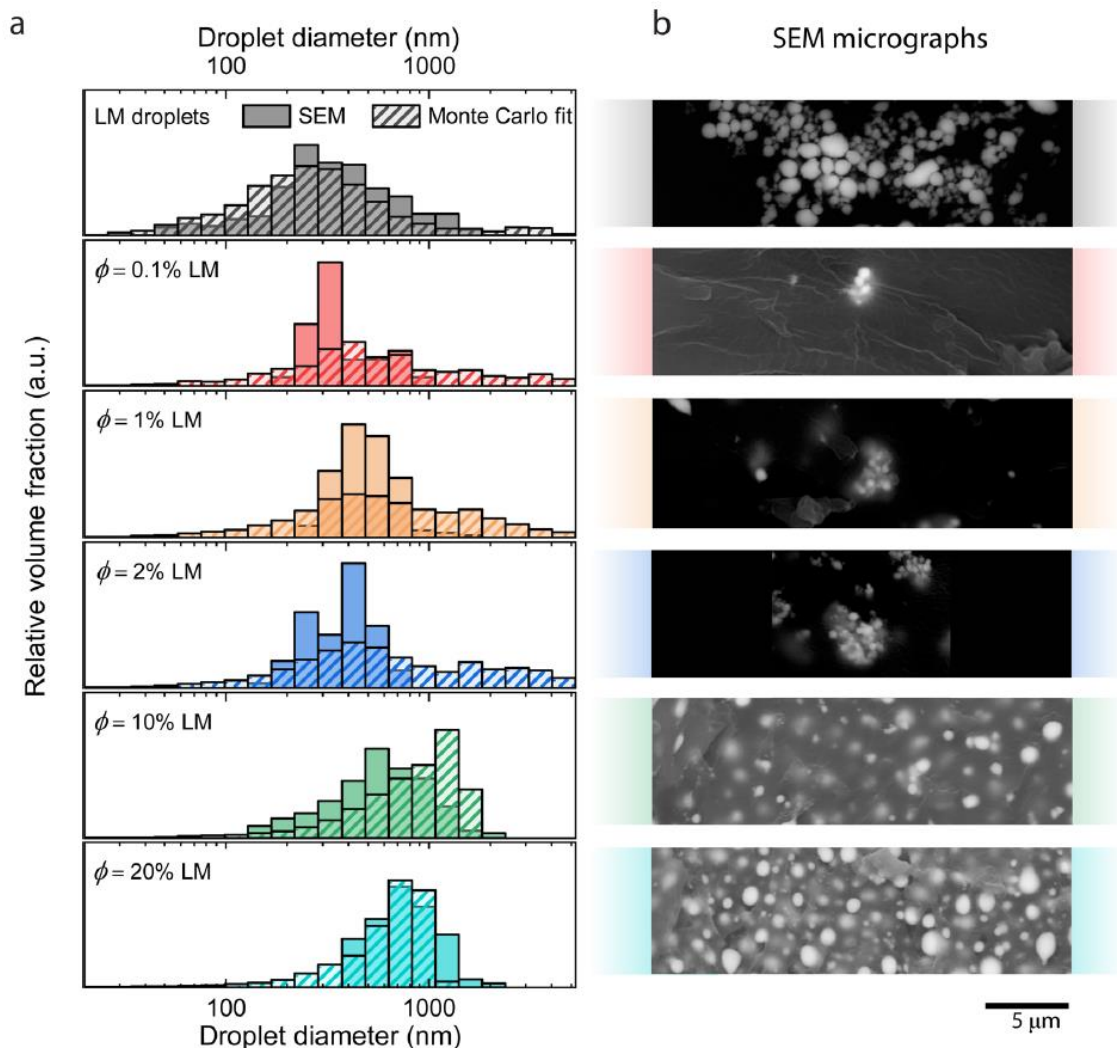


Figure 4.20. a) Size distributions of the LM droplets and composites at various LM loadings ($\Phi = 0.1, 1, 2, 10, 20\%$) overlaid on the histograms obtained from Monte Carlo fits on the scattering data. **b)** Representative SEM micrographs of the samples corresponding to the histogram overlays. The histograms have been normalized such that the total area of all bins is equal to 100%.

4.5 Conclusions

This work details the characterization of LM composite morphologies through a combination of scanning electron microscopy and X-ray scattering. Results from USAXS were interpreted using the Unified and Unified/Born–Green approaches to characterize the droplet dimensions, the mass fractal aggregate dimensions, and the interdroplet

interactions. The Unified, Monte Carlo, and maximum entropy particle size distribution methods were used to characterize the primary droplet and aggregate size distributions and revealed the presence of droplets with sizes spanning a wide range of length scales. The results from each method clearly reveal that the LM droplet sizes in the composites are slightly larger compared to the pristine droplets, which suggests that smaller droplets agglomerate and possibly coalesce to form larger droplets or clusters during the fabrication process. Future studies with varying mixing conditions and higher volume loading composites could provide more insight on coalescing mechanisms. For additional future studies, we will use this X-ray scattering method to systematically study the effects of a variety of important processing parameters such as mixing protocols, solvent choice, and interfacial compatibility on the dimensions of liquid metal composites.

The high electron density of EGaIn and other liquid metals, relative to the polymer matrix, positions X-ray scattering to be a sensitive and effective tool to study the morphology of a variety of nano-structured LM-containing systems. For example, X-ray scattering can be utilized to study the shape and size transformation of LM droplets in solutions,⁶⁸ and soft robots.⁶⁹ This method will be particularly useful in light of recent advancements of techniques to carefully control the size and distribution of the droplets in the 1–100 nm size range.⁷⁰ We anticipate the USAXS/SAXS/WAXS method, in combination with the scattering models presented here, will be attractive methods to non-destructively characterize global-averaged size distributions and polydispersity in many of these widely studied and utilized materials.

4.6 Recommendations for future work

This initial study, which involved composites from a single filler/matrix material, (EGaIn/PDMS) fabricated using a fixed set of processing conditions, can be expanded in many ways that would yield valuable insights into the aggregation and coalescing behavior of this interesting class of liquid filler composites. First, a systematic study on the effects of the mixing protocol on the EGaIn/PDMS system would help to elucidate the mechanism underlying the increasing droplet size that occurs when incorporating the droplets into the matrix. The simplest experiments would study this process for the droplet/solvent suspension in the absence of the polymer matrix. For example, the mixing speed (rpm) and mixing time could be independently tuned for the same batch of liquid metal droplets, and the effects of those processing conditions on the droplet and aggregate size should be studied with SEM image analysis and USAXS. The dispersing solvent could also be systematically tuned to understand the effects of the solvent/droplet interactions on the aggregation and agglomeration of particles. For example, more polar solvents might interact more favorably with the oxide layer of the LM droplets, resulting in less aggregation/agglomeration. Finally, a study could be conducted on the effects of added surfactants on the droplet and aggregate size, as the chemical structure of the surfactants could tune the droplet/solvent interactions. Once the process of aggregation had been established for the pure droplets and solvent, similar studies could be conducted studying the effects of the polymer matrix on the droplet and aggregate sizes. The USAXS experiments could be conducted at Virginia Tech, where we have observed excellent agreement between the data collected at Argonne National Laboratory and the Xenocs Xeuss 3.0 USAXS/SAXS/WAXS system (**Figure 4.22**).

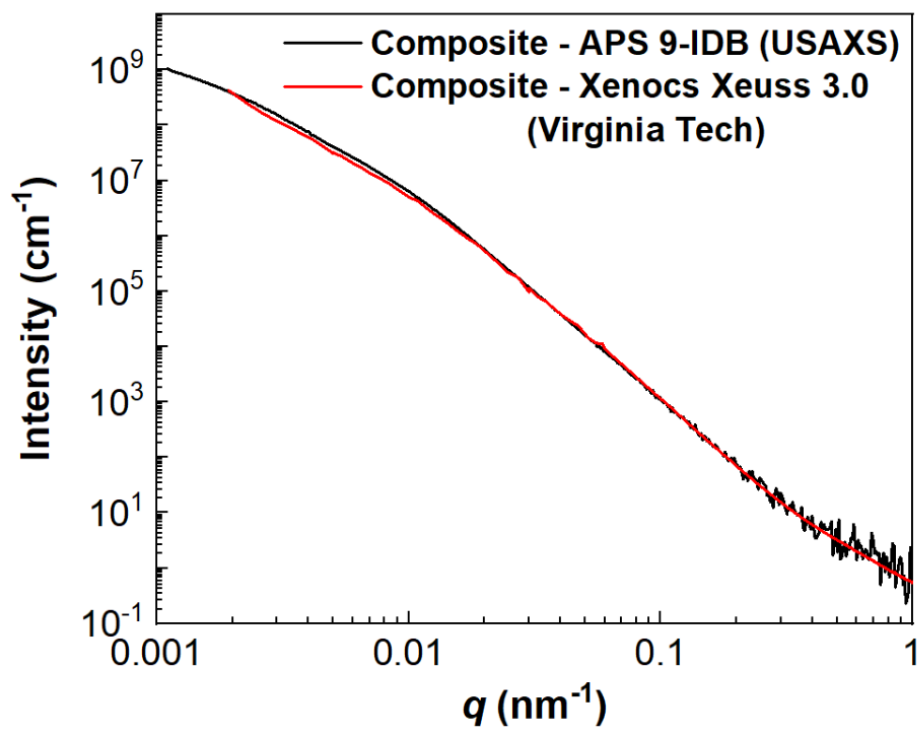
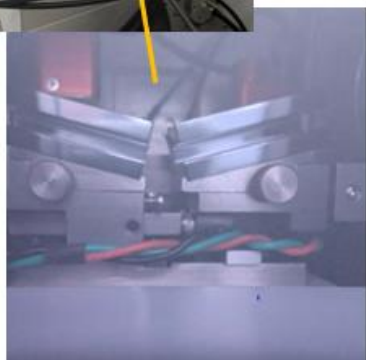
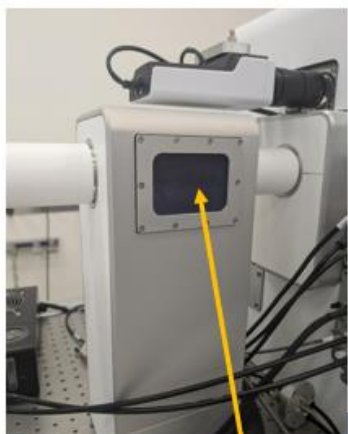


Figure 4.21. Comparison of USAXS profile of a LM composite collected at the APS, compared to the profile of the same material at Virginia Tech.



Monochromator (before sample)



Analyzer (after sample)

Figure 4.22. Photographs of the monochromator crystals and the analyzer crystals located before and after the sample, respectively, for the USAXS Bonse-Hart setup for the Xenoc Xeuss 3.0 system at Virginia Tech.

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Chapter 5. Rule of mixtures properties in binary blends of perfluorosulfonic acid copolymers: implications for recycling fuel cell and electrolyzer membranes

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5.1 Abstract

Recent efforts to advance a circular hydrogen economy have drawn attention to the need for recovering and recycling critical ionomer materials from end-of-life fuel cell and electrolyzer assemblies. In this work, we show that blending and casting of dispersions containing binary mixtures of structurally different PFSA (Syensqo Aquivion[®], 3M[™] PFSA, and Chemours Nafion[™]), provides a means to tailor integrated membranes with tunable properties from mixed PFSA sources. Dynamic mechanical analysis (DMA) reveals that the integrated membranes exhibit a single thermomechanical relaxation, T_{α} , consistent with a molecularly-mixed morphology. Small and wide-angle X-ray scattering (SAXS/WAXS) experiments of the membranes in the acid form reveal that the long-range spatial organization of PTFE-like crystallites can be systematically tuned through the blend composition. SAXS experiments of Cs⁺-form membranes reveal a single ionomer peak, which suggests that the sidechain aggregates formed in the integrated membranes are uniformly

composed of aggregates containing sidechains from both components. Finally, water vapor uptake, proton conductivity, and areal swelling experiments reveal a remarkably simple rules-of-mixtures behavior, dependent primarily on the average equivalent weight of the integrated membranes. This work will guide future research focused on closed-loop recycling and reprocessing of mixed PFSA waste streams for fuel cell and electrolyzer applications.

5.2. Introduction

Hydrogen fuel cells are electrochemical devices that convert the chemical energy of hydrogen fuel into electricity.¹⁻² Since water and heat are the principal byproducts from this reaction, hydrogen fuel is a promising alternative to hydrocarbon-based fossil fuels, which emit carbonaceous byproducts that contribute to climate change.³ A key component of the hydrogen fuel cell is the proton exchange membrane (PEM), which is responsible for proton transport from the anode to the cathode.⁴ PEMs are also heavily utilized in water electrolysis applications and thus have the potential to help generate hydrogen from sustainable sources (i.e., water and wind or solar power).⁵ For hydrogen fuel cells and water electrolyzers to be more widely adopted, the US Department of Energy states that PEMs must be cost-effective, high performance, and durable.⁶ Thus, a significant amount of research has been devoted to improving these aspects of PEMs.

The PEM of a hydrogen fuel cell or water electrolyzer is typically made from a polymer bearing a small mole fraction (typically 15- 25 mol%) of acidic groups that provide the material with sufficient proton conductivity while also maintaining its insolubility in water. Perfluorosulfonic acid (PFSA) membranes such as NafionTM are

the benchmark PEM materials, as their superacid sidechains provide high proton conductivity while the perfluorinated backbone provides chemical and mechanical stability.⁷⁻⁸ Hydrocarbon-based PEMs have also been developed as alternatives to perfluorinated PEMs, including sulfonated poly(ether ether ketone) (SPEEK)⁹ and sulfo-phenylated polyphenylenes such as PemionTM.¹⁰ Regardless of the type of polymer used in PEMs, there is increasing interest in improving the sustainability of PEM technology, through either recycling or re-using the polymers from used membrane electrode assemblies or offcuts from manufacturing.¹¹ Given the concerns regarding the negative environmental impacts and costs associated with the production of new perfluorinated materials,¹² the reusability of PFSA membranes is of great interest to the fuel cell, water electrolysis, and fluoropolymer communities.¹³ While a significant amount of research is being devoted to studying the recyclability and reprocessing of single component PFSA membranes,¹⁴⁻¹⁶ it must be recognized that a number of different PFSAs are currently utilized in commercial fuel cells or electrolyzers and often PFSAs utilized in the catalyst layers are different than the core membrane in catalyst coated membrane assemblies.¹⁷ Therefore, there is an imperative need to establish the compatibility of different PFSAs with one another as future multi-component waste streams will undoubtedly contain a wide variety of different commercial PFSAs.

Perfluorosulfonic acid polymers are generally characterized by a poly(tetrafluoroethylene) (PTFE)-based backbone and perfluoroether sidechains terminated in a sulfonic acid unit. A PFSA can be described by its equivalent weight (EW = grams polymer/mole SO₃H), related to the total acid content, as well as the length of the perfluoroether sidechain. NafionTM, initially a product of Dupont but now a product of Chemours, is the most well-studied PFSA, and has historically been

characterized by relatively high equivalent weights ($\text{EW} > 1,000 \text{ g PFSA/mol SO}_3\text{H}$) and a relatively long perfluoroether sulfonic acid sidechain.⁷ However, recent industrial developments have afforded new PFSA variants with different chemical structures. For example, the 3MTM PFSA is a PFSA with an intermediate sidechain length bearing four carbons.¹⁸ Syensqo's Aquivion[®], originally Dow Chemical Company's perfluorosulfonate ionomer (PFSI),¹⁹ is a PFSA with a short sidechain bearing two carbons. The greater availability of a wide variety of EWs for a given sidechain variant also allows the sidechain content to be tuned independent of the length of the sidechain. Each of these structural modifications of PFSAs has a subsequent effect on the properties of the PEM. For example, for a given PFSA sidechain length, PFSAs with a lower EW (greater $\text{-SO}_3\text{H}$ content) generally have higher proton conductivity and water uptake, whereas PFSAs with a higher EW (lower $\text{-SO}_3\text{H}$ content) generally have higher degrees of crystallinity (i.e., more crystallizable tetrafluoroethylene units between sidechains). Two comprehensive reviews by Kusoglu and Weber and García-Salaberri discuss the structure-property relationships of these different PFSAs in great detail.^{2, 8}

To our knowledge, only a few examples of blending one PFSA with another PFSA exist in the literature.²⁰⁻²² In the first example reported in 1994, Zaluski and Xu blended DuPont's NafionTM bearing a long sidechain ($\text{EW} = 1100 \text{ g mol}^{-1}$) with Dow's perfluorosulfonate ionomer (PFSI) bearing a short, two carbon sidechain ($\text{EW} = 800 \text{ g mol}^{-1}$).²⁰ The two PFSAs were blended by solution-processing the NafionTM and Dow membranes together in a high pressure and high temperature reactor. By heating the membranes in a 50:50 ethanol:water mixture at 250°C , the researchers were able to solubilize the polymers in a common solvent to obtain a multi-component dispersion. Then, the dispersion containing the blend was cast and dried at

130 °C to yield the blended membrane. These membranes showed significantly reduced crystallinity and proton conductivity compared to the single component membranes manufactured and obtained from Dupont and Dow.²⁰ In a more recent paper, Li⁺-neutralized NafionTM and Aquivion[®] PFSA dispersions were blended with one another to produce membranes for battery separator and electrolyte applications.²¹ In this study, Dombaycıoğlu and coworkers observed that the blended membranes at intermediate compositions displayed a synergistic increase in conductivity compared to the single component membranes; however, the morphologies of the blend membranes were not investigated.²¹ Finally, a recent paper from Kim and coworkers blended short and long sidechain PFSA to prepare multi-component membranes and multi-component binders for the catalyst layer of PEM fuel cells.²² Compared to the single component membranes, the authors postulated that the increased water uptake and proton conductivity of the PFSA blend membranes may be attributed to increased free volume. Similar to the work of Dombaycıoğlu and coworkers,²¹ this study only focused on a few limited compositions. Clearly, a fundamental understanding of composition-morphology-property relationships in blended PFSA membranes is needed to guide future developments in tailored membranes for energy applications.

In this work, we provide an in-depth study of the effects of dispersion-state blending of different commercial PFSA on the resulting properties in the integrated membranes. Membranes prepared by blending PFSA with different equivalent weights and sidechain lengths are shown to display a remarkably simple rule-of-mixtures in their properties, including water vapor uptake, proton conductivity, and areal swelling. Morphological analyses from small and wide-angle X-ray scattering (SAXS and WAXS) reveal that interdomain dimensions associated with the nanoscale hydrophilic and crystalline morphologies also follow a clear trend with respect to the

blend composition. Overall, this work provides evidence that commercial PFSA dispersions can be easily be blended to provide membranes with tunable properties and morphologies, paving the way for recycling mixed PFSA waste streams into valuable membranes for PEM fuel cell and electrolyzer applications.

5.3. Experimental Section

5.3.1 Materials

NafionTM (D2021CS, ca. 20wt% solids, 1100 EW LSC) alcohol/water dispersion was purchased from Ion Power. Aquivion[®] (D72-25BS, ca. 25 wt% solids, 720 EW C2) and Aquivion[®] (D98-25BS, ca. 25 wt% solids, 980 EW C2) water-based dispersions were purchased from the Fuel Cell Store. 3MTM Company provided the 725 EW C4 PFSA in powder form. Given the unknown and variable solvent compositions of the commercial C2 and LSC dispersions, the as-received dispersions were first dried in ambient conditions in a Petri dish for 48 hours to yield solid flakes of the PFSA. The residual solvent content of the solid flakes was determined by heating the flakes in a thermogravimetric analyzer (TGA 5500, TA Instruments) at 120 °C for 2 hours in a dry N₂ atmosphere.

5.3.2 Membrane Fabrication Process

Single-component PFSA dispersions were prepared by adding the solid PFSA flakes or powder to a pre-mixed nPrOH/H₂O mixture at 25 w/w% solids (mass solids/mass solvent = 0.25). All PFSA's other than Aquivion[®] at 720 EW C2 were re-constituted in a 60/40 w/w% nPrOH/DI H₂O mixture. However, due to the tendency of the Aquivion[®] 720 EW C2 PFSA to form high viscosity dispersions,²³ this PFSA was re-constituted in a 40/60 w/w% nPrOH/DI H₂O solvent mixture, yielding a

dispersion viscosity comparable to the other PFSA dispersions. Dispersions containing binary blends of different PFSA were prepared by combining the two separate, pre-formed dispersions at varying compositions (0/100, 25/75, 50/50, 75/25, 100/0) followed by stirring with a magnetic stir bar for 12-16 hours at room temperature at 300 rpm. Membranes were fabricated by casting the dispersions onto an industry-standard polyimide substrate²⁴ using an Elcometer 4340 automatic film applicator at room temperature to 14 mil (~350 μm) wet thickness. The substrate-supported membranes were then immediately placed in a preheated convection oven at 100 °C for 12 minutes to evaporate the solvent. After drying, the membranes were immediately transferred to a separate preheated convection oven at 200 °C for 12 minutes. The membranes were removed from the substrate by swelling with room temperature DI H₂O, then treated in an aqueous solution of 8M HNO₃ acid for 24-48 h to remove impurities, and then thoroughly rinsed with DI H₂O. The final membranes were in the H⁺-form and were approximately 30 ± 10 μm thick at ambient RH conditions measured by a digital micrometer (Mitutoyo). Unless otherwise specified, samples for the following experiments were used from this pretreatment procedure. The average equivalent weight of the integrated membranes was calculated as the weighted average equivalent weight of the blend components. Similarly, the average sidechain length of the integrated membranes was calculated as a weighted average of the sidechain length of the blend components. Details on how the sidechain lengths were calculated are discussed in detail later. The number of TFE units between sidechain was calculated using Equation 5.1,

$$EW = 100n + MW_{sc} \quad (5.1)$$

where EW is the equivalent weight of the PFSA (g PFSA/mol SO₃H), 100 is the molar mass (g mol⁻¹) of a TFE unit, n is the number of TFE units/mol sidechain, and MW_{sc} is the molecular weight of the monomer unit containing the sidechain.

5.3.3 Dynamic Mechanical Analysis Experiments

Specimens for dynamic mechanical analysis (DMA) were prepared by drying the membranes under reduced pressure at 70 °C for 12 hours, then cutting the membranes into 5.3 mm x 10 mm rectangular strips using a metal die. Temperature sweep experiments were performed using a TA Instruments Discovery DMA850 analyzer in tensile mode using an oscillatory strain of 10 μm. The specimens were analyzed at a frequency of 1 Hz from 30 °C to 200 °C with a heating rate of 2 °C/min.

5.3.4 Small/Wide Angle X-Ray Scattering Experiments

The integrated membranes were subjected to two different treatment procedures prior to X-ray scattering analysis. The first set of integrated membranes were simply dried at 70 °C under reduced vacuum for 24 h in the native H⁺-form to yield the dry, H⁺-form membranes. The second set of integrated membranes were soaked in a 1M CsOH aq. solution for 24 h prior to thoroughly rinsing with DI H₂O and drying at 110 °C under vacuum to yield the dry, Cs⁺-form membranes. Small, mid, and wide-angle X-ray scattering (SAXS/MAXS/WAXS) experiments were performed using a Xenocs Xeuss 3.0 SAXS/WAXS equipped with a GeniX 3D Cu HFVLF microfocus X-ray source utilizing Cu K_α radiation ($\lambda = 0.154$ nm). The sample-to-detector distance was 43 mm for WAXS, 370 mm for MAXS, and 900 mm for SAXS. The q -range was calibrated using standards: lanthanum hexaboride (for

WAXS) and silver behenate (for SAXS and MAXS). Two-dimensional scattering patterns were obtained using a Dectris EIGER 4M detector with various exposure times (SAXS: 2 hours, MAXS: 1 hour, WAXS: 30 minutes). Data reduction was performed using XSACT software provided by Xenocs, and the 1D profiles were corrected for sample thickness, background, and transmission. All scattering intensities are reported on an absolute intensity scale. The SAXS and MAXS profiles were merged into one dataset, referred to as simply “SAXS,” and plotted on an absolute intensity scale vs. the scattering vector, q . The WAXS diffraction profiles are plotted as relative intensity vs. the scattering angle 2θ .

5.3.5 Proton Conductivity Experiments

Prior to proton conductivity measurements, the membranes were equilibrated in room temperature DI H₂O for 24 hours. Next, the hydrated membranes were cut into rectangular strips measuring 1 cm x 3 cm and placed in a four-point probe conductivity cell (Bekktech) that was submerged in room temperature DI H₂O. Measurements were taken under fully hydrated conditions using a Solartron Electrochemical Interface SI 1287. The DC potential was swept twice from -0.2 to 0.2 V at 10 mV/s while the current was recorded. The sample was removed from the cell to measure the wet membrane thickness using a calibrated micrometer. Resistance values, R , were obtained from the slope of the potential, V , vs. current, I , curve, where $R=V/I$. Proton conductivity, σ , was calculated from: $\sigma = l/AR$, where l is the distance between the two inner (reference) electrodes, A is the cross-sectional area, and R is the resistance.

5.3.6 Water Vapor Sorption Experiments

Dynamic vapor sorption (DVS) water uptake experiments were performed using a TA Instruments Q5000 DVS analyzer. Membranes were cut into small pieces (ca. 2 mm²) and equilibrated at 25 °C, 0% relative humidity (RH) for 2 hours in the instrument. The RH was then ramped up from 0% RH to 95% RH in 10% RH increments. At each RH step, the sample was held until the weight change was less than 0.001% over a 5-minute period. The normalized water content (λ), expressed in units of mol H₂O/mol SO₃H, was calculated from Equation 5.2:

$$\lambda = \left(\frac{\Delta m}{m_i} \right) \left(\frac{EW}{18.02 \frac{g}{mol}} \right) \quad (5.2)$$

where Δm is the mass of water uptake, m_i is the dry mass of the membrane at 0% RH, and EW is the weighted-average EW (g mol⁻¹ SO₃H) of the PFSA.

5.3.7 Areal Swelling Experiments

Areal swelling of the membranes in 80 °C liquid water was determined by equilibrating at least four 2.5 cm x 2.5 cm membrane specimens in 80 °C DI H₂O for 1 hour and measuring the dimensions of the wet specimens using digital calipers. The same specimens were dried under reduced pressure at 70 °C for 24 hours, and the dry measurements were then recorded. The areal (in-plane) swelling was calculated using Equation 5.3:

$$\text{Areal swelling (\%)} = \frac{l_s w_s - l_d w_d}{l_d w_d} \times 100 \quad (5.3)$$

where l_s and w_s are the length and width of the hydrated specimens, respectively, and l_d and w_d are the length and the width of the dry specimens, respectively.

5.3.8 Computational Visualizations and Calculations

The PFSA sidechain lengths were estimated in Avogadro 1.2.0 computational software.²⁵ Structures consisting of a single monomer of each PFSA were constructed in Avogadro and the structures were then optimized in the software. The sidechain lengths were measured as the magnitude of the vector between the backbone carbon atom bearing the sidechain to the sulfur atom on the sidechain. VEGA ZZ 3.2.3.28 computational software was used to calculate the molecular volumes of the PFSA monomers.²⁶ First, the monomer structures were loaded into VEGA ZZ, and the energies were minimized before the molecular volume was calculated. The details regarding the calculations of the volume fraction of sidechains within the integrated membranes can be found in **Figure S5.5**, Table S1 (Supporting Information).

5.4. Results and Discussion

5.4.1. Membrane Fabrication Process

Each of the commercial PFSA variants used in this study exhibit a unique sidechain structure, shown in **Figure 5.1a**, with NafionTM having the longest sidechain (LSC), the 3MTM PFSA having an intermediate sidechain length bearing four carbons (C4), and Syensqo's Aquivion[®] having the shortest sidechain bearing two carbons (C2). The room temperature dispersion and casting techniques used to fabricate the integrated membranes have been used extensively to fabricate single component PFSA membranes.^{7-8, 27-28} Dispersion casting typically involves dispersing a PFSA in a solvent mixture followed by casting the dispersion on a substrate and processing the substrate-supported membrane at high temperature to remove the solvent and allow for morphological development (annealing) of the PFSA.²⁷⁻²⁸

The NafionTM and Aquivion[®] dispersions were received in a mixed alcohol/water solvent mixture and 100% water, respectively, whereas the 3MTM PFSA was received as a fine powder. To prepare the dispersions in a similar solvent mixture, the NafionTM and Aquivion[®] dispersions were first dried at ambient temperature and pressure for 48 hours in a PTFE dish. The solid PFSA flakes (NafionTM or Aquivion[®]) or the as received 3MTM PFSA powders were then re-constituted as dispersions in nPrOH/H₂O solvent mixtures at 25 wt% PFSA solids. Once the individual PFSA were fully dispersed in the solvent mixture (4-12 hours), the PFSA dispersions were combined at room temperature (**Figure 5.1b**) to form the integrated PFSA dispersion and mixed at 300 rpm for 12-16 hours at room temperature. Upon casting the blended dispersions onto a polyimide substrate, the dispersions were dried and annealed to allow for morphological development. An annealing temperature of 200 °C was selected because it is known to be an ideal processing temperature for the Aquivion[®] PFSA^s,³⁰ and above the α -relaxation temperature of each of the PFSA^s.⁸ Following the annealing step, a ~25-30 μ m thick membrane was obtained (**Figure 5.1b**). Binary blend compositions ranging from 0, 25%, 50%, 75%, to 100% were studied. Because 3MTM has recently discontinued manufacturing the C4 PFSA, data for blends containing the 3MTM C4 PFSA are presented in the Supporting Information, and discussion in the main text is reserved for blends containing only the Syensqo Aquivion[®] (C2) and Chemours NafionTM (LSC) PFSA^s.

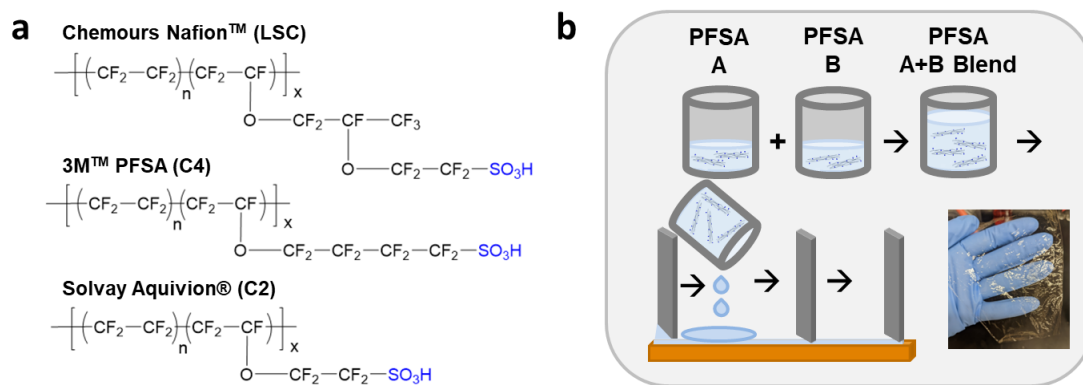


Figure 5.1. a) Chemical structures of various commercial PFSA highlighting the unique sidechain structures. b) Schematic showing the membrane fabrication process by blade-coating the blended dispersions. A photograph of a representative membrane is shown.

5.4.2. Thermomechanical Characterization

Dynamic mechanical analysis (DMA) was used to investigate the effect of the blend composition on the thermomechanical properties of the integrated PFSA membranes. The $\tan \delta$ vs. temperature curves of the dry, H^+ -form membranes containing blends of the C2 and LSC PFSA are shown in **Figure 5.2a-c**, and the data for the C4 blends is included in **Figure S5.1a,b**. DMA has been used extensively to characterize the thermomechanical properties of polymer blends and can provide insight into the degree of phase mixing between the blend components.²⁹ Provided the thermomechanical transitions of the blend components are sufficiently different from one another, the presence of two thermomechanical relaxations in a polymer blend typically suggests that isolated domains of the individual polymers are present in the blend (i.e., a heterogeneous, immiscible system), whereas a single thermomechanical transition at an intermediate temperature would suggest a homogeneous or molecularly-mixed polymer blend.

For neutralized PFSA (e.g., the sodium sulfonate form), the principal thermomechanical relaxation is the α -relaxation ($T_\alpha \approx 240$ °C for the 1100 EW LSC),

which is attributed to the onset of long-range mobility of the ionomer backbone and sidechains via a thermally-activated destabilization of the electrostatic network.³⁰ However, for acidified PFSA (i.e., in the -SO₃H form), the interactions between aggregated -SO₃H groups are principally hydrogen-bonding interactions, causing network destabilization at significantly lower temperatures.³¹ Thus, T_α for H⁺-form PFSA is still the dominant relaxation, but it is now observed near 100 °C, as shown for the PFSA in **Figure 5.2a-c**. It is also important to note that T_α is affected by the length of the PFSA sidechain. For example, the data in **Figure 5.2a** show that the T_α for the 1000 EW LSC PFSA is ~ 40 °C lower than that of the 980 EW C2 PFSA. This behavior has been attributed to a plasticization effect of the long sidechains of NafionTM compared to the shorter sidechains of the Aquivion[®] PFSA,⁸ and is a rather expected behavior for ionomers with variable length sidechains.³²⁻³³

Given the significant differences in T_α between the long and short sidechain PFSA, it is of interest to determine if blends of the different PFSA will yield two resolved α -relaxations (characteristic of distinct phases of the individual PFSA) or a single, compositionally-dependent α -relaxation (characteristic of a molecularly-mixed system). It is clear from the data in **Figure 5.2a** that blends of the long and short sidechain PFSA with essentially the same EWs display a single T_α that is compositionally-dependent and intermediate of the pure components, following a simple rule-of-mixtures. Therefore, since DMA is sensitive to phase dimensions of at least 5-10 nm or greater,³⁴ it is reasonable to conclude that the NafionTM and Aquivion[®] PFSA are molecularly-mixed in the blended membranes. Of course, a casual inspection of the similarities in the chemical structures of the two PFSA (**Figure 5.1a**) would suggest a miscible pair; however, it must be recognized that these membranes were formed from mixtures of colloidal dispersions as opposed to

molecularly-mixed true solutions.³⁵ Thus, at some point during the dispersion mixing, solvent evaporation, and/or annealing processes of membrane formation, NafionTM chains originally within their multi-chain aggregates in the dispersion apparently interchange with Aquivion[®] chains from their respective multi-chain aggregates leading to a molecularly-mixed morphology (i.e., polar domains containing aggregates of sidechains from both PFSA) with compositionally-dependent properties. Fundamentally, this finding raises a number of interesting questions for future investigations regarding the dynamics of the colloidal aggregates in PFSA dispersions and the chain interdiffusion dynamics during drying/annealing in PFSA film formation.

For integrated membranes in **Figure 5.2a** and **Figure S5.1** (Supporting Information), a single mechanical relaxation is observed with a peak temperature, T_α , appearing intermediate of the blend components. However, a clear rule-of-mixtures trend is not strictly observed for the integrated membranes containing the 720 EW C2 PFSA (**Figure 5.2b,c**). For these two blends, the lack of a clear compositional dependence is likely due to the minor change in solvent composition required to disperse the 720 EW C2 PFSA. Since the solvent composition is known to influence the microstructure of PFSA,²⁷ the integrated membranes containing the 720 EW C2 may not follow a precise rule-of-mixtures, as the solvent composition was slightly varied between the blend components. However, for all integrated membranes in which the solvent composition was identically matched between the blend components (980 EW C2 / 1000 EW LSC, 725 EW C4 / 980 EW C2, and the 725 EW C4 / 1100 EW LSC blends), the T_α is compositionally dependent between the blend components (**Figure 5.2a** and **Figure S5.1**, Supporting Information).

While a significant amount of research on the α -relaxation of PFSA has been concerned with the specific temperature, T_α , much less attention has been given to understanding the physical significance of the integration of $\tan \delta$ vs. temperature profiles in PFSA. In general, the integrated area under $\tan \delta$ is known to relate to the volume fraction of material undergoing the thermomechanical transition, with greater areas under $\tan \delta$ corresponding to greater volume fractions.²⁹ The integrated areas of $\tan \delta$ of the C2 and LSC blends are shown in **Figure 5.2d**, and the integrated areas of all blends are shown in **Figure S5.2** (Supporting Information). In the integrated membranes, the number of TFE units between sidechains (variable n , Equation 5.1) was estimated as the weighted-average number of TFE units (n) using value of n for each of the blend components. As apparent in **Figure 5.2d**, the integrated areas of $\tan \delta$ depend strongly on the number of TFE units between sidechains. In general, as the number of TFE units between sidechains increases, the integrated areas of $\tan \delta$ systematically decrease for each PFSA blend. This relationship is attributed to the crystallizability of the PTFE segments between sidechains, such that longer average segments of TFE units (greater n) yields more crystallizable copolymers in the integrated membranes. Since the molecular origin of the α -relaxation is associated with chain motions in the amorphous component of the PFSA, it follows that the total amount of material undergoing the α -relaxation decreases with increasing crystallizability of the integrated membrane. A similar relationship is observed for the blends containing the C4 PFSA (**Figure S5.2**, Supporting Information). As will be discussed below, the crystalline order in the integrated membranes can be systematically tuned through the blend composition.

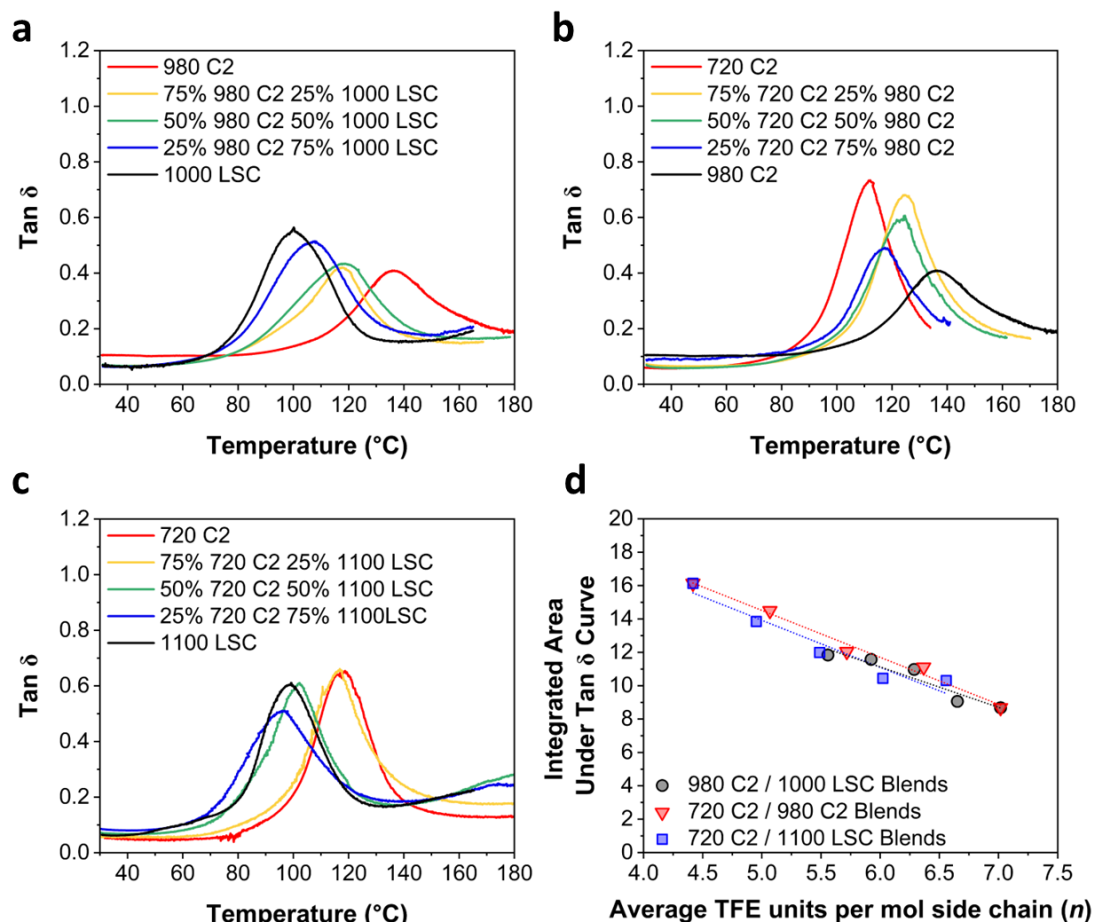


Figure 5.2. Variable-temperature DMA data revealing the $\tan \delta$ of the a) 980 EW C2/1000 EW LSC integrated membranes, b) 720 EW C2/980 EW C2 integrated membranes, and c) 720 EW C2/1100 EW LSC integrated membranes. d) Integration values for the area under the $\tan \delta$ curves, plotted as a function of the average number of TFE units between side chains (n).

5.4.3. Morphological Analysis

5.4.3.1. Crystalline Morphology Analysis

Small and wide-angle X-ray scattering (SAXS/WAXS) experiments were used to explore the crystalline morphologies of the integrated membranes over length scales ranging from less than 1 nanometer to tens of nanometers. For a given sidechain length, crystallinity in PFSA is known to increase with EW,³⁶⁻³⁷ as it is related to the number of crystallizable TFE units between pendant sidechains. When comparing different PFSA with the same EW, it is also known that PFSA with

shorter sidechains have, on average, longer runs of crystallizable TFE units between sidechains, and thus tend to yield membranes with greater crystalline order.⁸ These general trends (related to the weighted average n) are expected to be observed in blends of different PFSA, such that crystallizability could be independently tuned through the blend composition.

The WAXS profiles of the pure PFSA and integrated membranes are shown in **Figure 5.3** and **Figure S5.3** (Supporting Information). The diffraction patterns of all PFSA display two broad, amorphous halos centered at $16^\circ 2\theta$ and $39^\circ 2\theta$, respectively. The broad halo at $16^\circ 2\theta$ is assigned to interchain correlations within the amorphous phase, whereas the broad halo centered at $39^\circ 2\theta$ is assigned to intrachain correlations within the amorphous and crystalline phases.³⁸ In PFSA with high crystallizability (i.e., the 980 EW C2), a noticeable reflection centered at $18^\circ 2\theta$ is observed (**Figure 5.3a**). This crystalline reflection is assigned to the (100) family of planes of the hexagonal lattice within the PTFE-like crystallites in PFSA.³⁹ In contrast, the 100 reflection is undetectable in the scattering patterns of the 725 EW C4 membranes (**Figure S5.3**, Supporting Information), indicating very low degrees of crystallinity which is expected based on the small number of TFE units per repeat in this PFSA ($n = 3.5$).

While the (100) reflection is routinely used to measure the degree of crystallinity in highly crystalline PTFE,⁴⁰⁻⁴¹ the crystalline content of PFSA copolymers is profoundly reduced (compared to PTFE), and thus there is significant overlap between this weak crystalline reflection and the broad amorphous halo. Consequently, the low crystallinity limits the reliability of using WAXD in a quantitative analysis of the degree of crystallinity of PFSA. Qualitatively, however, the relative intensities of the (100) reflection to the amorphous halo track with the

blend composition. For example, the 720 EW C2 / 980 EW C2 series of blends (**Figure 5.3a**) compares a mixture of a much less crystallizable 720 EW C2 PFSA with a much more crystalline 980 EW C2 PFSA. For this series of blends, in which the sidechain length is held constant, it is clear that the relative intensity of the (100) reflection increases with increasing content of the more highly crystalline 980 EW C2 PFSA. Similar results are obtained for the 720 EW C2 / 1100 EW LSC blends (Figure 3b), and the intensity of the (100) reflection is even more pronounced in Figure 3c for the blends of 980 EW C2 and 1000 EW LSC PFSA.

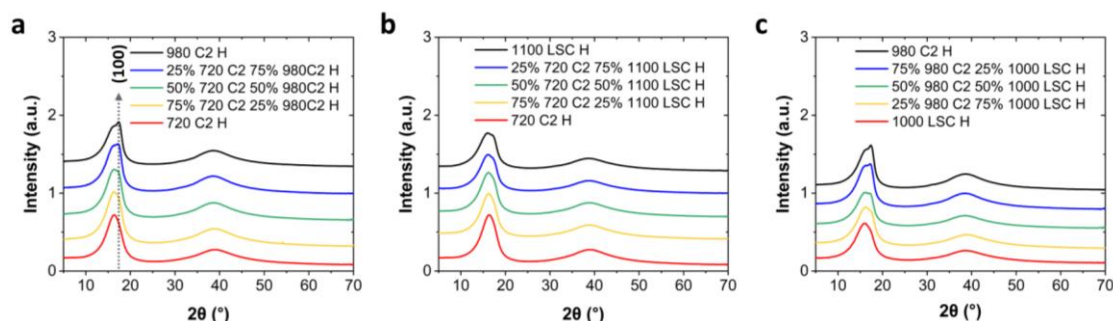


Figure 5.3. 1D WAXS patterns of the dry, H^+ -form membranes from the a) 720 EW C2/980 EW C2 blends, b) 720 EW C2/1100 EW LSC blends, c) 980 EW C2/1000 EW LSC blends. The curves are vertically offset for visualization purposes.

To investigate the long-range crystalline order within the hydrophobic component of the integrated membranes, SAXS experiments were performed on the same specimens used in the WAXS analyses. The SAXS patterns of the dry, H^+ -form PFSA and integrated membranes are shown in **Figure 4a-c** and **Figure S5.4** (Supporting Information). By measuring SAXS of the dry, H^+ -form PFSA, the scattering features associated with the crystalline morphology are effectively displayed.⁴² A single scattering maximum (commonly called the matrix knee),⁸ is observed around $q \approx 0.5\text{-}0.6 \text{ nm}^{-1}$. This scattering feature is attributed to spatial correlations of the PTFE-like crystallites in the hydrophobic phase,^{37, 43} with significant contrast in electron density between the crystalline and amorphous regions

of the copolymers. The most crystallizable PFSA, the 980 EW C2 PFSA, exhibits the greatest absolute scattering intensity as well as the sharpest scattering peak (**Figure 5.4a**), which suggests a high degree of crystalline order and periodicity of the PTFE-like crystallites. Blending the more highly crystalline 980 EW C2 with the less crystalline 720 EW C2 results in a systematic decrease in the intensity of the matrix knee in the SAXS profiles with increasing 720 EW C2 content in the integrated membranes (**Figure 5.4a**). A similar trend is noted for the 720 EW C2 / 1100 EW LSC blends (**Figure 5.4b**), 980 EW C2 / 1000 EW LSC blends (**Figure 5.4c**), and blends containing the 725 EW C4 PFSA (**Figure S5.4**, Supporting Information).

The Bragg spacings of the scattering maxima were used to estimate the average center-to-center distance between crystallites (i.e., the intercrystalline long period, d_{long}), and the values of d_{long} are plotted in **Figure 5.4d**. It was hypothesized that the long period would depend strongly on the volume fraction of non-crystallizable material in the integrated membranes, where greater volume fractions of non-PTFE material (i.e., sidechain monomer units) would increase the spacing between PTFE-like crystallites. To test this hypothesis, the volume fractions of non-crystallizable sidechains in each of the PFSA were first computationally determined from energy-minimized structures of the sidechains. The calculated molecular volume was 149 Å³ for the C2 sidechain and 240 Å³ for the LSC (Table S5.1, Supporting Information), which is over 1.5 times that of the C2 sidechain. These calculations show the profound impact that the additional atoms in the sidechain of NafionTM have on increasing the molecular volume, i.e., the bulkiness, of NafionTM sidechains (**Figure S5.5**, Supporting Information). Using the calculated molecular volumes and the known copolymer compositions, the volume fractions of sidechains in each PFSA were calculated. Details about these calculations are provided in the Supporting

Information, along with visual representations of the optimized structures (**Figure S5.5**, Table S1, Supporting Information).

As shown in **Figure 5.4d**, d_{long} correlates well with the volume fraction of sidechains in the integrated membranes. As the volume fraction of sidechains increases, the intercrystalline long period also increases. Again, this is consistent with the understanding that the pendant sidechains are excluded from the crystalline lattice. Thus, non-crystallizable sidechains contribute to filling the volume between PTFE-like crystallites and thus influence the average spacing between crystallites. A similar finding has been observed in linear low-density polyethylene (LLDPE) copolymers with varying amounts of short chain branches. Humbert and coworkers observed that the intercrystalline long period of polyethylene was greater at a higher content of sidechain branches, suggesting that the branch defects, which are excluded from the crystalline component, can influence the spacing between crystalline domains.⁴⁴ Overall, these findings show that blending PFSA into integrated membranes provides a means to control the long-range order of crystallites, and that the long-range order is strongly correlated to the volume fraction of non-crystallizable sidechains in the membranes.

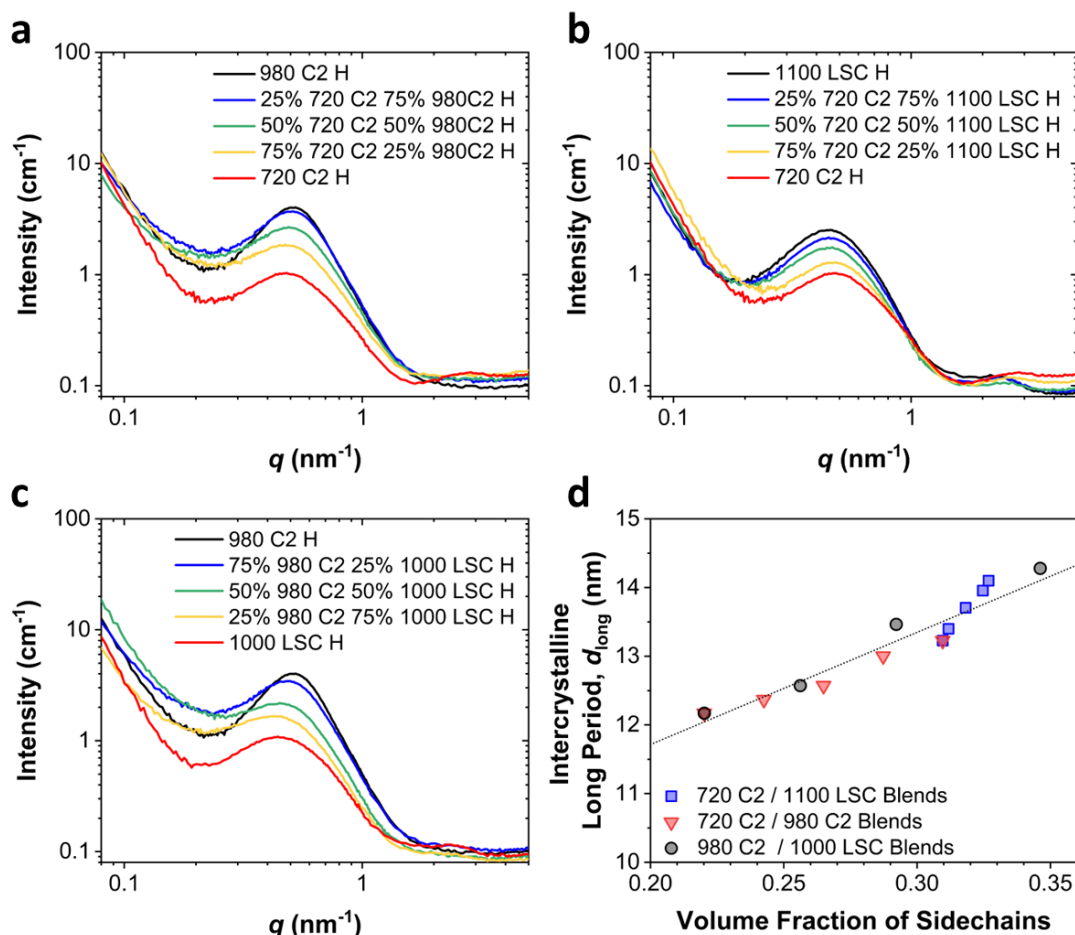


Figure 5.4. 1D SAXS patterns of the dry, H^+ -form membranes from the a) 720 EW C2/980 EW C2 blends, b) 720 EW C2/1100 EW LSC blends, c) 980 EW C2/1000 EW LSC blends, d) the intercrystalline long period obtained from the Bragg spacing of the scattering maxima, plotted as a function of the volume fraction of sidechains in the membranes. All scattering data are presented on an absolute intensity scale.

5.4.3.2. Hydrophilic Morphology Analysis

The morphology of PFSA membranes also consists of hydrophilic domains within the amorphous phase composed of regions of sulfonic acid aggregates which provide the membrane with percolated pathways for long-range proton transport. In this work, SAXS experiments were conducted to estimate the interaggregate dimensions in each of the membranes. The SAXS patterns of the single component, dry, Cs^+ form membranes are shown in **Figure 5.5a-c** and **Figure S5.6** (Supporting Information). It is well known that the scattering intensity from morphological

features of PFSA membranes can be altered by neutralizing the $\text{-SO}_3\text{H}$ group on PFSA membranes with various metal counterions.³⁶⁻³⁷ By conducting SAXS experiments on PFSA membranes in different counterion forms, the contrast between the morphological phases (e.g., crystalline, amorphous, and acid-containing aggregates) can be manipulated. For PFSA membranes, which display two SAXS features associated with the crystalline and hydrophilic domains, changing the counterion on the PFSA can allow these features to be enhanced or diminished due to systematic changes in electron density contrast.³⁶ For example, SAXS data from the dry H^+ form membranes yields a prominent intercrystalline long period feature (**Figure 5.4a-c**) but a very weak ionomer peak near $q \approx 2 \text{ nm}^{-1}$. In contrast, upon neutralization with an electron dense counterion, the dry Cs^+ -form membrane SAXS data reveals a significant reduction in the electron-density contrast between the PTFE crystals and the ionic matrix, causing a much weaker inter-crystalline long period peak relative to a much more prominent ionomer peak centered around $q \approx 2 \text{ nm}^{-1}$ (**Figure 5.5a-c** and **Figure S5.6**, Supporting Information). The scattering correlations associated with the ionomer peak are interpreted as the average center-to-center distance between aggregates of cesium sulfonate ion-pairs in the hydrophilic domains.³⁴ Neutralization is not believed to significantly alter the morphology of either the crystalline or hydrophilic domains, but it just changes the relative contrast, and thus intensity of the respective SAXS features.⁴³

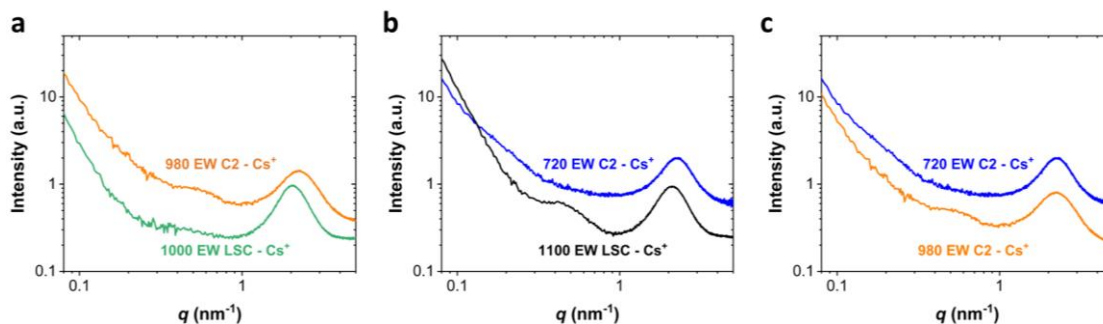


Figure 5.5. 1D SAXS patterns of the dry, Cs^+ form single component membranes, showing comparisons such as a) 980 EW C2 and 1000 EW LSC, b) 720 EW C2 and 1100 EW LSC, and c) 720 EW C2 and 980 EW C2.

The single component PFSA membranes display scattering profiles with Bragg spacing-chemical structure relationships that are consistent with prior comparisons made in the literature. For example, the effects of sidechain length on the interaggregate spacing can be considered by comparing the 980 EW C2 to the 1000 EW LSC SAXS profiles with essentially the same EW (**Figure 5.5a**). The Bragg spacing, which is interpreted as the average interaggregate distance (d_{agg}), was $d_{\text{agg}} \approx 2.8$ nm for the 980 EW C2 compared to $d_{\text{agg}} \approx 3.0$ nm for the 1000 EW LSC. This finding suggests that longer pendant sidechains yield greater interaggregate spacings which is consistent with comparisons of the C2 and LSC PFSA's made by Kusoglu and Weber who show that LSC PFSA's have larger interdomain spacings compared to C2 PFSA's at comparable EWs.⁸ SAXS studies of polystyrene-based ionomers with variable-length sidechains have revealed a similar relationship, showing that the Bragg spacing of the ionomer peak generally increases with the length of the acidic sidechain.³² The interaggregate spacing of the 1100 EW LSC was also greater than the 720 EW C2, albeit at non-comparable EWs (**Figure 5.5b**). At the same side chain length, the ionomer peak position of the 720 EW C2 was not significantly different

than the 980 EW C2 (**Figure 5.5c**), indicating essentially identical interaggregate dimensions in both C2 membranes.

In addition to the Bragg dimensions in the single component membranes, the widths of the SAXS ionomer peaks of the individual PFSA's were also characterized and compared to previously reported chemical structure-ionomer peak width relationships. At a similar EW, the ionomer peak of the 980 EW C2 is significantly broader than the peak observed in 1000 EW LSC (**Figure 5.5a**). In a prior study of polystyrene-based ionomers with variable-length sidechains,³² the full-width at half maximum (FWHM) of the SAXS ionomer peak has been postulated to correspond to the polydispersity in interaggregate distances and/or sizes. A broad range of interaggregate distances or sizes is thought to yield a broad peak (large FWHM), whereas narrow distributions of these dimensions yield a comparatively narrow peak (small FWHM). A similar interpretation has been made in the interpretation of SAXS ionomer peaks from PFSA's,^{18, 45} as the peak width has been related to the distribution in domain sizes and/or spacings. Based on these interpretations, a narrower ionomer peak (smaller FWHM) observed in the 1000 EW LSC compared to the 980 EW C2 (**Figure 5.5a**) suggests that the long sidechains of NafionTM result in more uniformly spaced ionic aggregates of more uniform size compared to those formed by the short sidechains in Aquivion[®]. The narrower distribution of aggregate dimensions in a long sidechain ionomer may be explained by the reduced steric constraints encountered by the ion pairs on the end of the long sidechains.³² For the LSC PFSA which has a greater distance between the PTFE backbone and the end of the sidechain, the ion pairs have a greater range of mobility. Therefore, it is easier for the ion pairs in Nafion to close-pack into uniformly spaced and/or sized aggregates.³² The FWHM of the 1100 EW LSC was also narrower than that of the 720 EW C2 (**Figure 5.5b**),

although the EWs are not comparable. At the same sidechain length, the FWHM of the ionomer peak in the 720 EW C2 was measurably less than that of the 980 EW C2 (**Figure 5.5c**). This finding suggests that there is less dispersity in the aggregate dimensions for the 720 EW C2 membrane than in the 980 EW C2 membrane.

Once the baseline morphologies of the blend components had been identified and differentiated, the morphologies of the integrated membranes were probed using the same SAXS experiments. A central question we sought to answer here was whether blended PFSA membranes would contain (I) two distinct populations of aggregates (i.e., aggregates resulting from long sidechains and aggregates resulting from short sidechains), or (II) mixed aggregates that contain both long and short sidechains within the same aggregate. As schematically illustrated in **Figure 5.6**, the scattering behavior of the integrated membranes could be expected to display a broad ionomer peak with two maxima if the long and short sidechain aggregates remained isolated (Case I), or a relatively narrow ionomer peak with a single maximum and a compositionally dependent position if the aggregates contained a mixture of both long and short sidechains (Case II). Case I represents what one would expect if isolated PFSA aggregates of the blend components were completely preserved in the integrated membranes. In this case, signatures of both ionomer peaks would be present in the SAXS pattern of the integrated membranes, and the breadth of the peak would be greater than the peaks from the blend components, spanning the width of the ionomer peaks from PFSA A to B. Case II represents what one would expect if the PFSA membranes in the blends come together to form new aggregates containing sidechains from both PFSA membranes. In this case, a single ionomer peak would be present in the integrated membranes and exhibit an intermediate peak maximum and breadth to the blend components.

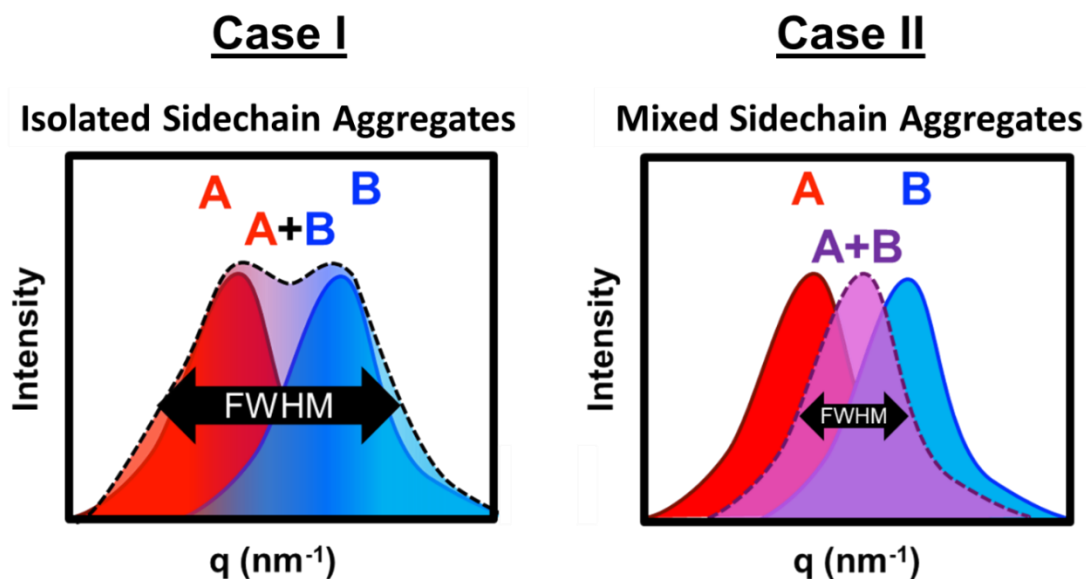


Figure 5.6. Schematic figure representing two cases of SAXS ionomer peak profiles in the integrated membranes. In both cases, polymer A, a long sidechain PFSA (solid red), and polymer B, a C2 PFSA (solid blue) have distinctly different ionomer peak positions. In Case I, the scattering pattern of a 50/50 blend (purple dotted line) contains two ionomer peaks from polymer A and polymer B, indicating that isolated long sidechain aggregates from polymer A and isolated short sidechain aggregates from polymer B are preserved in the blend membrane. The FWHM of the blend is broader than the FWHM of the blend components. In Case II, the scattering pattern of a 50/50 blend (purple dotted line) contains a single ionomer peak with an intermediate peak position and FWHM of the blend components, suggesting that the aggregates contain sidechains from both PFSA.

As shown in **Figure 5.7a-c** and **Figure S5.6** (Supporting Information), a single ionomer peak is observed in the SAXS patterns of the integrated membranes at each composition of PFSA A/PFSA B. The average interaggregate distance (d_{agg}) (**Figure 5.7d-f**) and the FWHM of the ionomer peak (**Figure 5.7g-i**) are plotted as a function of the blend composition. Remarkably, the interaggregate distance (**Figure 5.5d-f**) and FWHM (**Figure 5.7g-i**) systematically track linearly with the blend composition. These observations align with Case II (**Figure 5.6**) and intriguingly suggest that the aggregates in the integrated membranes contain sidechains from both

PFSAs. A similar trend is noted for the scattering behavior of the blends containing the C4 PFSA (**Figures S5.7, S5.8**, Supporting Information). These SAXS results are also consistent with the DMA data discussed above (**Figure 5.2**), which again revealed a single α -relaxation in the integrated membranes, suggestive of a molecularly-mixed hydrogen bonded network. Overall, results from these experiments are highly supportive of a molecularly-mixed morphology on the length scale of the sidechain aggregates and suggest that at some point during the dispersion, casting, and/or drying steps of membrane fabrication, the distinct multi-chain aggregates from the two different PFSA dispersions disassociate and reassemble to form aggregates containing both PFSA sidechains.

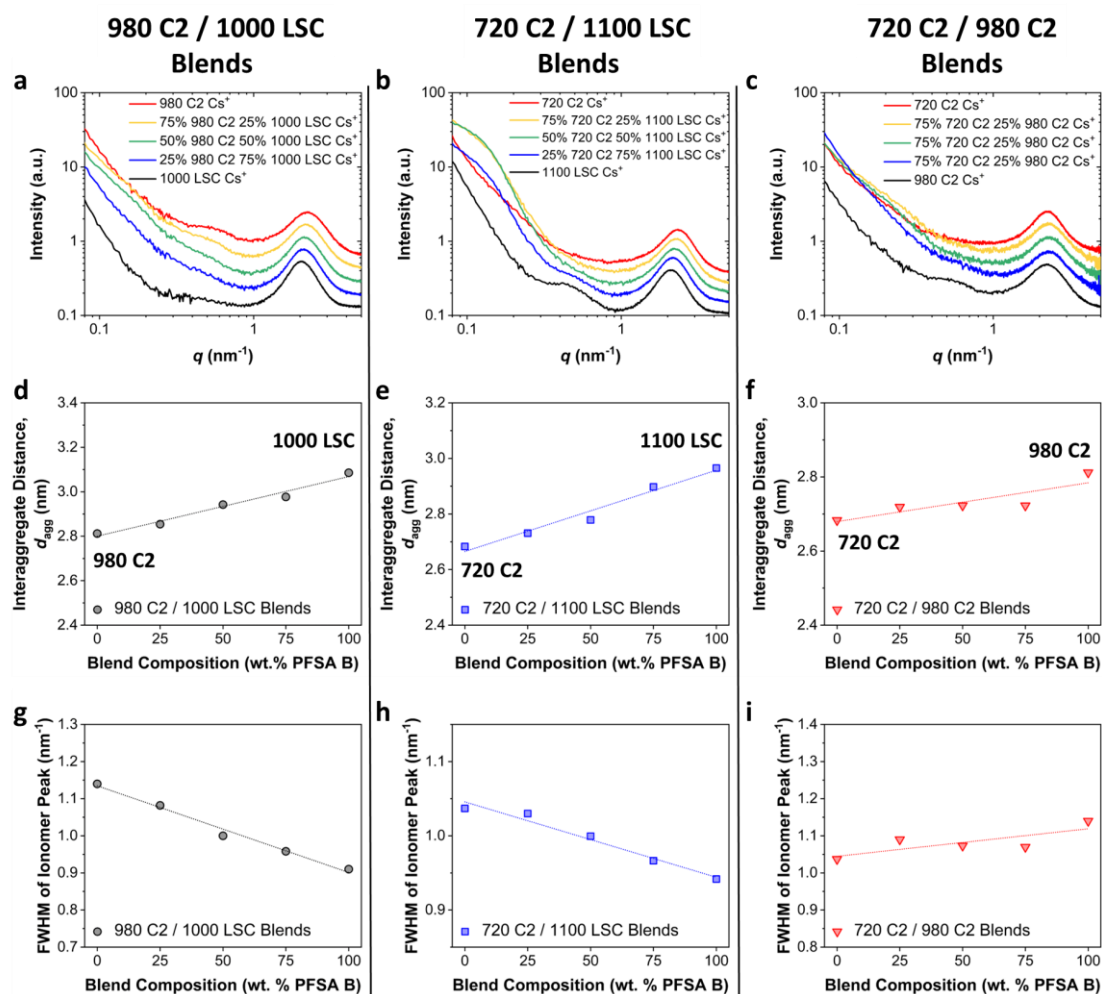


Figure 5.7. 1D SAXS patterns of the dry, Cs⁺ form membranes from the a) 980 EW C2/1000 EW LSC blends, b) 720 EW C2/1100 EW LSC blends, and c) 720 EW C2/980 EW C2 blends. In d-f) the interaggregate distance obtained from the Bragg spacing of the ionomer peak is plotted as a function of the blend composition for the respective blends. In g-h) the FWHM of the ionomer peak is plotted for the corresponding integrated membranes. The parameters in d-i) are plotted as a function of the wt.% of PFSA B in the PFSA A/PFSA B binary blend.

The SAXS experiments on the Cs⁺ form membranes may also be used to study how the various aspects of the PFSA chemical structure (e.g., EW and sidechain length) influence the interaggregate distance and the FWHM of the ionomer peak. The EW and sidechain length in the integrated membranes were calculated as a compositionally-dependent, weighted-average of the EW and sidechain length of the binary blend components, and hereafter referred to as the average EW and average

sidechain length. The interaggregate distance (d_{agg}) is plotted as a function of the average EW in **Figure 5.8a**. For the 720 EW C2 / 980 EW C2 integrated membranes containing PFSA with identical sidechain lengths, d_{agg} changes very little with the average EW of the membrane. In contrast, d_{agg} systematically increases in the 720 EW C2 / 1100 EW LSC blends as the content of the higher EW 1100 EW PFSA increases. With nearly the same EW, d_{agg} increases abruptly with average EW, yet still systematically, in the 980 EW C2 / 1000 EW LSC blends.

In contrast to the well-behaved d_{agg} versus average EW trends in **Figure 5.8**, we note that the d_{agg} of the 725 C4 / 980 EW C2 integrated membranes shows an opposite trend: d_{agg} of the 725 EW C4 systematically decreases with the addition of the higher EW 980 EW C2 (**Figure S5.7a**, Supporting Information). When considering all five blends plotted as a function of the average EW (**Figure S5.7a**, Supporting Information), it is clear that there are inconsistent trends with respect to the relationship between the interaggregate spacing and the average EW of the membrane. In addition to variations in average EW of the integrated membranes, it is also important to recognize that in many of these blends, there is also a mixture of different sidechain lengths (e.g., C2/LSC, C2/C4, and C4/LSC). Therefore, the inconsistencies in the d_{agg} -EW trends could be attributable to conflicting effects from differences in average sidechain length. To better understand the influence of sidechain length on the interaggregate distance, d_{agg} is plotted as a function of the average sidechain length in **Figure 5.8b**. Interestingly, d_{agg} systematically increases as the average sidechain length increases for the C2/LSC blends. Moreover, in contrast to the inconsistencies with the d_{agg} -EW trends, a systematic trend of increasing d_{agg} with average sidechain length is preserved with the C4 blends (**Figure S5.7b**, Supporting Information). In complete agreement with d_{agg} versus sidechain length

trends observed for conventional ionomers,³² the data in **Figure 5.8b** show that the same relationship is observed with respect to the *average* sidechain length, which can easily be tuned by simply blending PFSA with different pendant lengths. Therefore, the fact that d_{agg} tends to increase with sidechain length regardless of the EW differences between the PFSA suggests that the length of the acidic sidechain is more influential in determining the interaggregate spacing than the acid content (EW).

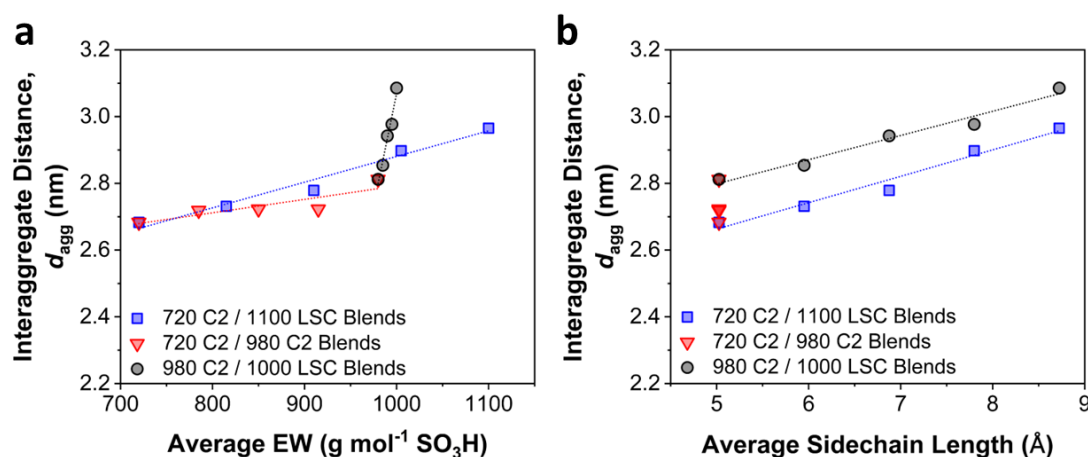


Figure 5.8. The interaggregate distance obtained from the Bragg distance of the ionomer peak is plotted as a function of the a) the average EW or b) the average sidechain length in the integrated membranes containing the C2 and LSC PFSA.

The FWHM was also analyzed as a function of the blend composition to understand how the various aspects of the PFSA chemical structure impact the FWHM of the SAXS ionomer peak. The FWHM of the SAXS ionomer peak is plotted as a function of the average EW in **Figure 5.9a**. Again, the FWHM is understood to correspond to the polydispersity in interaggregate distances.³² As shown in **Figure 5.9a** and **Figure S5.8a** (Supporting Information), the EW-FWHM relationship is not obvious. However, when plotting the FWHM of the SAXS ionomer peak as a function of the average sidechain length in **Figure 5.9b** and **Figure S5.8b**

(Supporting Information), a clearer relationship is observed. As the average sidechain length increases, the FWHM of the SAXS ionomer peak tends to decrease, suggesting a narrower distribution of aggregate dimensions (interaggregate spacing and/or aggregate size). Overall, the SAXS experiments on the aggregate morphologies in the integrated membranes reveal clear composition-morphology relationships that exist in binary blends of PFSA.

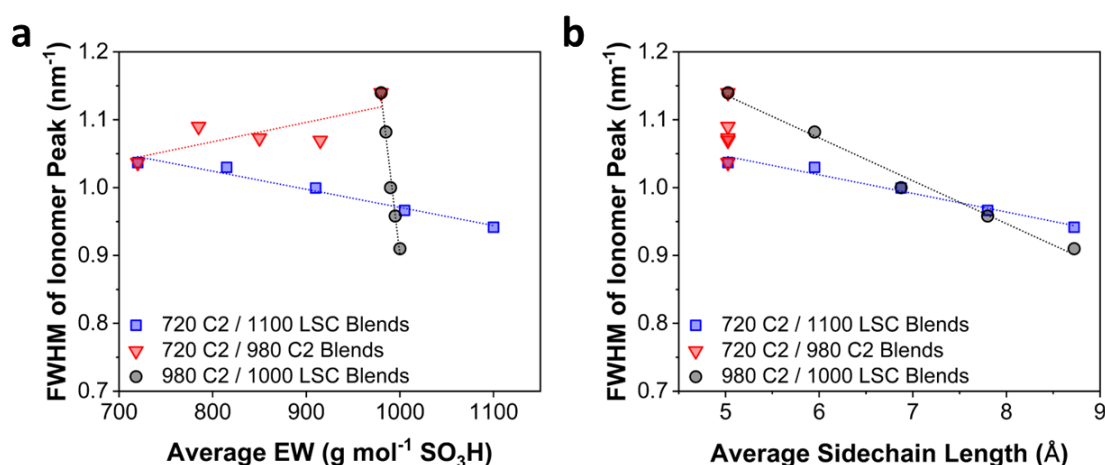


Figure 5.9. The FWHM of the ionomer peak is plotted as a function of the a) the average EW or b) the average sidechain length in the integrated membranes containing the C2 and LSC PFSA.

5.4.4 Physical Property Characterization

Finally, three key physical properties of the integrated membranes were investigated, including water vapor uptake, proton conductivity, and areal (in-plane) swelling. The water vapor uptake of the single component and integrated membranes was measured via dynamic vapor sorption experiments over a wide range of relative humidities (**Figure S5.9**, Supporting Information). The maximum water vapor uptake of the membranes, observed at 95% RH, is plotted vs. the average EW in **Figure 5.10a** and **Figure S5.10a** (Supporting Information). When comparing the single

component membranes, the lower EW 720 EW C2 membrane exhibited the highest water uptake (ca. 26 wt. %), whereas the higher EW 1100 EW LSC membrane exhibited the lowest water uptake (ca. 15 wt. %). This result was expected, as the water vapor uptake is inherently related to the total ion content of the material (EW).⁸ Based on the SAXS results discussed above that showed that the average interaggregate spacing in the integrated membranes was intermediate that of the single blend components (**Figure 5.7d-f**), it was expected that the physical properties related to the hydrophilic domain would follow a simple rules-of-mixtures. Notably, the water vapor uptake of the integrated membranes follows a profoundly linear relationship with respect to the blend composition, systematically decreasing with increasing average EW of the membrane (**Figure 5.10a**). As expected, the differences in water vapor uptake were negligible for the 980 EW C2 and 1000 EW LSC integrated membranes at roughly the same EW.

The proton conductivity of the membranes under fully hydrated conditions is shown in **Figure 5.10b**. As expected, the lower EW 720 EW C2 membrane displayed a higher proton conductivity than the higher EW 1100 EW LSC membrane which is again known to relate to the total ion content.⁸ Similar to the water vapor uptake, the proton conductivity of the integrated membranes follows a direct linear relationship and systematically decreases with increasing EW of the membrane (**Figure 5.10b**).

The areal (in-plane) swelling of the membranes when exposed to 80 °C H₂O was measured, which represents the maximum dimensional changes the membrane may experience in a hydrogen fuel cell or water electrolyzer. Consistent with the water vapor and proton conductivity results, the areal swelling of the membranes is the greatest for membranes with a higher average ion content (**Figure 5.10c**). Moreover, the dimensional changes of the integrated membranes systematically

decrease (in a linear fashion) with an increase in the average EW. Similar EW-property relationships are observed in the membranes containing the C4 PFSA (Figure S5.10, Supporting Information).

Overall, these results support the structure-property relationships that have been studied in single component PFSA membranes for many decades. The systematic trends observed in these critical properties also lend further support that blends of these PFSA yield molecularly-mixed systems with no unusual heterogeneities associated with processing of mixed dispersions. Therefore, the observed morphology-property relationships from the integrated membranes demonstrate that the well-established and time-honored structure-property relationships of PFSA can be systematically tailored by simply blending PFSA with different structures and physical properties. From a sustainability perspective, it is now clear that reconstituted/recycled membranes from mixed PFSA feedstocks are expected to have valuable and predictable properties in future PEMFC or electrolyzer applications.

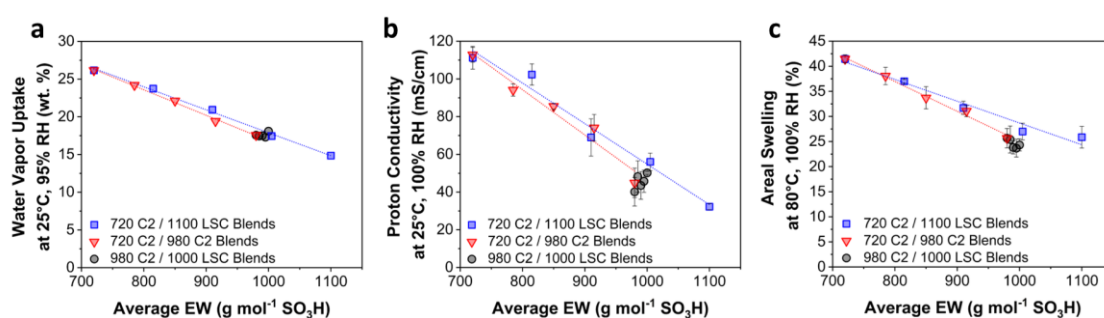


Figure 5.10. a) Dynamic water vapor sorption at 25 °C, 95% RH, b) proton conductivity in ~25 °C DI H₂O, c) in-plane dimensional changes of the membranes in 80 °C H₂O compared to fully dry dimensions.

5.5. Conclusion

In this work, dispersions of commercial PFSA (Chemours NafionTM, Syensqo Aquivion[®], 3MTM PFSA) having unique sidechain lengths and equivalent weights were blended and cast to yield integrated membranes. The integrated PFSA membranes were shown to be well-mixed on many length scales, ranging from the dimensions between the sidechain aggregates to the dimensions between PTFE-like crystallites. The key physical properties of the integrated membranes were shown to follow a remarkably similar rule-of-mixtures, including proton conductivity, water vapor uptake, and areal swelling. Overall, this work demonstrates that commercial PFSA can be combined into a single membrane to yield an integrated membrane with intermediate and predictable properties. Blending commercial PFSA will be necessary to further commercialize recycling efforts because PFSA binders in electrodes are generally different than the PFSA membranes in a given membrane electrode assembly (MEA). Future work will be required to evaluate/optimize blend compositions for electrode layers paired with blended membranes in integrated MEAs. Moreover, the utilization of end-of-life feed streams will require critical considerations of chemically degraded PFSA once recycling protocols become standardized.

5.6 Acknowledgements

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5.7 Supporting Information

Rule-of-mixtures properties in binary blends of perfluorosulfonic acid copolymers: implications for recycling fuel cell and electrolyzer membranes

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*Moore**

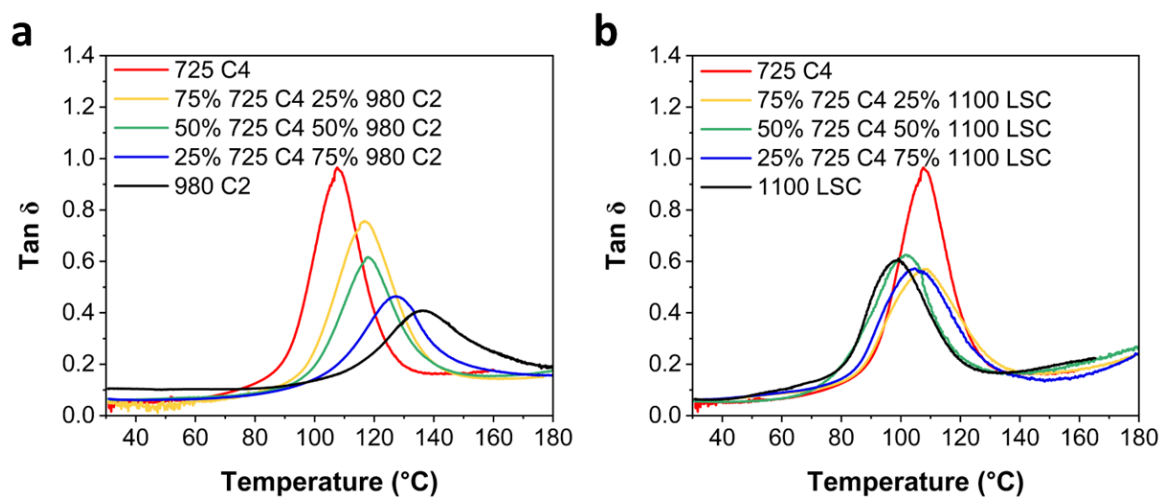


Figure S5.1. Variable-temperature DMA data revealing the tan δ of the a) 725 EW C4/980 EW C2 single component and integrated membranes, b) 725 EW C4/1100 EW LSC single component and integrated membranes.

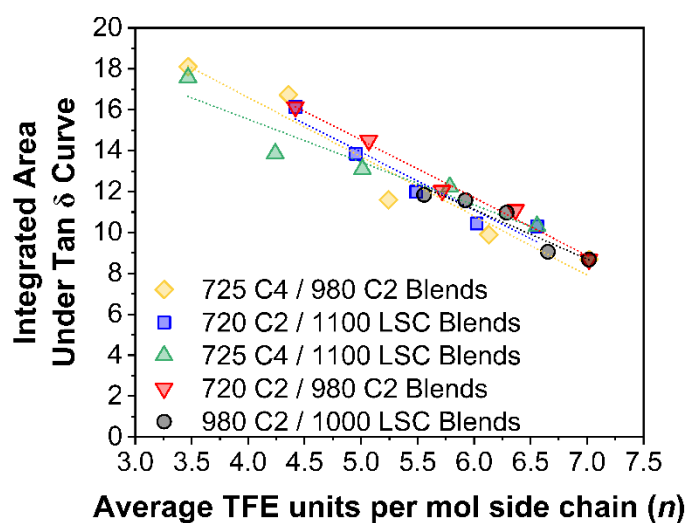


Figure S5.2. Integration values for the area under the $\tan \delta$ curves for the H^+ -form integrated membranes, plotted as a function of the average number of TFE units between side chains (n).

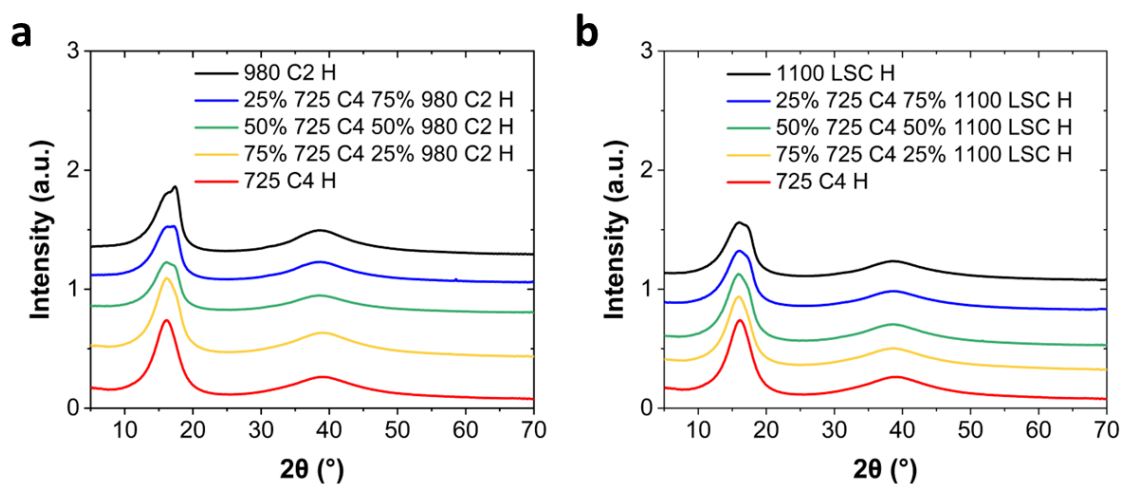


Figure S5.3. 1D WAXS patterns of the dry, H^+ -form membranes from the a) 725 EW C4/980 EW C2 blends, b) 725 EW C4/1100 EW LSC blends. The curves are vertically offset for visualization purposes.

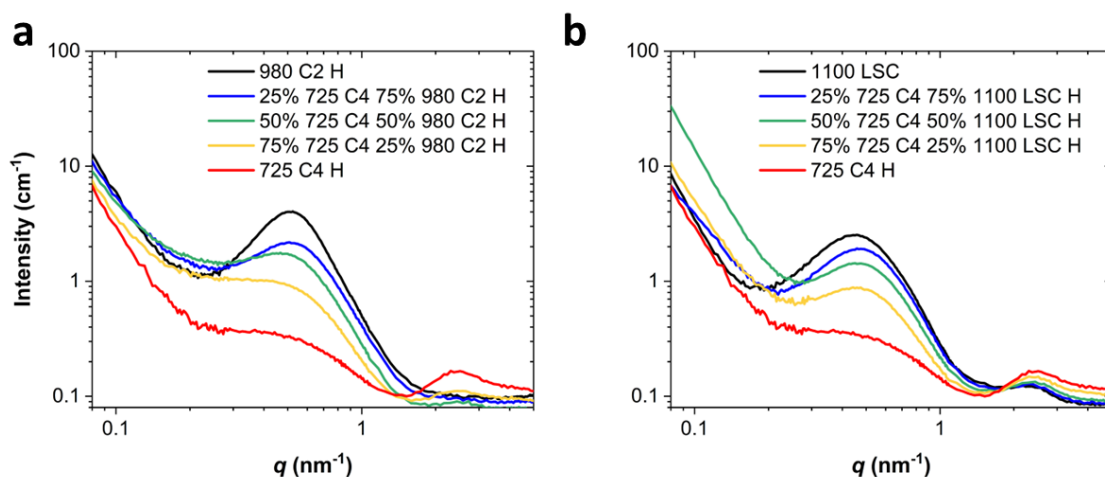


Figure S5.4. 1D SAXS patterns of the dry, H⁺-form membranes from the a) 725 EW C4/980 EW C2 blends, b) 725 EW C4/1100 EW LSC blends.

Calculating the volume fraction of sidechains in the integrated membranes

The molecular volumes of the analogues to the monomers are shown in **Figure S5** with optimized/energy-minimized structures, and the molecular volumes calculated in the VEGA XX software are listed in **Table S1**. The total volume of one mole of PFSA (sidechain repeat + TFE units per repeat) was calculated from Equation S5.1,

$$\text{Total Volume} = 1 \times Vol_{SC} + n \times 75.2 \text{ \AA}^3 \quad (\text{S5.1})$$

where Vol_{SC} is the volume of the monomer unit containing the sidechain, m is the number of TFE units between sidechains, and $75.2 \text{ \AA}^3$ is the molecular volume of a single hexafluoroethane unit. The sidechain fraction of the total volume was calculated from Equation S5.2, shown below.

$$\text{Volume fraction of sidechains} = \frac{1 \times Vol_{SC}}{\text{Total volume}} \quad (\text{S2})$$

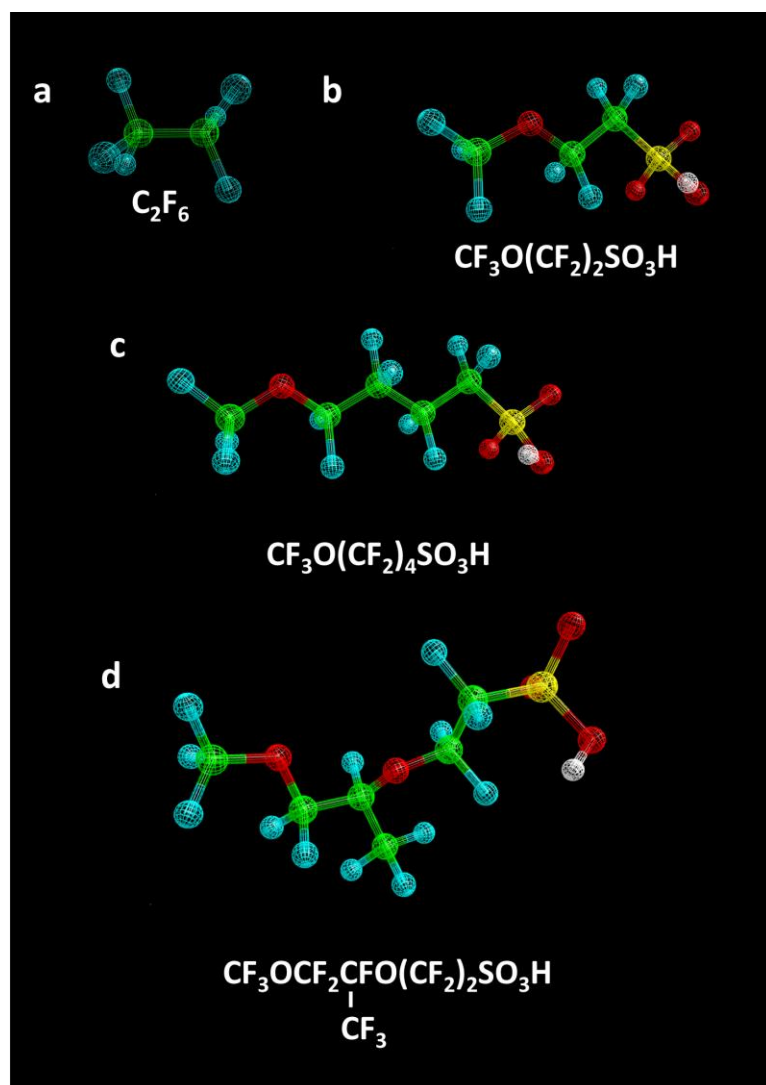


Figure S5.5. Energy-minimized structures of the comonomer analogues, including a) hexafluoroethane, b) the C2 sidechain-containing comonomer, c) the C4 sidechain-containing comonomer, and d) the LSC-containing comonomer.

Table S5.1. Calculated molecular volumes of the optimized structures shown in Figure S5.

Structure	Calculated Molecular Volume [$\text{\AA}^3$]
Hexafluoroethane	75
C2 Sidechain-Containing Comonomer	149
C4 Sidechain-Containing Comonomer	202
LSC-Containing Comonomer	240

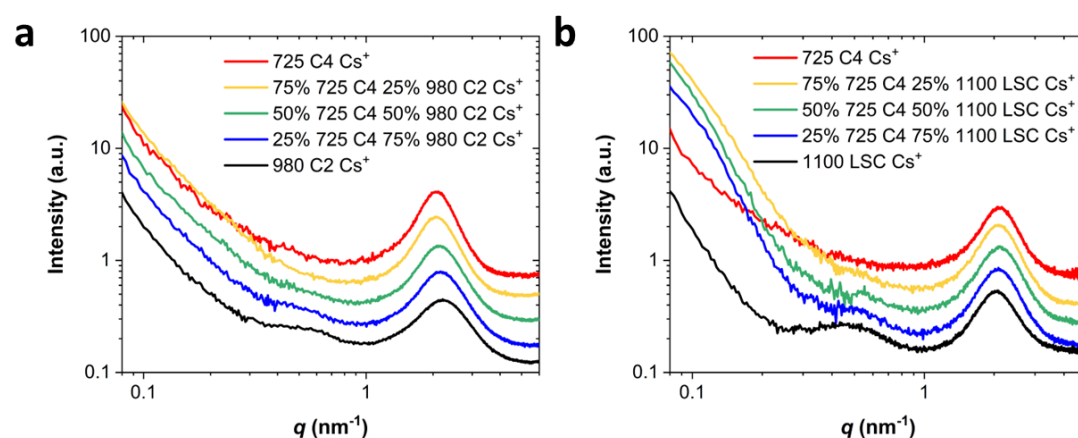


Figure S5.6. 1D SAXS patterns of the dry, Cs^+ form membranes from the a) 725 EW C2/980 EW C2 blends and the b) 725 EW C4/1100 EW LSC blends.

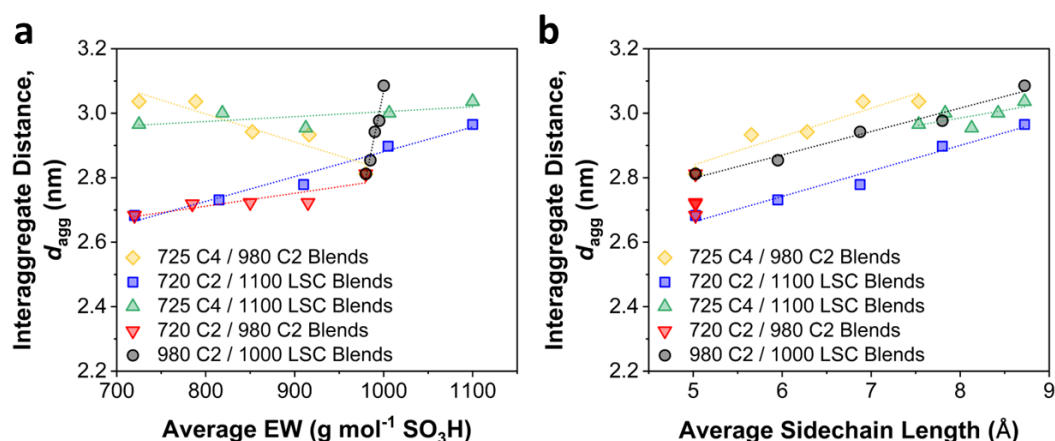


Figure S5.7. The interaggregate distance (d_{agg}) obtained from the Bragg distance of the ionomer peak is plotted as a function of the a) the average EW or b) the average sidechain length for all compositions of the integrated membranes. All blends are shown for comparison.

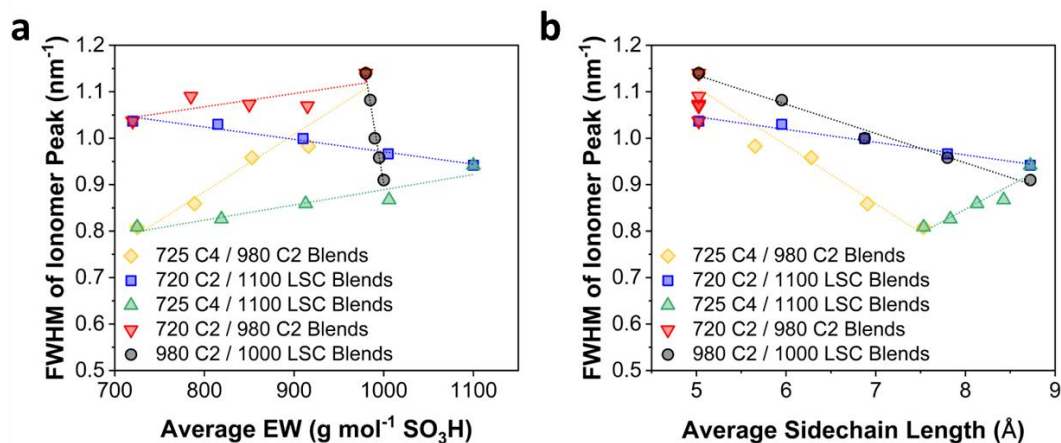


Figure S5.8. The FWHM of the ionomer peak is plotted as a function of the a) the average EW or b) the average sidechain length for all compositions of the integrated membranes. All blends are shown for comparison. In contrast to the other blends, the 725 EW C4 has a narrower ionomer peak (smaller FWHM) than the 1100 EW LSC. The remarkably high acid content and essentially amorphous character of the 725 EW C4 may lead to a more regularity in the interaggregate spacing compared to the other PFSA.

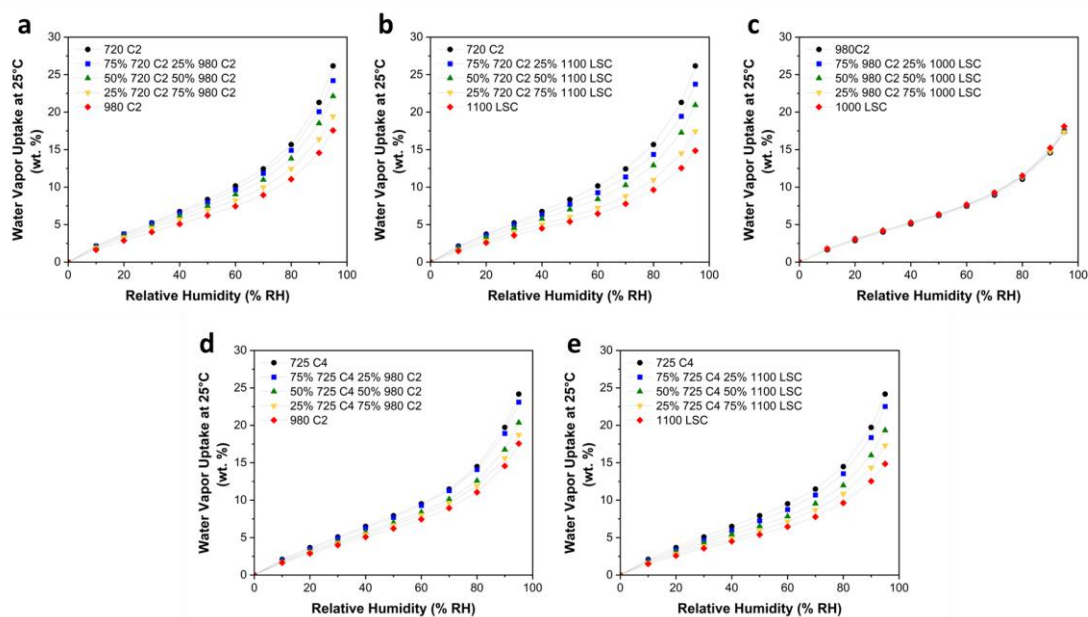


Figure S5.9. Water vapor sorption isotherms conducted at 25 °C for the a) 720 EW C2/980 EW C2 blends, b) 720 EW C2/1100 EW LSC blends, c) 980 EW C2/1000 EW LSC blends, d) 725 EW C4/980 EW C2 blends, e) 725 EW C4/1100 EW LSC blends.

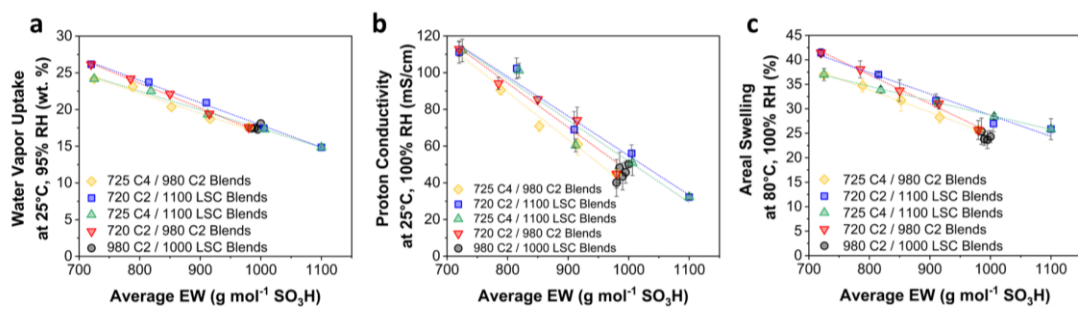


Figure S5.10. a) Dynamic water vapor sorption at 25 °C, 95% RH, b) proton conductivity in ~25 °C DI H₂O, c) dimensional changes of the membranes in 80 °C H₂O. All blends are shown for comparison.

5.8 Future Work

One area of research that could be thoroughly studied is the application of these blended membranes in membrane electrode assemblies (MEA) for hydrogen fuel cells. Testing the integrated membranes under fuel cell operating conditions would provide additional evidence that this blending process could be applied at scale. We have conducted initial fuel cell experiments on the integrated membranes of the 720 EW C2 / 1100 EW LSC blends, since those PFSA's are the most dissimilar in sidechain length and equivalent weight. MEAs were prepared using a hot press method, in which two gas diffusion electrodes are pressed onto the membrane at elevated temperature and pressure to create good contact between the membrane and the electrodes.⁴⁶ Our initial fuel cell experiments failed due to the presence of electrical shorts in the MEAs. In general, successful fuel cell experiments cannot be conducted if there is an electrical short in the cell. This result indicated that at some point during the hot press process, the electrodes were coming into contact with one another leading to an electrical shortage. Investigation of the surface of the electrodes with laser profilometry/optical microscopy resulted in the image shown in **Figure 5.11**. As can be seen in the images, the surface of the electrode consisting of the catalyst particles was extremely rough, which could result in the particles piercing the membrane during the hot press process.

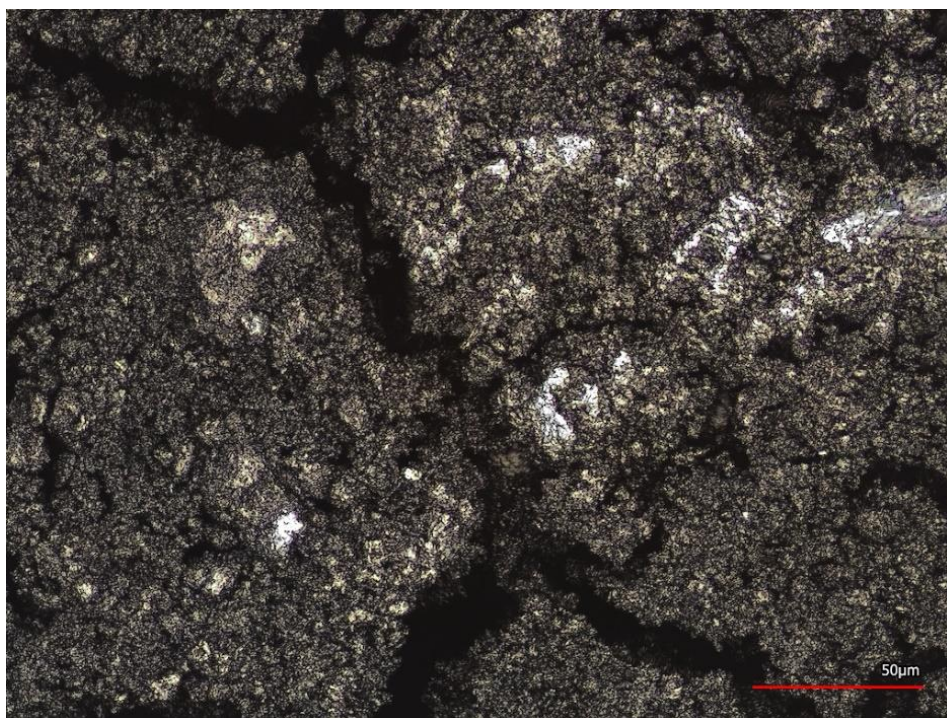


Figure 5.11. Laser profilometry image of the surface of the gas diffusion electrode used in the preliminary fuel cell studies of blended membranes.

Future work should focus on eliminating electrical shorts in MEAs of integrated membranes. First, thicker membranes could be cast on industrial processing equipment leading to a greater membrane thickness and therefore resistance to puncturing by the electrodes. Second, different electrodes should be studied to understand how the surface morphology of the electrode influencing the electrical shorting of the MEA. Third, catalyst-coated membranes could be prepared which would likely dramatically reduce the electrical shorting issue, but would also result in membrane-to-membrane variability across the blend composition.

The presence of gross electrical shorts in MEAs can easily be detected using a potentiostat and conductive blocks shown in **Figure 5.12** prior to fuel cell testing. As outlined in the Springer Handbook of Electrochemical Energy, a simple test using Ohm's Law can be conducted by applying a current of 1 mA and measuring the voltage across the cathode and the electrodes.⁴⁷ Next, the resistance can be determined

from the slope, and resistance values greater than $500 \Omega \text{ cm}^2$ are considered adequate and free from gross shorts.⁴⁷ The primary advantage of this test is that the presence of electrical shorts can be screened using a simple potentiostat before the MEA is setup for more complex fuel cell experiments.



Figure 5.12. A custom copper testing geometry designed and manufactured by Scribner, LLC for testing the gross electrical shortage of MEAs prior to fuel cell testing. The MEA is placed in the center of the setup, with copper blocks underneath and on top of the MEA, creating a sandwich. The leads are connected to a potentiostat.

Another area for future investigation could involve a comprehensive study of the mechanical properties of integrated membranes from binary blends of PFSA. Preliminary stress-strain data collected on the 720 EW C2 / 1100 EW LSC blends is shown in **Figure 5.13**. The mechanical behavior of the blends seems to follow a clear rule-of-mixtures throughout the blend composition. Other membranes from blends of the same sidechain length and similar equivalent weights should be studied to

understand whether the mechanical properties of integrated membranes can be controlled by the formulation of the blend.

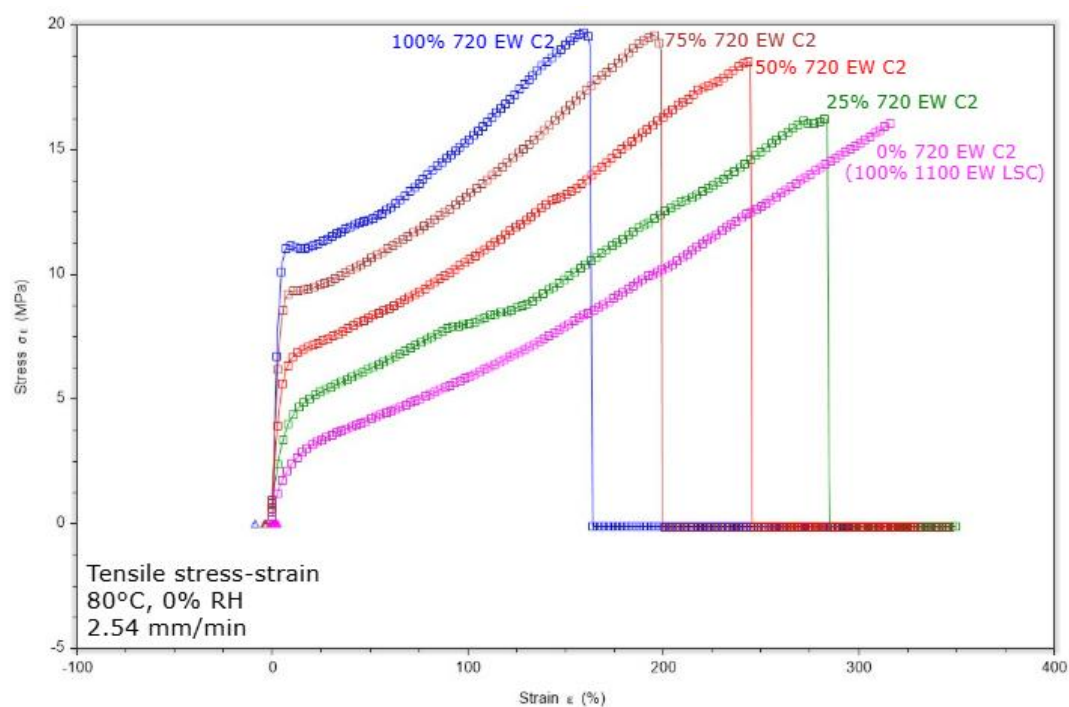


Figure 5.13. Stress-strain profiles of membranes from the 720 EW C2 / 1100 EW LSC series.

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Chapter 6. Morphological and Computational Analysis of Additively Manufacturable Polyimide Precursors: Implications for Rationally Designing New Polyimide Structures

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6.1 Abstract

In this work, photocurable polyimide precursors are additively manufactured via vat photopolymerization and thermally post-processed into bulk polyimide discs. Two polyimide structural variants were additively manufactured, post-processed, and characterized: the conventional pyromellitic dianhydride / 4,4'-oxydianiline (PMDA/ODA), and one based on PMDA / 4,4'-diaminodiphenyl sulfone (PMDA/DDS). The morphologies of both variants were studied as a function of post-processing temperature. Scanning electron microscopy experiments reveal that the bulk morphologies of all printed parts are homogeneous below 350 °C. Post-processing at and above 350 °C

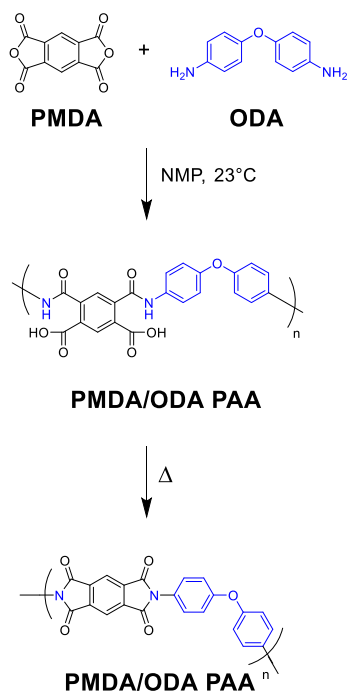
results in prevalent internal voids, which are more severe in the PMDA/DDS parts. Small/wide-angle X-ray scattering experiments reveal that the crystalline domains in PMDA/DDS parts are more loosely organized than the PMDA/ODA parts. Atomistic simulations reveal that the sulfone linkage of PMDA/DDS disrupts pi-stacking of aromatic rings of neighboring chains, resulting in a profound reduction in interaction strength between adjacent polymer units in PMDA/DDS compared to PMDA/ODA. Ultimately, the reduced thermal stability of PMDA/DDS parts is attributed to disordering of the PMDA/DDS crystallites. This work presents the first in-depth study of the structure-morphology relationships of additively manufacturable polyimide precursors throughout post-processing. These insights will inform future work focused on the development of new polyimides with stable semicrystalline morphologies.

6.2 Introduction

Aromatic polyimides are high-performance polymers with exceptional physical properties including high thermal stability, high glass transition temperatures, and excellent chemical resistance.¹ These valued properties of polyimides allow them to be utilized in thermally and mechanically demanding applications, such as aerospace² and defense research areas.³ The benchmark aromatic polyimide prepared from pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA), commonly recognized as the tradename Kapton® (Dupont).⁴ The conventional approach to preparing poly(4,4'-oxydiphenylene pyromellitimide) (PMDA/ODA) involves a two-step synthesis. In the first step, PMDA is polymerized with ODA to yield the ring-opened PMDA/ODA poly(amic acid) (PAA) (**Figure 6.1a**), which is soluble in common organic solvents such as NMP and DMSO.¹ Organic solutions of the PAA are commonly cast onto a substrate into a two-

dimensional (2D) form factor. In the second step of this conventional approach, the PMDA/ODA PAA cast solution is heated to evolve the solvent and drives the thermally-driven cyclodehydration reaction, yielding the PMDA/ODA polyimide film.¹ Throughout this paper, PMDA/ODA polyimides prepared from this conventional two-step PAA approach will be denoted as PMDA/ODA_(PAA).

a) Conventional Polyimide Preparation



b) Polysalt Polyimide Preparation

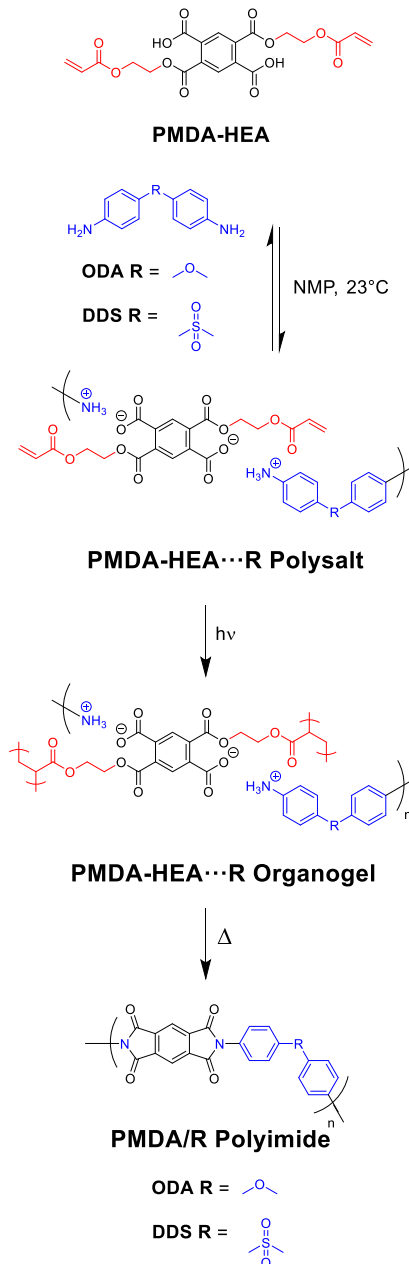


Figure 6.1. a) Schematic of the conventional synthesis of PMDA/ODA polyimides through the formation of a poly(amic acid). b) Schematic representing the supramolecular polysalt approach. In this method, PMDA-HEA reacts with a diamine to form a supramolecular polysalt. UV irradiation of printed polysalt solution solidifies the structure, forming an organogel. Thermal treatment of the printed part drives the cyclodehydration reaction and volatilizes the acrylic scaffold to afford the aromatic polyimide.

Despite their excellent physical properties, aromatic polyimides like PMDA/ODA are challenging to process into more complex, three-dimensional (3D) shapes for many reasons. First, directly additively manufacturing (AM) the polyimide after heat treating the PAA is not possible because the ring-closed polyimide is not soluble or melt-processable due to strong intermolecular interactions ($T_g > 300\text{ }^{\circ}\text{C}$).^{1,3} Second, even in the soluble PAA form, polyimide precursor solutions lack the means for quick solidification to enable multi-layer manufacturing. For these reasons, aromatic polyimides have traditionally been limited to 2D form factors (films).

There have been many synthetic developments in designing polyimide precursors that meet the requirements for various AM techniques including UV-assisted direct-ink-write (DIW) and VPP.⁵⁻¹¹ Generally, these strategies leverage a polyimide precursor that has been modified with photosensitive acrylate chemical groups. These acrylic moieties are subsequently crosslinked with UV light throughout the printing process, yielding a composite network consisting of the polyimide precursor with a polymerized acrylic scaffold. This composite network provides a sufficiently high gel modulus to enable multi-layer manufacturing. Subsequently, post-processing the AM part at elevated temperatures drives the ring-closing cyclodehydration reaction of the polyimide precursor to form the polyimide, while simultaneously volatilizing the photosensitive polymer group. In this approach, the acrylic group can be referred to as a “scaffold,” as it provides the gel modulus for printing the polyimide precursor and can be volatilized after printing, yielding the 3D polyimide structure.

One of the latest approaches for VPP AM is shown in **Figure 6.1b**.⁵ In this approach, a supramolecular “polysalt” structure is formed by mixing hydroxyethyl acrylate

(HEA)-functionalized PMDA (PMDA-HEA) and ODA in solution. The acrylic functionality on the PMDA unit provides the photosensitivity which will ultimately forms the polymerized acrylic scaffold, as well as higher solution viscosities required for AM.⁵ The polysalt solutions have been previously printed via VP AM, where subjecting the printed polysalt solution to UV radiation polymerizes the acrylate, resulting in the formation of the organogel. Once the print is complete, thermally post-processing the printed part liberates forms the polyimide and also liberates the acrylic scaffold (see discussion of **Figure 6.2**, below).

In the latest studies on the supramolecular polysalt approach, it was found that the PMDA/ODA polysalt was not stable in solution.⁶ This was attributed to the Michael addition side reaction involving the more nucleophilic ODA unit compared to DDS, which led to consumption of the acrylate, increasing the viscosity and subsequently limiting the ability to print the solution.⁶ Weyhrich and coworkers found that slightly modifying the chemical structure of ODA to 4,4-diaminodiphenylsulfone (DDS) significantly improved the polysalt solution stability leading to increased shelf life; the side reaction with the acrylic unit was avoided by using DDS.⁶ The authors further demonstrated that complex 3D lattices from the PMDA/DDS polysalt could be manufactured. However, the morphologies of the PMDA/DDS_(PS) parts were not studied in detail and compared to the PMDA/ODA_(PS) parts. Moreover, complex lattices were formed in the prior work, but bulk, printed disc-shaped parts were not manufactured or explored.

Throughout this paper, polyimides prepared from this supramolecular polysalt approach will be denoted as either PMDA/ODA_(PS) or PMDA/DDS_(PS) when comparing to materials prepared from the conventional PAA approach, PMDA/ODA_(PAA). In this work,

we characterize the morphologies of bulk PMDA/ODA_(PS) and PMDA/DDS_(PS) printed discs prepared via the polysalt synthetic approach with VPP AM. The effect of post-processing the parts at temperatures ranging from 100 °C to 400 °C is explored to understand how the part morphology develops throughout the post-processing procedure. The morphologies of the parts prepared through the polysalt approach are characterized via scanning electron microscopy (SEM) and small/wide-angle X-ray scattering experiments (SAXS/WAXS) and compared to the reported morphologies of conventional polyimides found in the literature. Finally, atomistic simulations via electronic-structure calculations help explain the observed differences between the PMDA/ODA and PMDA/DDS systems, yielding key insights into the effects of polyimide chain packing on the part morphology and stability during post-processing.

6.3 Methods

6.3.1 Materials

Pyromellitic dianhydride (PMDA), 2-hydroxyethyl acrylate (HEA), hydrochloric acid, and anhydrous 1-methyl-2-pyrrolidone (NMP, under Argon) were purchased from Thermo Fisher Scientific and used as received. 4,4'-oxydianiline (ODA), 4,4'-diaminodiphenyl sulfone (DDS), phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO), and triethylamine (TEA) were purchased from MilliporeSigma and used as received.

6.3.2 Polysalt Solution Preparation

PMDA-HEA was prepared as previously reported.¹ To make approximately 50 mL of polysalt solution at 40wt% solids loading, PMDA-HEA (15 g, 0.033 mol) and anhydrous NMP (32.50 g, 31.62 mL) were added to a 250 mL two-neck round bottom flask covered

with aluminum foil to protect from light and stirred with an overhead mixer at approximately 120 rpm until dissolved. The diamine, either ODA or DDS, was then added in a molar equivalence to the PMDA-HEA and the mixture stirred until dissolved. Finally, the photoinitiator BAPO was added in a quantity comprising 2 wt% of the dissolved solids (~0.45 g depending on the diamine) and stirred until dissolved. All resins were used day of to avoid impacts of degradation in solution reported in PMDA/ODA polysalt.¹

6.3.3 Printing/Post-Processing Procedure

An ASIGA MAX X bottom-up mask projection vat photopolymerization system was used to fabricate all additively manufactured parts. This system was equipped with a 385 nm UV LED capable of outputting 21 mW/cm² max irradiance. A resin working curve experiment was conducted to select the appropriate UV dose to cure 100 μ m layers with 25 μ m of overcure to encourage good layer adhesion. For example, at 20 mW/cm² irradiance, PMDA/ODA polysalt was observed to have a critical exposure (E_c) of 34.1 mJ/cm² and a depth of penetration (D_p) of 0.17 mm resulting in a cure time of 3.52 sec to cure 125 μ m of resin at the same irradiance. The first layer was irradiated 2-3 times that of the subsequent layers to promote build plate adhesion. The minimum system travel speed of 0.15 mm/sec was used for all build plate moves to apply minimal force to the part throughout the print.

Following printing, parts were patted dry and then dried under vacuum at 80 °C for 72 hours. Parts were then thermally post processed to various temperatures at a rate of 0.5 C/min with a 4-hour isothermal hold at final temperature. Thermal post processing up to 240 °C was performed under vacuum in a Yamato Scientific ADP 300C vacuum oven. Samples that were post processed to higher temperatures were first taken to 240 °C under

vacuum and then transferred to an MTI Corporation GSL 1700X tube furnace for further thermal post processing under N₂.

6.3.4 Thermogravimetric Analysis

Thermogravimetric experiments were performed on a TA Instruments TGA 550 in a nitrogen environment. Temperature ramp experiments were performed with a ramp rate of 10 °C/min on 2-5 mg of sample up to 800 °C.

6.3.5 Small/Wide-Angle X-Ray Scattering

Small, mid, and wide-angle X-ray scattering (SAXS/MAXS/WAXS) experiments were performed on a Xenocs Xeuss 3.0 SAXS/WAXS equipped with a GeniX 3D Cu HFVLF microfocus X-ray source utilizing Cu K- α radiation ($\lambda = 0.154$ nm). The sample-to-detector distance was 43 mm for WAXS, 370 mm for MAXS, and 900 mm for SAXS, and the q -range was calibrated using lanthanum hexaboride and silver behenate standards. Two-dimensional scattering patterns were obtained using a Dectris EIGER 4M detector with various exposure times (SAXS: 2 hours, MAXS: 1 hour, WAXS: 30 minutes). Data reduction was performed using XSACT software provided by Xenocs, and the 1D profiles were corrected for sample thickness, background, and transmission. The SAXS, MAXS, and WAXS profiles were merged into one dataset and plotted on an absolute intensity scale vs. the scattering vector, q . The scattering profiles were modeled in SasView.

6.3.6 Scanning Electron Microscopy

The internal morphologies of printed specimens were analyzed using a Zeiss LEO 1550 field-emission scanning electron microscope (FE-SEM) with in-lens detection. Parts were freeze-fractured and mounted vertically on carbon tape using a 90° stub, then sputter coated with 5 nm of iridium using a Leica EM ACE600 sputter coater.

6.3.7 Computational Experiments

Two separate sets of electronic structure calculations were employed to obtain a fundamental atomistic understanding of the structure and properties of the materials in this work. First, the geometry of the PMDA/ODA, and PMDA/DDS polyimides in the crystalline phase were obtained via periodic density-functional theory (DFT) calculations with the Vienna Ab Initio Simulation Package (VASP 5.4.4).¹²⁻¹³ The exchange and correlation energy were computed with the Perdew-Burke-Ernzerhof (PBE) functional and a plane-wave cutoff of 400 eV. The D3BJ empirical-dispersion correction was utilized in all simulations to model non-covalent interactions.¹⁴ The force convergence criterion in the geometry optimizations of the variable-length cubic unit cell was 0.02 eV/atom and an energy convergence criterion of 1.0×10^{-7} eV ensured a smooth geometry convergence. Simulated powder X-ray diffraction patterns for each of the two computed unit cells were computed in the VESTA software suite with the RIETAN-FP algorithm.¹⁵⁻¹⁷ Using the optimal unit-cell geometries from the periodic calculations capped with hydrogen atoms, we performed a second set of molecular-orbital DFT calculations that characterized the interaction energy between neighboring polymer chains in the solid. In order to model a bulk crystal, the atomic positions within a chain were not allowed to relax. The interaction energies were computed using the B97D¹⁸ functional and the def2-TZVP¹⁹ basis sets in the Gaussian 09²⁰ program suite. The def2-TZVP basis set was chosen because it is reportedly able to approximate the basis set limit for DFT, while also remaining computationally efficient.¹⁹ Further efficiency was gained via the use of density fitting with the universal def2 set.²¹ The long-range dispersion-corrected generalized gradient functional, B97D, was

chosen primarily due to its ability to intrinsically correct for noncovalent interactions, such as those that facilitate aggregation in aromatic polymer systems.²²⁻²⁴

6.4 Results and Discussion

6.4.1 Thermal Analysis

To understand how the composition of the printed parts evolves throughout the thermal post-processing procedure, the printed parts of PMDA/ODA_(PS) and PMDA/DDS_(PS) heated to 100, 150, 200, 240, 300, 350, 400, and 450 °C were analyzed using thermogravimetric analysis (TGA). Thermograms for PMDA/ODA_(PS) and PMDA/DDS_(PS) printed parts post-processed to varying temperatures are shown in **Figure 6.2**, along with the thermograms for neat poly(PMDA-HEA) and PMDA/ODA_(PAA). It is useful to first investigate the thermal properties of the benchmark polyimide and neat poly(PMDA-HEA) scaffold. The PMDA-HEA film was post-processed to 240 °C to completely remove NMP and the PMDA/ODA_(PAA) film was post-processed to 350 °C to remove NMP and complete thermal imidization. The mass loss profile for the neat polyimide film, PMDA/ODA_(PAA), is shown in **Figure 6.2a**, and the first derivative of the mass loss profile is shown in **Figure 6.2b**. Consistent with prior literature,²⁵ neat PMDA/ODA_(PAA) has high thermal stability, with the onset of degradation occurring at $T > 500$ °C (**Figure 6.2a**). The mass loss profile reveals a single mass loss step centered around $T = 600$ °C which is related to the decomposition of the polyimide backbone.²⁵ In contrast, neat poly(PMDA-HEA), i.e., the acrylic scaffold, displays a single mass loss event at much lower temperatures (**Figure 6.2a**) which is associated with degradation of the polyacrylate backbone.²⁶ The onset of mass loss for neat poly(PMDA-HEA) is $T \approx 330$ °C and the peak in mass loss is around $T \approx 440$ °C, which is similar to poly(HEA) which has been previously

reported in the literature.²⁶ As discussed later, the onset volatilization of poly(PMDA-HEA) that occurs at $T < 400$ °C will have a profound effect on the resulting internal microstructure of the printed parts.

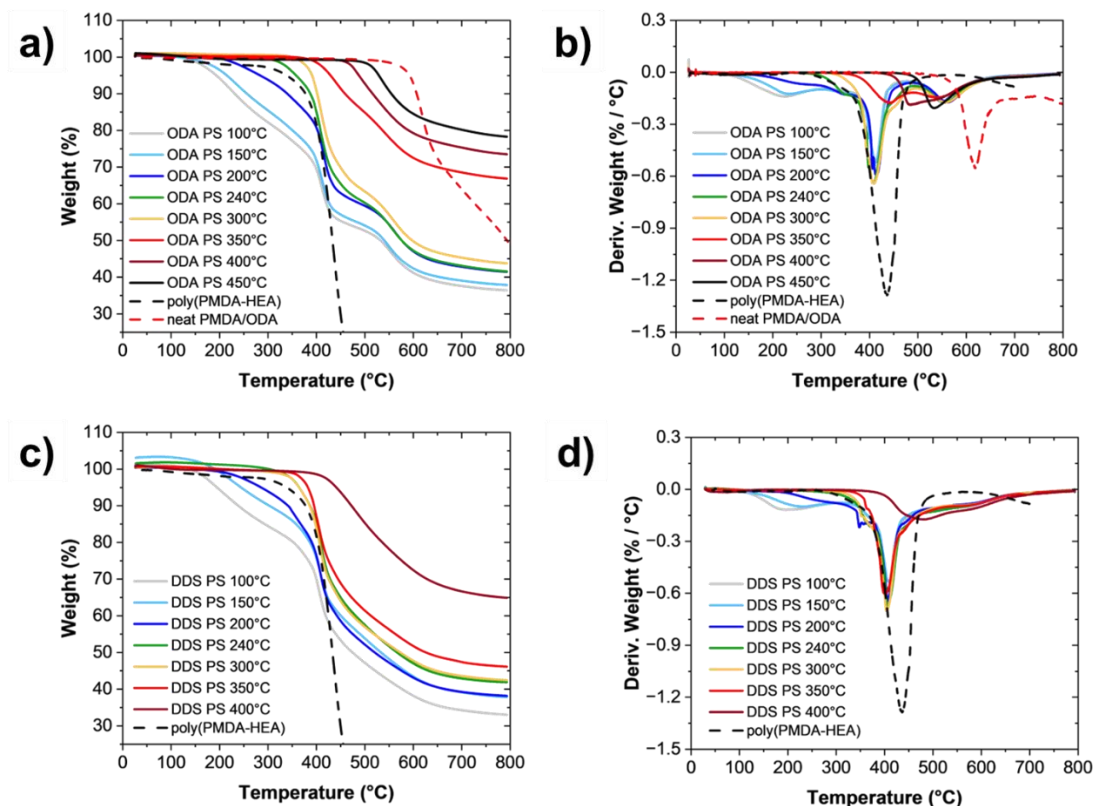


Figure 6.2. TGA thermograms showing mass loss (**a and c**) and the first derivative of mass loss (**b and d**) for PMDA/ODA polysalt parts (**a and b**) and PMDA/DDS polysalt parts (**c and d**) post-processed to various temperatures.

Figure 6.2 a,b show the thermograms for the PMDA/ODA_(PS) parts processed at various temperatures. In the printed PMDA/ODA_(PS) parts processed below 240 °C, an initial mass loss event is observed, which appears as a subtle peak in the first derivative of the mass loss (**Figure 6.2b**). This mass loss has been assigned to the water loss associated with imidization, which was expected as these samples are known to be partially imidized

at these relatively lower temperatures.^{6, 27} In the printed PMDA/ODA_(PS) parts processed below 400 °C, a second mass loss event associated with the volatilization of poly(PMDA-HEA) is apparent at $T = 410$ °C. The presence of poly(PMDA-HEA) in the printed parts processed below 400 °C demonstrates that $T \geq 400$ °C are required to fully volatilize the acrylic scaffold. Below $T = 400$ °C, a multi-component material consisting of polyimide precursor, polyimide, and polyacrylate is present. For the PMDA/ODA_(PS) samples processed at 400 °C and 450 °C, the mass loss of the polyacrylate scaffold is not observed (**Figure 6.2a**). Instead, a single, high-temperature broad mass loss event is present which is associated with the degradation of the polyimide backbone. Overall, the TGA data of the PMDA/ODA_(PS) series reveals that parts processed at $T < 400$ °C are hybrid polyacrylate-polyimide parts, whereas the PMDA/ODA parts processed at $T \geq 400$ °C are predominately polyimide parts.

Similar thermal stability experiments were performed on the PMDA/DDS_(PS) series, and the thermograms are shown in **Figure 6.2 c,d**. This series also reveals a low-temperature mass loss peak with an onset of $T = 100$ °C, which is again likely related to the water loss that occurs during imidization (**Figure 6.2d**). Like the PMDA/ODA_(PS) series, the PMDA/DDS_(PS) materials processed below 240 °C reveal a mass loss event which could be associated with incomplete imidization. A second mass loss event is observed with an onset temperature of 500 °C and a peak mass loss temperature of 600 °C (**Figure 6.2d**). Consistent with prior studies,⁶ this mass loss step is assigned to the poly(PMDA-HEA) backbone degradation. The third mass loss event associated with the polyimide degradation is far less discernible in PMDA/DDS_(PS) parts compared to the PMDA/ODA_(PS) series. It is hypothesized that this may be due to polyimide degradation

occurring at lower temperatures and overlapping with the polyacrylate volatilization step. As will be discussed in detail later, the thermal stability of the PMDA/DDS_(PS) is lower than PMDA/ODA_(PS) printed parts.

6.4.2 SEM Analysis

The internal structures of the printed parts were analyzed via scanning electron microscopy (SEM). The freeze-fractured internal surfaces of the PMDA/ODA_(PS) printed parts post-processed up to various temperatures are shown in **Figure 6.3**. The 125X magnification images are shown in **Figure 6.3 a-e** and the 1000X magnification images of the same parts are shown in **Figure 6.3 f-j**. In the printed PMDA/ODA_(PS) parts post-processed up to 100 °C, 200 °C, and 300 °C, the internal morphology is consistently homogeneous, revealing no significant physical features (**Figure 6.3**). Furthermore, no obvious phase separation is observed, which supports that the polyimide domains and the polyacrylate domains are well-mixed on this length scale. Additionally, there are no visible borders between the print layers that make up the part thickness. This suggests that polysalt chains from one layer can efficiently diffuse into another layer, forming a uniform part. No print layers were observed in any of the parts examined.

In the 400 °C PMDA/ODA_(PS) part, a few, small internal voids approximately 10 μm in diameter begin to appear (**Figure 6.3i**). This is in contrast with conventional PMDA/ODA (Kapton®) which is known to possess a homogeneous film morphology absent of any macrovoids or pores. As discussed previously, the onset of volatilization for poly(PMDA-HEA) acrylic scaffold is $T = 330$ °C. Therefore, these internal voids likely represent poly(PMDA-HEA) regions that subsequently volatilized during the thermal treatment step. In the part post-processed to 450 °C, the internal voids increase in size and

number (**Figure 6.3e**). Example internal voids approximately 50 μm in diameter are shown in **Figure 6.3j**. Clearly, the volatilization of the acrylic scaffold at 400 $^{\circ}\text{C}$ and 450 $^{\circ}\text{C}$ has a strong effect on the structure of these bulk printed parts. In the lattices prepared from the same polysalts, these voids were not observed,⁵ likely because the open lattice structure provided more efficient pathways for the acrylic scaffold to escape out of the thinner struts. In the lattices, the acrylic scaffold byproducts likely diffuse more easily through the polyimide matrix and exit the printed part. However, in the bulk parts studied here, it is expected that the acrylic scaffold byproducts are not able to effectively diffuse through the polyimide matrix, leading to macroscopic eruptive voids at the location of volatilization.

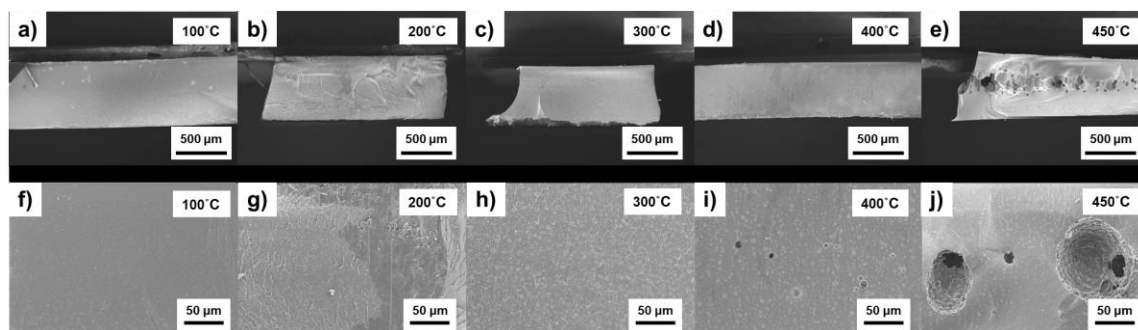


Figure 6.3. SEM images of freeze-fractured internal surfaces of the PMDA/ODA_(PS) printed parts that were post-processed up to **a,f**) 100 $^{\circ}\text{C}$, **b,g**) 200 $^{\circ}\text{C}$, **c,h**) 300 $^{\circ}\text{C}$, **d,i**) 400 $^{\circ}\text{C}$, and **e,j**) at 450 $^{\circ}\text{C}$. Images **a-e** were collected at 125X magnification, whereas images **f-j** were collected at 1000X magnification. All images were taken at room temperature.

The internal structure of the PMDA/DDS_(PS) printed parts was also characterized via SEM and compared to the PMDA/ODA_(PS) printed parts. The freeze-fractured internal surfaces of the PMDA/DDS_(PS) printed parts post-processed up to various temperatures are shown in **Figure 6.4**. The 125X magnification images are shown in **Figure 6.4 a-e** and the 1000X magnification images of the same parts are shown in **Figure 6.4 f-j**. Similar to the PMDA/ODA printed parts, the absence of distinct layers in all images again suggests efficient interlayer chain diffusion. Images of the PMDA/DDS_(PS) printed parts post-

processed to 100 °C, 200 °C, 300 °C, and 350 °C reveal a primarily homogeneous morphology on this relatively large length scale. Again, this suggests that no obvious bulk phase separation of the polyacrylate and the PMDA/DDS_(PS) is present.

For the PMDA/DDS_(PS) printed part post-processed to 400 °C, the internal structure is fully characterized by internal voids approximately 50-100 μm in diameter (**Figure 6.4e**). It is important to note that the PMDA/DDS_(PS) parts were completely voided when processed at 400 °C, which is 50 °C lower than the temperature where the PMDA/ODA_(PS) parts reveal voids (**Figure 6.3**). This result reveals that simply replacing the ether linkage with a sulfone has an influence on the thermal stability of the part morphology and the temperature at which voids become prevalent. The origin of these differences will be discussed in detail in the computational analysis section below. Macroscopic voids are sometimes thought of as detrimental to polymer parts in terms of their mechanical properties.²⁸ However, voids in manufactured parts have found utility in applications that require internal porosity, such as additively manufacturable absorbents for environmental remediation efforts.²⁹

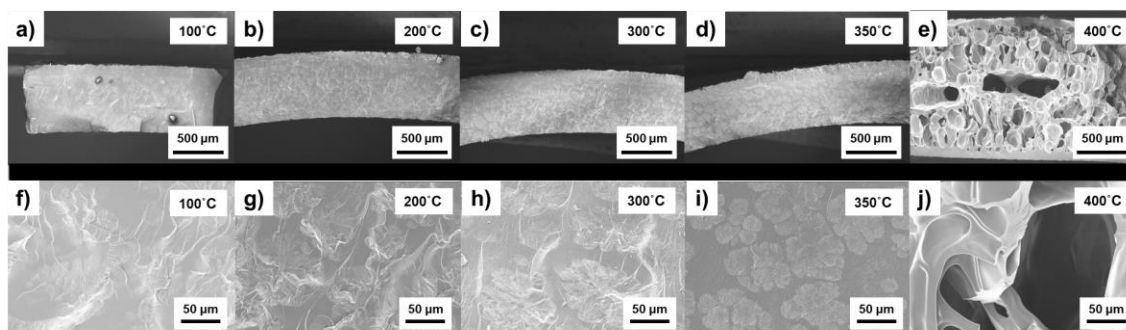


Figure 6.4. SEM images of freeze-fractured internal surfaces of the PMDA/DDS_(PS) printed parts that were post-processed up to **a,f**) 100 °C, **b,g**) 200 °C, **c,h**) 300 °C, **d,i**) 350 °C, and **e,j**) at 400 °C. Images **a-e** were collected at 125X magnification, whereas images **f-j** were collected at 1000X magnification. All images were taken at room temperature.

6.4.3 SAXS/WAXS Analysis

6.4.3.1 Comparison of polysalt to PAA-derived Polyimides

Small and wide-angle X-ray scattering experiments were performed to investigate the morphologies of the printed parts on the nanoscale. First, the morphology of the PMDA/ODA_(PAA) control film was compared to the PMDA/ODA_(PS). The merged SAXS/WAXS profile of the conventional PMDA/ODA_(PAA) polyimide film is shown in **Figure 6.5**. The scattering pattern for the printed PMDA/ODA_(PS) polyimide part is also shown for comparison. In the wide-angle region of the scattering profile ($5 < q < 40 \text{ nm}^{-1}$), diffraction features arising from the smallest interchain and intercrystallite distances appear. Polyimides are generally understood to crystallize in chain extended morphologies, with PMDA/ODA crystallizing in an orthorhombic unit cell with the crystallographic direction c corresponding to the polymer chain axis.³⁰

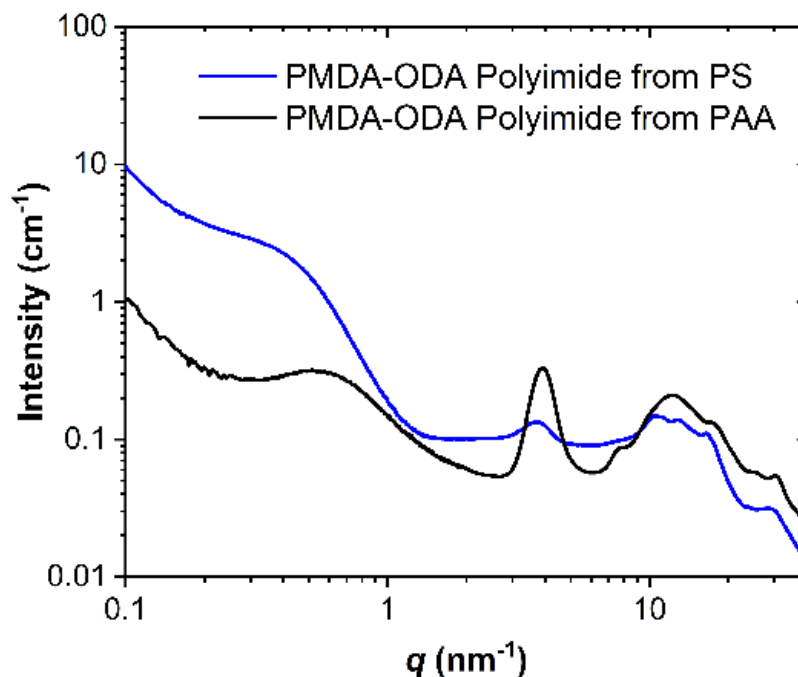


Figure 6.5. Merged SAXS/MAXS/WAXS profiles of a printed PMDA/ODA_(PS) part processed to 450 °C, along with the profile for conventional PMDA/ODA_(PAA) processed to the same temperature. Both profiles were collected at room temperature.

In the mid-angle region of the scattering profiles ($2 \text{ nm}^{-1} < q < 8 \text{ nm}^{-1}$), a characteristic scattering peak centered around $q \approx 4 \text{ nm}^{-1}$ is present for both the PMDA/ODA_(PAA) and PMDA/ODA_(PS) polyimides (**Figure 6.5**). This scattering feature is assigned to the periodic intrachain spacing along the chain axis corresponding to the (002) family of planes.³¹ This crystalline reflection is a characteristic scattering feature observed in many polyimides and is related to the length of the monomer unit.³⁰⁻³¹ The location of this feature is in a similar position for both materials, suggesting similar *c*-axis dimensions for both polyimides prepared from different precursors, as expected.

In the small-angle region of the scattering profiles ($0.1 \text{ nm}^{-1} < q < 2 \text{ nm}^{-1}$), a strong scattering feature appears in both polyimides between $0.3 \text{ nm}^{-1} < q < 1 \text{ nm}^{-1}$. This feature

has been associated with the long-range spatial correlations of crystalline domains, and is commonly known as the *intercrystalline* long period.³² The Bragg spacing of the intercrystalline long period is commonly interpreted as the average center-to-center distance between crystalline domains. As will be shown later, this dimension changes as the material is post-processed to different temperatures.

Finally, at $q < 0.3 \text{ nm}^{-1}$, the scattering profiles of both PMDA/ODA polyimides display an upturn in intensity which is indicative of heterogeneities in electron density $> 100 \text{ nm}$ in size. For the PMDA/ODA_(PS) polyimide, the scattering at low q is an order of magnitude greater than the scattering in the PMDA/ODA_(PAA) polyimide (**Figure 6.5**). This is likely associated with the $\sim 10 \text{ }\mu\text{m}$ diameter internal voids formed from volatilization of the acrylic scaffold which are significant at a post-processing temperature of $450 \text{ }^{\circ}\text{C}$ (**Figure 6.3e**). It is important to note that while the exact sizes of these internal voids are too large to measure with SAXS, the SAXS intensity at low q is highly sensitive to the presence of the voids.

6.4.3.2 Ex-Situ Variable-Temperature Experiment – PMDA/ODA

To study how the morphology of the polysalt transforms into the polyimide morphology, the printed parts with final post-processing temperatures ranging from $100 \text{ }^{\circ}\text{C}$ to $400 \text{ }^{\circ}\text{C}$ (DDS) or $100 \text{ }^{\circ}\text{C}$ to $450 \text{ }^{\circ}\text{C}$ (ODA) were investigated via SAXS/WAXS. Merged SAXS/WAXS profiles of the PMDA/ODA_(PS) part series are shown in **Figure 6.6a** for each post-processing temperature, and each region of the scattering profile was investigated. The wide-angle region of the scattering profile ($5 < q < 40 \text{ nm}^{-1}$) provides information about how the structure within the crystalline domains develops as a function of processing temperature. An initial type of diffraction pattern persists up to processing

temperatures of 300 °C (**Figure 6.6a**). These low-temperature diffraction patterns in the polysalt are comparable to those that have been observed in PMDA/ODA_(PAA) processed at similar temperatures,³³ so assignments were made based on existing literature of PMDA/ODA_(PAA) polyimides (**Figure 6.6b**). This result demonstrates that the complex polysalt organogel morphology that is formed in the initial printed parts does not significantly alter the crystalline structure of PMDA/ODA_(PS), even at low temperatures when the acrylic scaffold is still present in the material.

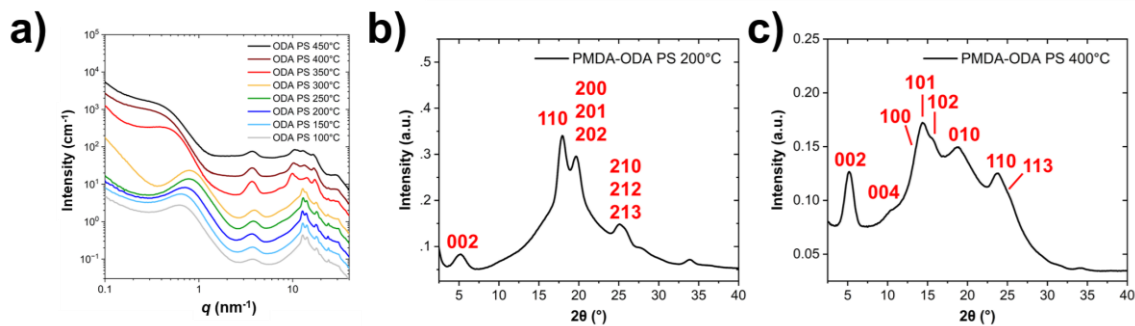


Figure 6.6. a) Merged SAXS/MAXS/WAXS profiles of printed PMDA/ODA_(PS) parts post-processed at temperatures 100 °C to 450 °C. All profiles were collected at room temperature. The scattering profiles have been vertically offset for visualization purposes. WAXS profile of PMDA/ODA_(PS) post-processed to b) 200 °C, revealing the low-temperature “Type I” crystal form, and c) 400 °C, revealing the high-temperature “Type II” crystal form.

A significant transformation in the crystalline morphology appears between processing temperatures of 300 °C and 350 °C (**Figure 6.6a**).⁵ This development has been observed in conventional PMDA/ODA_(PAA) processed at 330 °C and has been previously described as a crystal phase transformation of the PMDA/ODA polyimide.³³ This high-temperature diffraction pattern of PMDA/ODA_(PS) was comparable to that of PMDA/ODA_(PAA) reported in the literature, so crystallographic assignments were made based on literature values (**Figure 6.6c**).³³ At these temperatures, the majority of the acrylic

scaffold is removed from the printed parts, so it is reasonable that this high-temperature polyimide diffraction pattern is similar regardless of the precursor identity.

For processing temperatures ≥ 150 °C, the mid-angle region ($2 \text{ nm}^{-1} < q < 8 \text{ nm}^{-1}$) of the scattering profiles displays a characteristic scattering peak centered around $q \approx 4 \text{ nm}^{-1}$ that is commonly observed in scattering profiles of polyimides (**Figure 6.6a**). As noted previously, this scattering feature is assigned to the periodic intrachain spacing along the chain axis corresponding to the (002) crystalline plane.³¹ This feature grows in intensity and sharpens as the post-processing temperature increases, which is expected as higher processing temperatures drive the formation of the polyimide structure and therefore the ordered polyimide morphology. The 1D correlation function has been previously used to quantify the intercrystallite domain spacing (i.e., the long period) in polyimides,³⁴ so a similar analysis was conducted in this work to study how the domain spacing developed throughout the imidization protocol. In **Figure 6.7**, the long period is plotted as a function of the processing temperature. The long period slightly decreases between processing temperatures 100 °C to 300 °C, but increases dramatically at 350 °C and 400 °C. The increase in the long period at elevated temperatures in polyimides has been reported to be due to the melting of thin crystallites between larger primary crystallites.³⁵

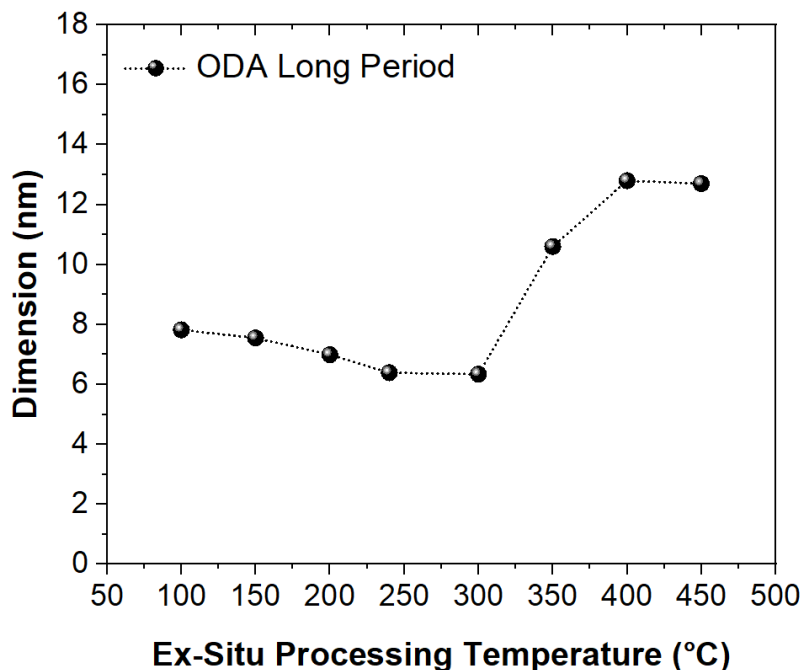


Figure 6.7. The intercrystalline long period from the 1D correlation function analysis on the SAXS feature for the PMDA/ODA_(PS) parts.

6.4.3.3 Ex-Situ Variable-Temperature Experiment – PMDA/DDS

Similar SAXS/WAXS experiments were conducted on the PMDA/DDS_(PS) parts post-processed at various temperatures. Merged SAXS/WAXS profiles of the PMDA/DDS_(PS) part series are shown in **Figure 6.8a** for each post-processing temperature and each region of the scattering profile was subsequently analyzed. At $T < 400$ °C, the WAXS diffraction pattern is relatively unchanged, unlike PMDA/ODA_(PS) which showed an abrupt change in diffraction pattern. Unlike the PMDA/ODA materials, there are no known literature reports of PMDA/DDS poly(amic acids) or polyimides to assign the diffraction patterns in polymers. However, computational experiments discussed below provide valuable insight into the origins of its crystalline reflections. Interestingly, the WAXS pattern of PMDA/DDS_(PS) post-processed at 400 °C is absent of crystalline reflections, suggesting a primarily amorphous morphology.

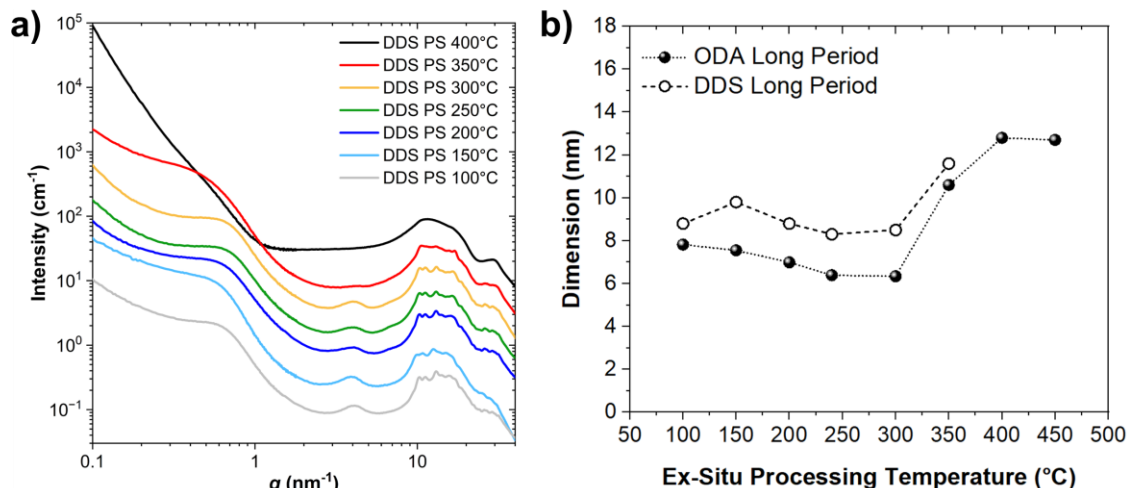


Figure 6.8. a) Merged SAXS/MAXS/WAXS profiles of PMDA/DDS(*PS*) post-processed at temperatures 100 °C to 450 °C. All profiles were collected at room temperature. The scattering profiles have been vertically offset for visualization purposes. **b)** The intercrystalline long period from the 1D correlation function analysis on the SAXS feature for the PMDA/DDS(*PS*) and PMDA/ODA(*PS*) parts.

In the mid-angle region of the scattering profile, a peak at $q \approx 4 \text{ nm}^{-1}$ is observed (**Figure 6.8a**). Further supported by computational experiments below, this feature is assigned to the (002) family of planes. Interestingly, this scattering feature is broader than the same feature in patterns of PMDA/ODA(*PS*) (**Figure 6a**), which suggests that the PMDA/DDS chains are less ordered along the chain axis compared to PMDA/ODA polyimides. The small-angle region of the scattering profiles ($0.1 \text{ nm}^{-1} < q < 2 \text{ nm}^{-1}$) reveals the intercrystalline long period. This feature in the PMDA/DDS(*PS*) series is broader and more “knee-like” than the long period peak observed in the PMDA/ODA(*PS*) series, which is sharper and more clearly defined (**Figure 6a**). This suggests that the crystalline domains in PMDA/ODA(*PS*) exhibit greater long-range order than those in PMDA/DDS(*PS*). The 1D correlation function analysis was performed, and the extracted long period values are shown in **Figure 6.8b**. For the same post-processing temperature, the long period of

PMDA/DDS_(PS) is greater than that of PMDA/ODA_(PS), which indicates that the average center-to-center crystalline domain spacing is greater. These differences in crystalline morphologies are further supported by the atomistic simulations presented below. Finally, it is notable that the final PMDA/DDS_(PS) profile for the 400 °C sample is essentially amorphous via SAXS and WAXS, which suggests that at some point between 350 °C and 400 °C, the polyimide crystallites become disordered or disappear completely. The intense scattering at low q (i.e., below $q = 0.4 \text{ nm}^{-1}$) is attributed to the presence of voids in this specimen (**Figure 6.4e**).

6.4.4 Computational Analysis

6.4.4.1 Prediction of Unit Cell Parameters

In an effort to better understand the observed morphological differences between the PMDA/ODA and PMDA/DDS polyimides, several computational experiments using atomistic models of the samples were performed. First, periodic DFT calculations were employed to model the polyimide geometries in the solid aggregate state, which was believed to best represent the conformations of the polymer chains in their respective crystallites. From these calculations, simulated unit cells of both PMDA/ODA and PMDA/DDS polyimides were obtained to provide ordered chain conformations in the crystal structure (**Figure 6.9**). The computed energy-minimized unit cell of both polyimides was orthorhombic, which is commonly observed in polyimides with similar chemical structures.³⁰ The computationally-predicted lattice parameters of the PMDA/ODA polyimide ($a = 6.22 \text{ \AA}$, $b = 3.62 \text{ \AA}$, $c = 32.62 \text{ \AA}$) were in excellent agreement with experimental values determined from oriented conventional, PAA-derived PMDA/ODA films reported in the literature ($a = 6.25 \text{ \AA}$, $b = 3.92 \text{ \AA}$, $c = 32.0 \text{ \AA}$).³⁰ The

full predicted powder x-ray diffraction pattern of PMDA/ODA polyimide is shown in **Figure S6.1**.

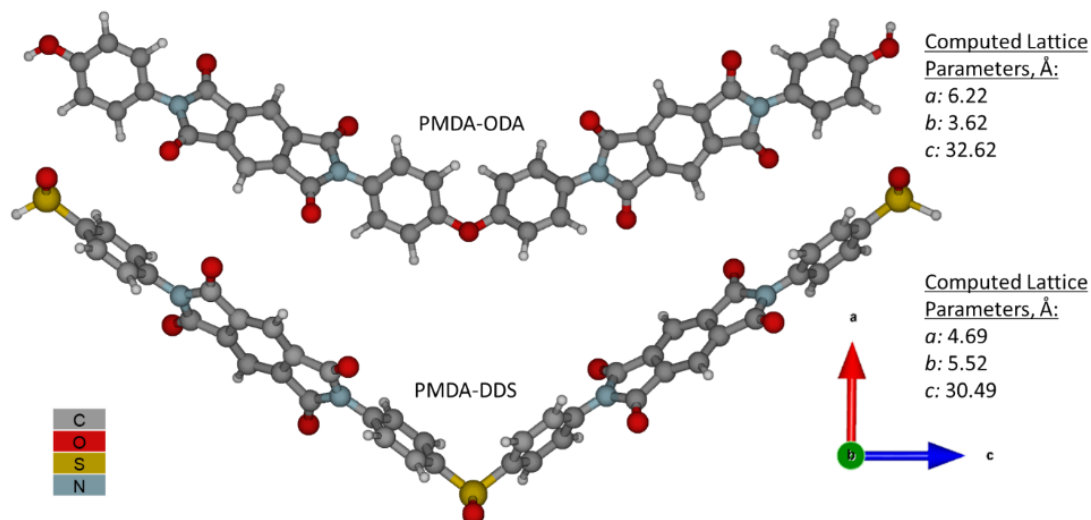


Figure 6.9. Visualization of the computed PMDA/ODA polyimide and PMDA/DDS polyimide unit cells and accompanying lattice parameters. Both unit cells are orthorhombic with interaxial angles deviating less than 1° from perpendicular. The dangling bonds across unit cells have been saturated with H atoms.

Next, the experimentally-derived lattice parameter c for PMDA/ODA_(PS) was compared to the computational prediction. Using the well-resolved (002) reflection observed in experimental data for PMDA/ODA_(PS) at 350 °C at $q = 3.70 \text{ nm}^{-1}$ (**Figure 6a**), the c -axis dimension was calculated as 33.62 Å, just a 1% difference from the predicted value ($c = 32.62 \text{ Å}$). This result confirms that the crystallites formed in the polysalt-derived polyimides are comparable in morphology to those formed in conventional, PAA-derived polyimides. The comparison additionally provides credibility to the computational model to predict structures that are consistent with those observed experimentally.

Agreement between the computational model and experimental literature values for PMDA/ODA provided confidence that the computational calculations could predict

structural information for the experimentally unresolved PMDA/DDS material with no previously reported crystallography. The computationally-predicted c -axis dimension for PMDA/DDS polyimide was $c = 30.49 \text{ \AA}$, which is several Angstroms less than that predicted and observed for PMDA/ODA polyimide. Assuming the peak at $q = 4.01 \text{ nm}^{-1}$ (**Figure 6.8a**) corresponds to the (002) family of planes, a c -axis dimension of $c = 31.30 \text{ nm}$ can be obtained, which is within 3% of the calculated value. This shows that the results from both computation and experiment support a smaller c -axis dimension in PMDA/DDS compared to PMDA/ODA. The full predicted powder x-ray diffraction pattern of PMDA/DDS polyimide is shown in **Figure S6.1**.

6.4.4.2 Interaction Energies of Polymer Chains (*Dimer Model*)

As shown in **Figure 6.9**, the most significant difference between the crystalline structures of the two polymers is that the pyromellitic dianhydride unit of the DDS variant is rotated approximately 90° in-plane relative to the ODA variant. We hypothesize that this rotation of the aromatic ring dramatically weakens the strength of the polymer chain interactions in PMDA/DDS crystallites, which leads to failure in PMDA/DDS_(PS) parts at elevated temperatures. To quantitatively test this hypothesis, a computational experiment was performed to approximate the relative strength of the polymer chain interactions in each polyimide aggregate. Specifically, the interaction energies between two adjacent polymer strands in the crystalline solids were calculated using molecular-orbital DFT. Starting with the PMDA/ODA polyimide, two pairs of dimers were constructed to examine the interaction between neighboring polymer chains along the a - and b -axes (**Figure 6.10**). For PDMA/ODA, the a -axis interaction energy is nearly three times weaker than along the b -axis. This observation can be rationalized by the presence of strong interactions between

both the pyromellitic dianhydride units and the aniline of neighboring unit cells when stacked along the *b*-axis (**Figure S6.2a**). The overall interlayer interaction along the *b*-axis is primarily composed of pi-stacking of the aromatic rings and hydrogen bonding between C-H groups in one chain and electron-rich C=O hydrogen bond acceptors in a neighboring chain (8 such hydrogen bonds are formed between the two polymer strands when stacked along the *b*-axis). Additionally, the interlayer stacking distance along the *b*-axis is 3.62 Å, which is in good agreement with the interlayer separation of other pi-stacking interactions, such as graphite.³⁶⁻³⁷ In comparison, neighboring PMDA/ODA polymer chains along the *a*-axis cannot establish pi-stacking because the aromatic rings are not parallel, and form merely four hydrogen-bonds (**Figure S6.2a**).

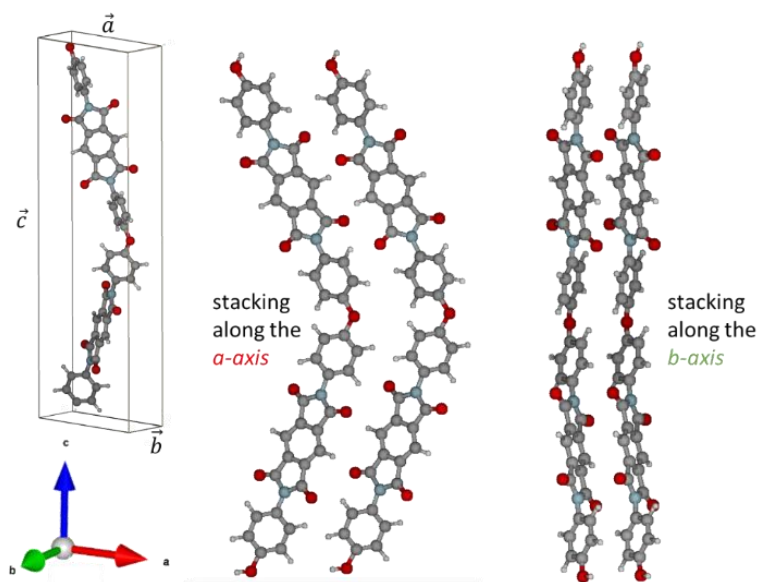


Figure 6.10. Visualization of the dimer models for PMDA/ODA that were used to investigate the interactions between neighboring polymer chains. The shown interlayer separations follow from the computed unit cell parameters.

An analogous set of dimer structures were constructed for PMDA/DDS and the interaction energies were subsequently computed (**Figure S6.2b**). Again, the pyromellitic

dianhydride unit in the PMDA/DDS polymer is predicted to be rotated $\sim 90^\circ$ in-plane relative to the PMDA/ODA structure. As a result, PMDA/DDS neighboring chains engage in pi-stacking along the *a*-axis rather than the *b*-axis described above for PMDA/ODA dimer. Nevertheless, the interaction along the pi-stacking direction is $\sim 25\%$ weaker for PMDA/DDS compared to PMDA/ODA (**Table 6.1**). This difference in energy is likely a result of the greater interchain separation between polymer units in the PMDA/DDS crystallites. Specifically, the bulkier sulfone linkage hinders packing as compact as within PMDA/ODA. Quantitatively, the aromatic moieties of adjacent PMDA/DDS and PMDA/ODA chains are separated by 4.69 and 3.62 Å respectively, corroborating the weaker interaction between PMDA/DDS polymer strands.

For the PMDA/DDS interchain interactions along the *b*-axis, a slight enhancement (10 kJ/mol) in the relative interaction energy was observed when compared to the analogous PMDA/ODA dimer (83.1 vs 72.9 kJ/mol, respectively for PMDA/DDS and PMDA/ODA). We attribute this difference to the additional (8 total) hydrogen bonds formed in the PMDA/DDS structure. Importantly, the four additional hydrogen bonds are formed between the oxygens of the sulfone and the C-H donors of the neighboring aniline rather than oxygens found along the pyromellitic dianhydride unit. In summary, the PMDA/ODA dimer is capable of stronger (+48 kJ/mol per unit cell) pi-stacking interactions than the analogous PMDA/DDS dimer structure. The calculations of interaction energies using dimers along specific directions illuminate fundamental differences in the packing of chains for PMDA/DDS and PMDA/ODA along specific crystallographic axes.

6.4.4.3 Interaction Energies of Polymer Chains (*Bulk Model*)

Finally, to more accurately quantify the strength of the interchain interactions in the bulk polymer phase, a more expansive cluster model was constructed. In this model, the cumulative strength of the chain interactions along both the a and b -axis are considered. To accomplish this, a 3-by-3 supercell of 9 interacting unit cells was created in the ab -plane (each polymer unit cell is capped with hydrogen atoms along the c -axis). This model offers insight into the lability of the polymer crystallites observed in the experiments by providing the energy required to liberate a single surface polymer unit from the bulk formed by the other 8 chains. There are three possible locations within this supercell for a surface chain to desorb: (i) a corner, (ii) the central surface chain located along the a -axis, and (iii) the central surface chain along the b -axis (**Figure 6.11**).

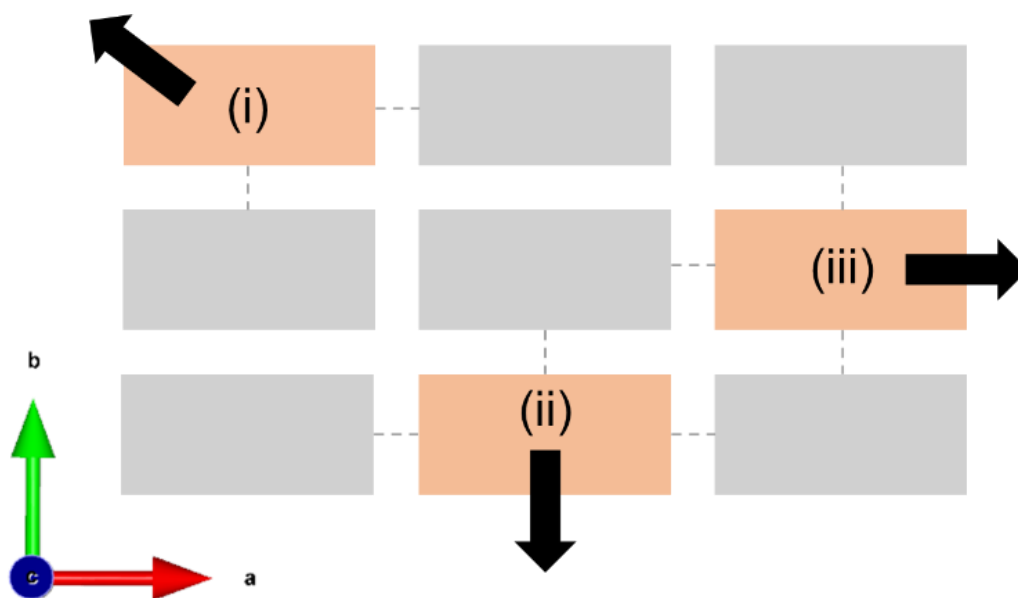


Figure 6.11. Depiction of the model 3x3 polymer aggregate used in this study. Each rectangle represents one polymer chain visualized in the ab -plane. Unique polymer desorption sites are labeled (i, ii, iii). Dashed lines represent interactions between polymer chains analogous to those calculated in **Figure S6.2**.

Expressions for the total interaction energies for a polymer unit in each position are given in **Figure S6.3a**. These net interaction energies were calculated by taking the sum of the individual interaction energies along each face of the unit cell. An example calculation for desorption of a PMDA/ODA unit cell in position (ii) is provided by **Figure S6.3b**. Calculations from this model yielded the energy required to desorb a set of 3 uniquely bound polymer units (**Table 6.1**).

Table 6.1. Dimer interaction energies along the *a* and *b*-axes (E_a and E_b , respectively) and desorption energies for unique polymer desorption sites (i, ii, iii) within the 3x3 polymer aggregate model.

Energy (kJ/mol)	PMDA/ODA	PMDA/DDS
E_a	72.9	161.7
E_b	210.1	83.1
$E_{\text{desorb(i)}}$	283.0	244.8
$E_{\text{desorb(ii)}}$	355.9	406.5
$E_{\text{desorb(iii)}}$	493.1	327.9

Taking all the interaction energies from i, ii, and iii together, the presence of the sulfone linkage reduces the combined interaction strength of the three unique polymer units by over 150 kJ/mol per unit cell. This difference in interaction strength translates into a 6-fold relative enhancement in polymer desorption rate at 400 °C temperature when swapping the ether linkage for the sulfone (**Table 6.2**). While the reduced dimensionality models are comprised of only two monomers along the *c*-axis, the interaction strength is

expected to scale linearly with the degree of polymerization. Thus, the difference in interaction strengths revealed with the model of this work are exacerbated in the actual printed parts.

6.5 Conclusions

In conclusion, the morphology of polyimides prepared from photocurable, AM precursors is studied through a combination of scanning electron microscopy, X-ray scattering, and atomistic DFT calculations. Parts based on the benchmark polyimide chemical structure, PMDA/ODA, reveal highly ordered crystalline morphologies and strong interchain interactions that yield robust morphologies at $T \leq 350$ °C. Slightly modifying the chemical structure to PMDA/DDS results in less ordered crystalline morphologies and weaker interchain interactions that facilitate void formation at elevated temperatures. Overall, SAXS experiments are revealed to be sensitive to the presence of voids in printed parts, so this characterization technique may find applications in detecting nano or microvoids in a variety of printed parts. Additionally, we suspect that the computational models reported in this paper could be used to enable the rational design of new polyimide structures with tailored crystalline morphologies.

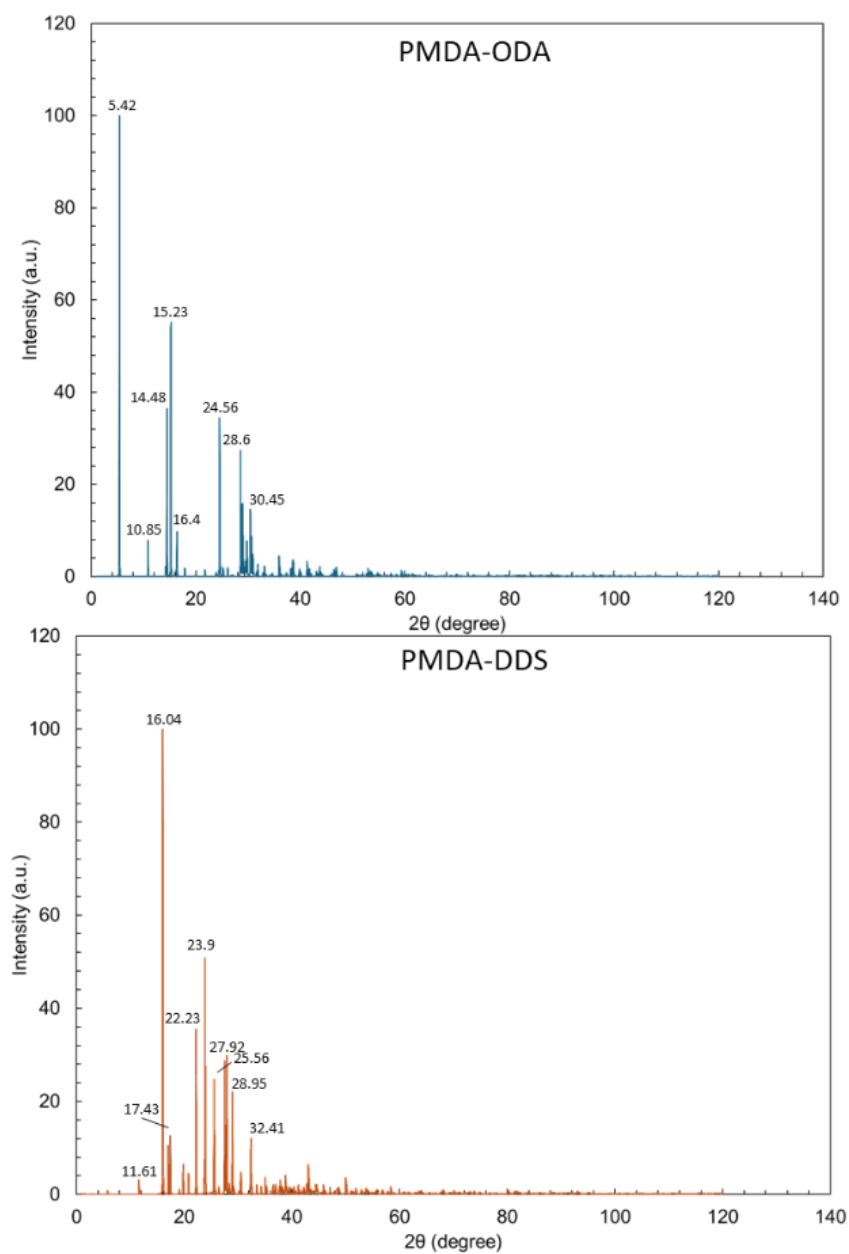


Figure S6.1. Simulated powder diffraction patterns for the DFT-computed PMDA-DDS and PMDA/ODA unit cells. All major peaks within the first 40° 2θ are denoted. The simulated spectra were produced from incident X-rays of $\lambda = 1.54059 \text{ \AA}$.

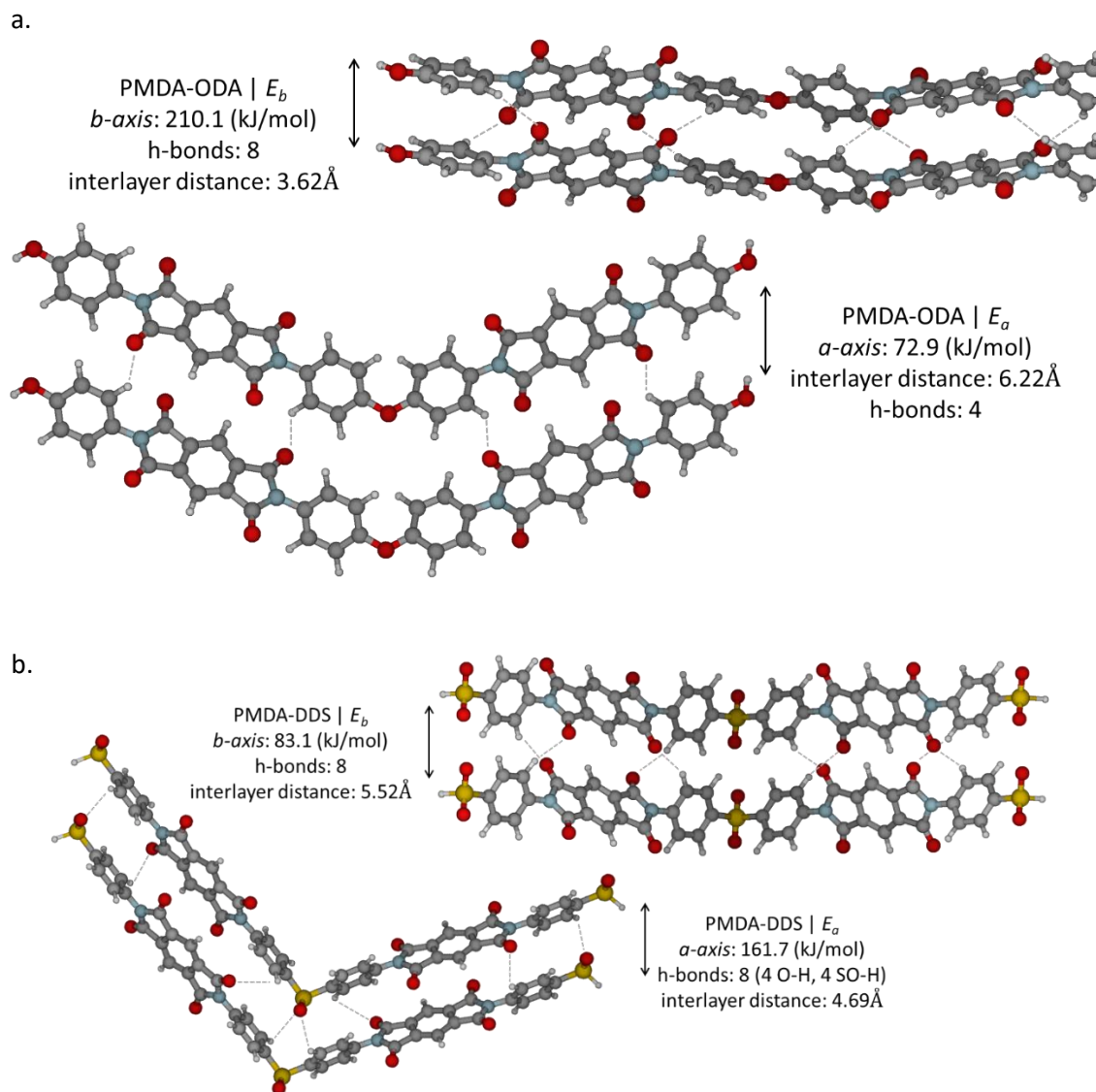


Figure S6.2. Interaction energies, hydrogen bond count, and interlayer distances for neighboring **a)** PMDA/ODA and **b)** PMDA/DDS chains stacked along the b and a -axes respectively. Hydrogen bonds are denoted with dashed lines.

c

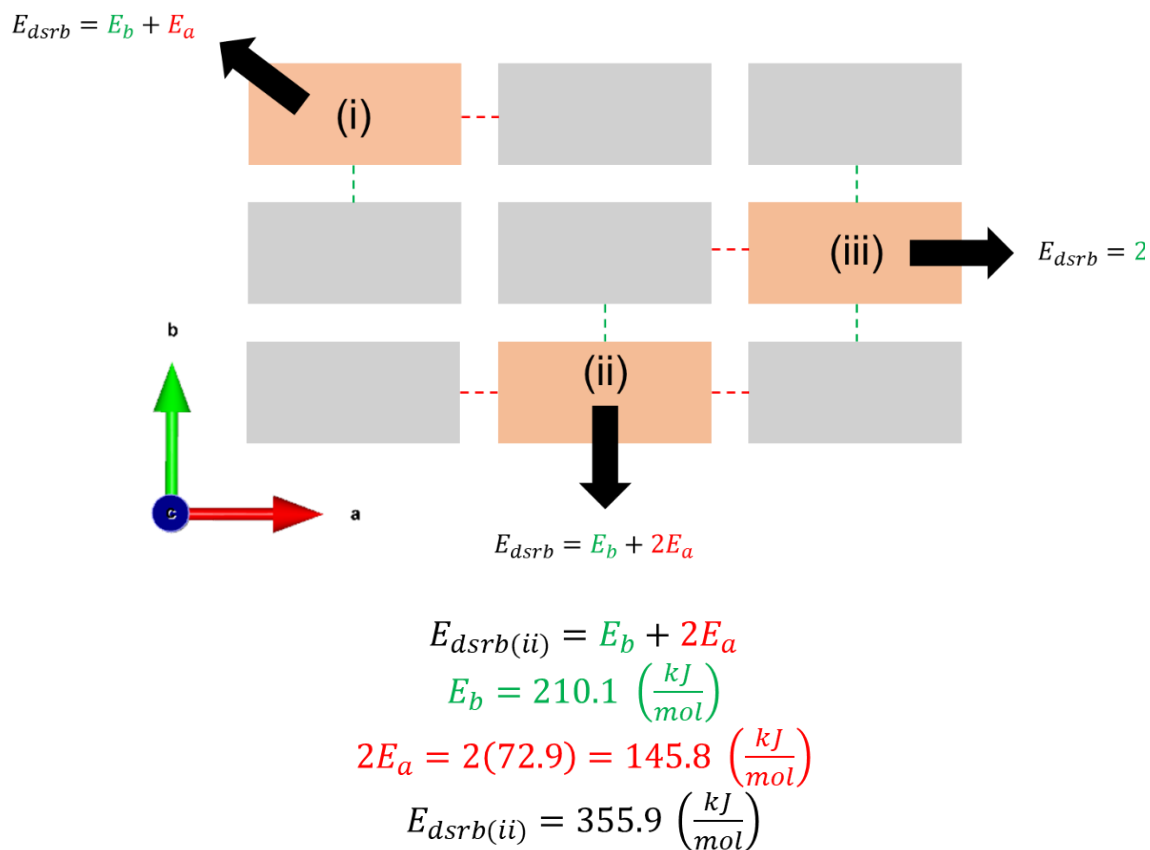


Figure S6.3. A) Desorption energy expressions for each of three (i, ii, iii) polymer desorption sites. B) Example calculation for desorption of a polymer chain from position (ii) for the PMDA-ODA polymer. Energetic data (E_a and E_b) available in Figure S6.2.

Table 6.2. Comparison of estimated thermal desorption rate constants between the most strongly bound PMDA/ODA (position “ii”) and PMDA/DDS (position “iii”) monomers from the 3x3 polymer aggregate model. The color gradient runs linearly across a log-scale ranging from 10^{-38} to 10^{-10} s⁻¹; corresponding colors were applied to each entry of a matching magnitude. Rate constants were calculated using the Eyring Equation and polymer desorption energies as the energies of activation for the desorption process.

T (°K)	PMDA-ODA k (hr ⁻¹)	PMDA-DDS k (hr ⁻¹)
473.15	1.28E-38	4.69E-29
523.15	2.26E-33	1.01E-24
573.15	4.90E-29	3.84E-21
623.15	2.15E-25	3.92E-18
673.15	2.73E-22	1.44E-15
723.15	1.30E-19	2.35E-13
773.15	2.79E-17	1.99E-11
823.15	3.14E-15	9.86E-10

6.6 Future Work

One route for future work could involve studying additively manufactured parts of blends of PMDA/ODA and PMDA/DDS polyimides. One interesting question is, do the strength of the PMDA/ODA crystallites act as reinforcements to the PMDA/DDS system? Blending 1%, 10%, 20%, and higher amounts of PMDA/ODA into the PMDA/DDS system would allow for this to be studied. SAXS experiments tracking the intercrystalline long period could be used to study the long-range organization of crystallites in these mixed systems. SEM experiments, coupled with investigating the scattering intensity at low q , could reveal the effect of the blend composition on the void formation in the printed parts.

As discussed in Chapter 2, there are other experimental techniques that could be used to characterize the morphology the printed parts. X-ray microtomography as a non-destructive 3D imaging technique could track the formation of void networks with time. Because it is a bulk imaging technique, the connectivity and volume fraction of voids could be determined. The results could be compared to the results from additional SAXS analysis such as the scattering invariant, which could provide a volume fraction of porosity when the electron density of each phase is known.³⁸ If these experiments were performed at a beamline, the results could be collected *in-situ* to directly correlate the temperature to the void formation and connectivity.

Finally, another area of research based on this work could involve intentionally engineering voids in polyimide parts to create aerogels. This area of research is active and involves tailoring the chemical structure, crosslinking, and drying methods of polyimides to create a porous morphology.³⁹ Based on the work presented here, it would be interesting to study the parameters that allow for control over the pore size distribution. Factors would

include heating rate during post-processing, nonsolvent induced phase separation, and scaffold engineering, to reduce the thermal stability of the scaffold and induce void formation earlier during post-processing. Such systems with controlled porosity may produce materials with low thermal conductivity and low dielectric constants that make these materials applicable in additional applications.

6.7 Acknowledgements

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Chapter 7. Collaborative Studies Utilizing X-ray Scattering

7.1. Phase separated morphologies in blocky copolymers

7.1.1 Blocky bromination of poly(ether ketone ketone) (PEKK) as a means to preserve crystallizability and rapid crystallization kinetics¹

Michelle E. Pomatto, Erin R. Crater, Garrett F. Godshall, Robert B. Moore

Polymer Chemistry **2024**, 15 (7), 609-621.

Background

Poly(ether ketone ketone) (PEKK) (**Figure 7.1**) is a semicrystalline thermoplastic copolymer² which can gel into a solvent-swollen, physically crosslinked network via a thermally-induced phase separation (TIPS) mechanism with diphenylacetone (DPA) as the solvent.¹ The properties of these physically crosslinked, semicrystalline gel networks have been extensively studied by members of the Moore Group, including their porosity, modulus, and hierarchical morphology.³⁻⁸ A fascinating finding from these scientific investigations is that the physically crosslinked and semicrystalline gels can be used to template the formation of blocky copolymers by performing the post-polymerization functionalization reaction in the gel state.^{1, 9-14} This result is in contrast with homogeneous reactions which yield a random functionalization distribution. Functionalizing semicrystalline polymers in a blocky sequence has been shown to yield higher degrees of crystallinity, faster crystallization kinetics, and thicker crystalline lamella than their random counterparts at similar degrees of functionalization.^{1, 9-13, 15}

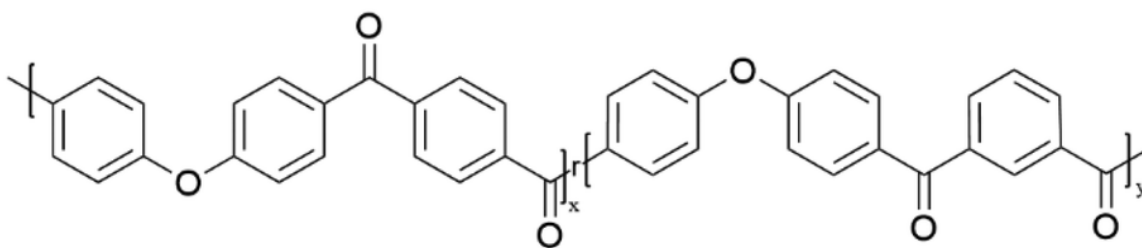


Figure 7.1. The chemical structure of poly(ether ketone ketone) (PEKK), a copolymer with a terephthalic comonomer, denoted by x , and an isophthalic comonomer, denoted by y . For PEKK 80/20, $x = 80$ and $y = 20$.

As mentioned previously, the semicrystalline polymer of interest by Pomatto and coworkers was PEKK 80/20. This copolymer of PEKK, containing a relatively high amount of terephthalic units compared to isophthalic units, has been shown to have high degrees of crystallinity and fast crystallization kinetics,² making the copolymer an excellent candidate to form semicrystalline gels and to study the effects of functionalizing in the gel state. In this work, the functionalization reaction that was chosen was bromination, as prior work in the Moore Group demonstrated that similar semicrystalline polymers including poly(ether ether ketone) (PEEK)¹⁶ and syndiotactic polystyrene (sPS)^{10, 14} could be brominated in the gel state to form blocky copolymers.

Pomatto and coworkers synthesized a series of randomly and blocky brominated PEKK 80/20 copolymers as shown in **Figure 7.2**.¹ The randomly and blocky brominated PEKK copolymers were prepared in matched sets with similar degrees of bromination between random and blocky to understand the effects of the comonomer distribution on the morphology of the copolymers. Randomly brominated copolymers were prepared by brominating PEKK in the homogeneous solution state. PEKK is randomly brominated in the solution state, where each solubilized polymer chain has equal access to the functionalizing reagents. In contrast, PEKK is blocky brominated when the same

reaction is performed in the heterogeneous, semicrystalline gel state. In the gel state, the solvent-swollen amorphous PEKK chains have greater access to the brominating reagents compared to the chains in the crystalline lamella. This leads to relatively longer runs of unfunctionalized, pristine PEKK comonomers, leading to a “blocky” microstructure.¹ The pristine runs of PEKK are crystallizable, leading to the apparent increase in crystallinity in blocky vs. randomly functionalized PEKK copolymers.

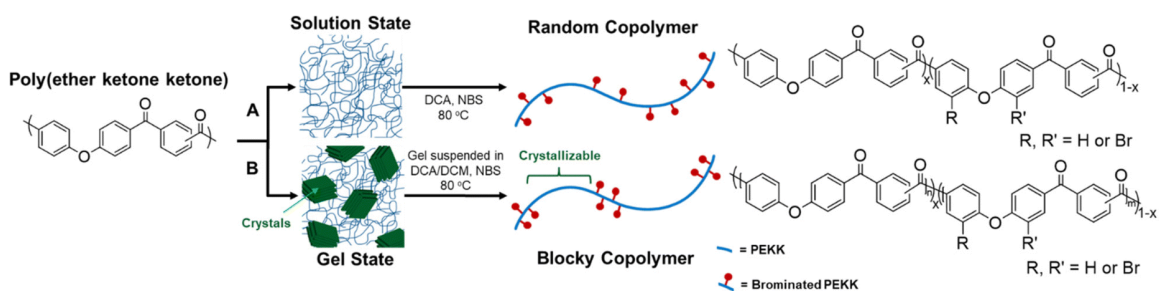


Figure 7.2. Schematic showing the post-polymerization bromination routes of poly(ether ketone ketone) (PEKK). Bromination in the homogeneous solution state results in a random copolymer, whereas bromination in the heterogeneous, semicrystalline gel state results in a blocky copolymer.

Experimental

Samples for small, mid, and wide-angle X-ray scattering/diffraction (SAXS, MAXS, WAXS/D) analysis were prepared using the following methods. The solvent-extracted PEKK aerogel was placed in a 1 mm thick metal washer with Scotch® Magic™ tape windows on either side. The PEKK, rBrPEKK, and bBrPEKK copolymer samples were prepared in differential scanning calorimetry (DSC) pans that were subsequently treated in a DSC. Samples were loaded into a Tzero DSC pan, heated to 400 °C at 10 °C min⁻¹ in nitrogen and isothermally held at 400 °C for 3 minutes to remove all thermal history. Samples were then rapidly cooled at 100 °C min⁻¹ to 280 °C and held for 30 minutes to allow for crystallization to occur. After 30 minutes, the samples were cooled at

10 °C min⁻¹ to room temperature. The samples were then removed from the pan using tweezers and a razor blade and utilized for SAXS/MAXS/WAXS/D analysis.

The SAXS, MAXS, WAXS/D experiments were performed on the solid samples using a Xenocs Xeuss 3.0 SAXS/WAXS system equipped with a GeniX 3D Cu HFVLF microfocus X-ray source utilizing Cu K- α radiation ($\lambda = 0.154$ nm). The sample-to-detector distance was 900 mm for SAXS, 370 mm for MAXS, and 43 mm for WAXD. The q -range was calibrated using a silver behenate standard for SAXS and MAXS, and a lanthanum hexaboride standard for WAXD. The exposure times were 2 h, 1 h, and 30 min for SAXS, MAXS, and WAXD, respectively. The two-dimensional scattering patterns were collected using a Dectris EIGER 4M detector in an evacuated chamber and reduced using the XSACT software to obtain azimuthally integrated intensity versus scattering vector q profiles, where $q = (4\pi/\lambda)\sin(\theta)$, θ is one half of the scattering angle and λ is the X-ray wavelength. The data were normalized for background, thickness, and absolute intensity, and the SAXS/MAXS/WAXD profiles were merged into a single dataset for visualization purposes.

Results and Discussion

Small, mid, and wide-angle X-ray scattering experiments (hereafter referred to as SAXS/WAXS experiments) were performed to characterize the phase-separated microstructure of the starting material, gel, and functionalized copolymer products. First, the merged SAXS/WAXS pattern of the solvent-extracted PEKK/DPA aerogel was collected, shown in **Figure 7.3**. Characterizing the solvent-extracted gel rather than the solvent-swollen gel can be advantageous, as it leads to increased scattering contrast between the morphological features of the gel. At high q ($q > 10$ nm⁻¹), the WAXS region

of the scattering profile reveals crystalline reflections consistent with those reported for form I polymorph of neat PEKK.¹⁷ This data confirms the presence of lamellar crystallites in the gel that would be used to template the blocky functionalization of PEKK in later steps. At lower q , a broad knee-like scattering feature is centered around $q \approx 0.4 \text{ nm}^{-1}$. A similar scattering feature has been observed in poly(ether ether ketone) (PEEK)/DPA aerogels by Spiering and coworkers,⁴ along with poly(phenylene sulfide) (PPS) aerogels by Godshall and coworkers,³ and is attributed to scattering from the crystalline lamella. The oscillations observed between $q \approx 0.6$ and 2 nm^{-1} have also been observed in similar gels and are thought to arise from the structure factor associated with the spatial distribution of lamella in the semicrystalline gel.⁴ Overall, the X-ray scattering data of the PEKK aerogel confirms the semicrystalline structure of the gel used to template the blocky functionalization reaction.

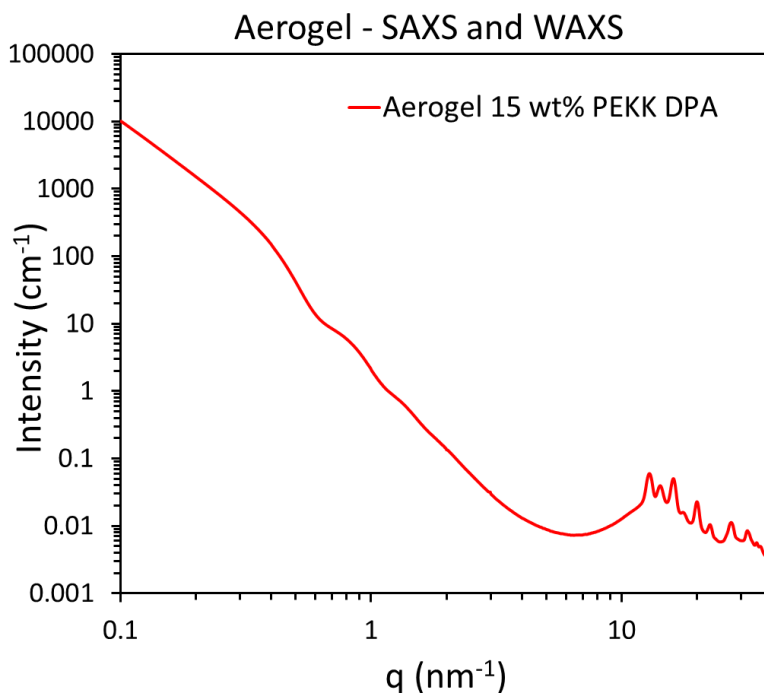


Figure 7.3. Merged SAXS/WAXS profile of the 15 wt.% PEKK/DPA solvent-extracted aerogel.

Next, the morphologies of blocky and randomly brominated copolymers of poly(ether ketone ketone) (PEKK) were studied via SAXS/WAXS to understand the effects of the copolymer microstructure and degree of bromination on the phase-separated morphology of the films. The merged SAXS/WAXS patterns of the random BrPEKK copolymers are shown in **Figure 7.4a**, and the same results are shown for the blocky BrPEKK copolymers in **Figure 7.4b**. At wide angles ($q > 8 \text{ nm}^{-1}$), the WAXS region of the random copolymers (**Figure 7.4a**) reveal crystalline reflections arising from the intracrystalline spacings in form I crystallites of pristine PEKK, similar to those observed in bulk PEKK (**Figure 7.4a**) and the PEKK aerogel (**Figure 7.3**).¹⁷ As mentioned previously, the lamellar crystallites in PEKK copolymers are understood to form from the pristine PEKK segments, as the functionalized (i.e., brominated) comonomers would be

excluded from the crystalline lamella, acting as defects to the unit cell structure. Therefore, it is expected that the crystalline reflections, and therefore the unit cell crystal structures, would be similar between the PEKK copolymers and pristine PEKK.

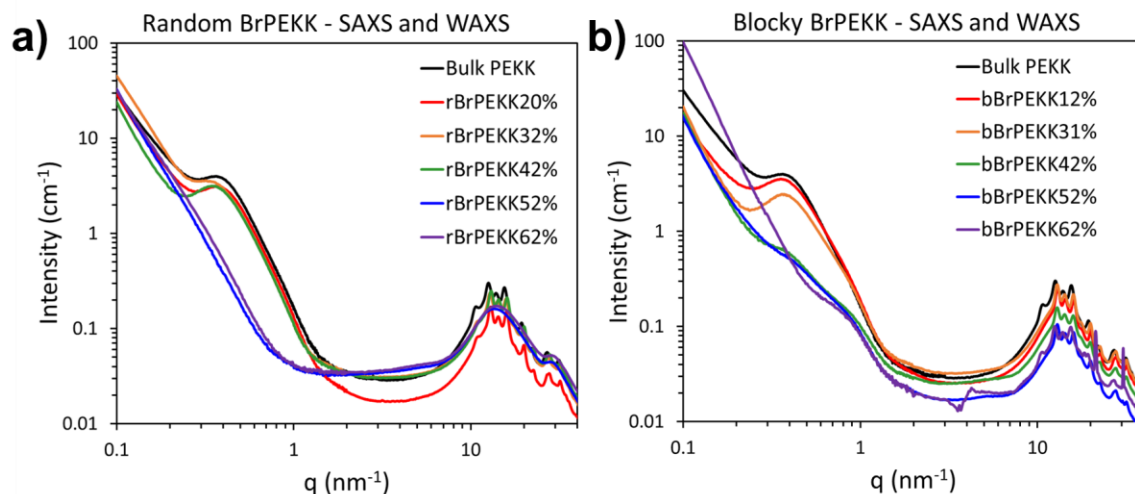


Figure 7.4. Merged SAXS/WAXS patterns of **a)** randomly brominated PEKK copolymers, and **b)** blocky brominated PEKK copolymers. All samples were isothermally crystallized from the melt at 280°C for 30 minutes under a nitrogen atmosphere.

The vertically offset WAXS profiles of the random and blocky brominated PEKK copolymers are shown in **Figure 7.5a** and **Figure 7.5b**, respectively. At low degrees of bromination (< 52 mol%), randomly brominated PEKK copolymers again display crystalline reflections consistent with the form I crystalline form of PEKK.¹⁷ At 52 and 62 mol% of functionalization, the randomly brominated PEKK copolymers reveal a broad amorphous halo (**Figure 7.5a**) indicating a lack of crystallinity. This observation was consistent with the lack of melting transitions observed via DSC for these materials and is expected as high degrees of functionalization decreases the crystallizability of the copolymers due to increasing number of defects to the crystalline unit cell structure.

The WAXS profiles of the blocky brominated PEKK copolymers are shown in **Figure 7.5b**. In contrast to the random copolymers, the WAXS profiles for all blocky copolymers display crystalline reflections, supporting that crystallinity is retained even at high mol% of functionalization. As discussed previously, the preservation in crystallinity in the blocky copolymers is due to the non-random, block-like sequence of units that preserves longer, uninterrupted runs of the crystallizable, pristine PEKK segments. Interestingly, the 62 mol% blocky brominated PEKK copolymer displays new crystalline reflections shown via the black arrows in **Figure 7.5b**. These new peaks could be attributed to another crystal form of PEKK, but further studies would be needed to confirm this. 2D orientation WAXS experiments, in which the polymer film is physically drawn along a given axis, could help determine the origins of the new peaks in the bBrPEKK62%. For example, the 2D WAXS pattern images yielding features at ca. 30° and 45° 2θ , shown as arrows in **Figure 7.5b** would likely display anisotropies in the 2D pattern from an oriented film. The anisotropies, whether along or perpendicular to the orientation direction, would provide insight into the crystallographic axes where these atoms are located.

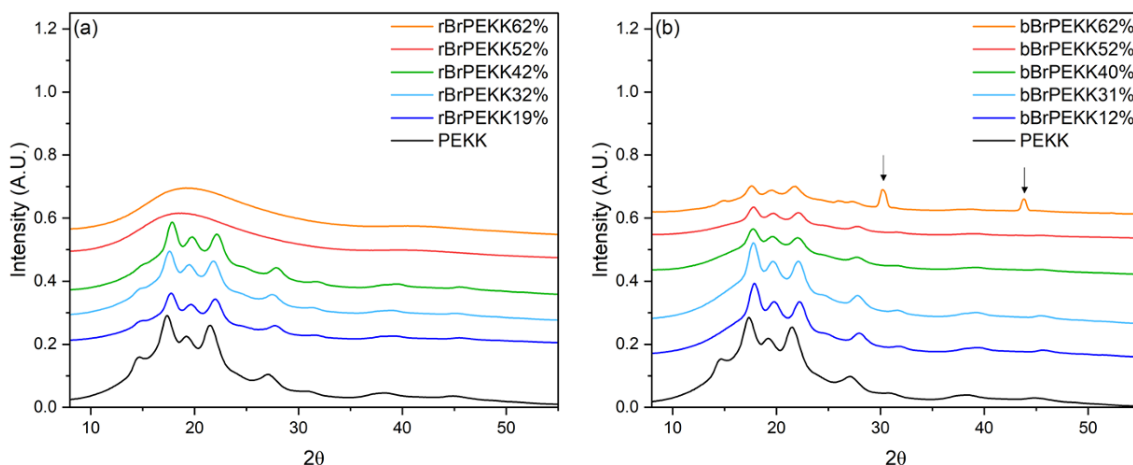


Figure 7.5. Vertically offset WAXS profiles of **a)** randomly brominated PEKK copolymers and **b)** blocky brominated PEKK copolymers.

At small angles ($q < 1 \text{ nm}^{-1}$), a prominent peak is observed centered around $q \approx 0.5 \text{ nm}^{-1}$ (**Figure 7.4a**). This peak is known as the intercrystalline long period and the peak position corresponds with the average center-to-center distance between lamellar crystallites, and is observed in many semicrystalline polymers. As expected, an intercrystalline long period peak is observed for the semicrystalline PEKK copolymers, whereas the SAXS region of rBrPEKK52% and rBrPEKK62% is featureless, consistent with the amorphous morphology observed in the WAXS profiles (**Figure 7.5a**). The SAXS patterns for the low mol% blocky copolymers, bBrPEKK12% and bBrPEKK 31%, reveal the characteristic interlamellar long period peak (**Figure 7.4b**), that was also observed in the semicrystalline random copolymers (**Figure 7.4a**). However, for the high mol% blocky copolymers, the SAXS region is characterized by two knee-like features (**Figure 7.4b**). The second knee at higher q , centered around $q \approx 0.5 \text{ nm}^{-1}$ might be due to the structure factor contributions from the intercrystalline long period, similar to those observed in the aerogel SAXS pattern (**Figure 7.3**). However, further studies are needed to confirm this.

7.1.2 Tailoring the microstructure of sulfonated poly(ether ketone ketone) through blocky functionalization in the gel state: a facile route to enhanced crystallizability and proton conductivity¹³

Michelle E. Pomatto, Erin R. Crater, Mark S. McCrary, Robert B. Moore

Polymer **2025**, 334, 128706.

Background

Previous work in the Moore Group has detailed the blocky sulfonation of sPS⁹ and PEEK.¹¹ Sulfonated polymers are heavily utilized as proton exchange membranes in hydrogen fuel cells, with the perfluorosulfonic acid copolymer NafionTM (Chemours) being the industry standard.¹⁸ As discussed in Chapter 5, the two primary requirements for proton exchange membranes include high proton conductivity, which determines the efficiency of a fuel cell, and the membrane mechanical stability, which is a factor in determining the lifespan of the fuel cell. There is a growing interest in developing fully hydrocarbon-based proton exchange membranes, due to the negative externalities associated with the production and breakdown of fluorinated materials.¹⁹ Sulfonated PEEK has been proposed a potential alternative to perfluorosulfonic acids (PFSAs), due to the ability to control the degree of sulfonation by the post-polymerization reaction conditions, and the presence of crystallinity.¹¹ In this study, post-polymerization sulfonation reactions of poly(ether ketone ketone) (PEKK) were performed in the homogeneous solution state to yield randomly sulfonated PEKK copolymers and in the heterogeneous, semicrystalline gel state, to yield blocky sulfonated PEKK.¹³ The principles of blocky sulfonation of PEKK are the same as those discussed for bromination of PEKK, and others blocky, gel state functionalization

reactions, and are presented in **Figure 7.6**. The goal of this study was to understand how the sequence of the sulfonic acid units influenced the resulting morphology of the membrane, ultimately helping to explain some of the observed differences in physical properties between the two classes of materials.

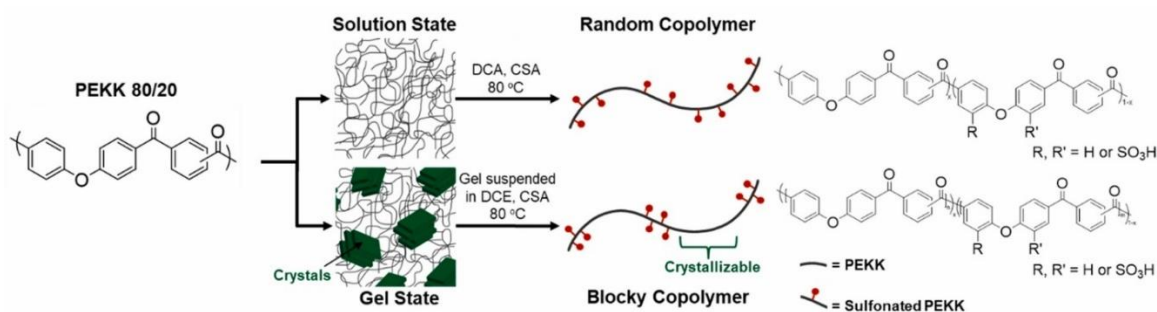


Figure 7.6. Schematic showing the post-polymerization sulfonation routes of poly(ether ketone ketone) (PEKK). Sulfonation in the homogeneous solution state results in a random copolymer, whereas sulfonation in the heterogeneous, semicrystalline gel state results in a blocky copolymer.

Experimental

The PEKK, rSPEKK, and bSPEKK copolymer membranes (Cs^+ -form) for small, mid, and wide-angle X-ray scattering/diffraction (SAXS, MAXS, WAXS) analysis were solvent-cast and prepared as described in the work by Pomatto and coworkers.¹³ Prior to analysis, Cs^+ -form membranes were dried at 100 °C for a minimum of 12 h under vacuum. The SAXS, MAXS, WAXS experiments were performed on the solid samples using a Xenocs Xeuss 3.0 SAXS/WAXS system equipped with a GeniX 3D Cu HFVLF microfocus X-ray source utilizing Cu K- α radiation ($\lambda = 0.154$ nm). The sample-to-detector distance was 900 mm for SAXS, 370 mm for MAXS, and 43 mm for WAXS. The q -range was calibrated using a silver behenate standard for SAXS and MAXS, and a lanthanum hexaboride standard for WAXS. The exposure times were 2 h, 1 h, and 30 min

for SAXS, MAXS, and WAXS, respectively. The two-dimensional scattering patterns were collected using a Dectris EIGER 4 M detector in an evacuated chamber and reduced using the XSACT software to obtain azimuthally integrated intensity versus scattering vector q profiles, where $q = (4\pi/\lambda)\sin(\theta)$, θ is one half of the scattering angle and λ is the X-ray wavelength. The data were normalized for background, thickness, and absolute intensity, and the SAXS/MAXS/WAXS profiles were merged into a single dataset for visualization purposes. The merged profiles are named “SAXS/WAXS” profiles for brevity.

Results and Discussion

PEKK, rSPEKK and bSPEKK copolymers were analyzed by small and wide-angle X-ray scattering (SAXS/WAXS) to study the differences between the blocky and random microstructures. The SAXS/WAXS profiles of PEKK, rSPEKK and bSPEKK membranes as-cast then converted to the Cs⁺-form are shown in **Figure 7.7b**. The peaks observed in the wide-angle region ($q > 10 \text{ nm}^{-1}$) in PEKK and b17 are attributed to the crystalline reflections of pristine PEKK crystallites indicating retention of crystallinity in bSPEKK, in agreement with DSC data.¹³ Conversely, r14 and b36 exhibit amorphous halos due to the significant reduction in crystallinity (X_c of 4 % and 7 %, respectively).²⁰ Additionally, an amorphous halo is prevalent for r35 due to complete lack of crystallizability. This is consistent with the observations from the WAXS experiments of the brominated PEKK copolymers, discussed above, which showed the retention of crystalline reflections at higher mol% functionalization in the blocky copolymers, whereas the respective random copolymers were primarily amorphous.

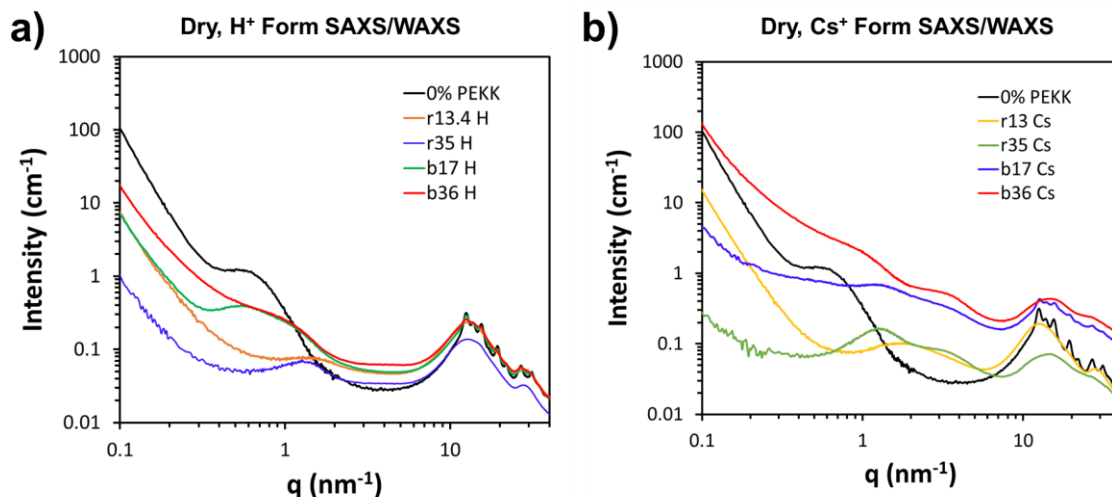


Figure 7.7. Merged SAXS/WAXS profiles of **a)** Dry, H⁺-form random and blocky sulfonated PEKK membranes, as-cast and dried under vacuum. **b)** Dry, Cs⁺-form random and blocky sulfonated PEKK membranes, as-cast and dried under vacuum.

In the mid-angle region ($1 < q < 10 \text{ nm}^{-1}$), two broad scattering features are observed at $q = \sim 1.3 \text{ nm}^{-1}$ and $\sim 3.6 \text{ nm}^{-1}$ for each of the SPEKK samples. These two features are attributed to the contrast in electron density related to the ionic component of the SPEKK ionomers.¹² Similar to polystyrene-based ionomers discussed in detail in Chapter 3, the ionomer peak is attributed to the presence of nano-phase separated ionic aggregates which exhibit interdomain dimensions that result in the appearance of a scattering feature.²¹ This is further supported by the observation that this feature becomes more pronounced with increasing mol% sulfonation, which increases the volume fraction of the ionic phase.

The SAXS/WAXS patterns of the dry, H⁺-form shows no evidence of a scattering maximum in the mid-angle region of $1 < q < 10 \text{ nm}^{-1}$ (**Figure 7.7a**). In the dry, H⁺-form, the primary scattering feature is assigned to the intercrystalline long period peak, appearing at $0.3 < q < 2 \text{ nm}^{-1}$. This feature is related to the average center-to-center distance between

PEKK crystallites, as it is also observed in non-ionic, neat PEKK (**Figure 7.7**). Clearly, in the dry Cs⁺-form, there are overlapping and convoluted scattering features from the broad ionomer peak and the interlamellar scattering of the crystalline component (**Figure 7.7b**). When comparing the blocky and random microstructures, the ionic feature observed at $q = \sim 1.3 \text{ nm}^{-1}$ appears at a lower q in the blocky samples compared to the random analog. Fitting this SAXS feature to the shape-independent Guinier model results in an average dimension of $R_g \approx 14 \text{ nm}$ for this feature.²² This relatively large ionic domain is attributed to efficient blocking up of the sulfonate functionalities leading to larger aggregate dimensions compared to those in the random analog. Efficient blocking up of the sulfonate group is supported by increased proton conductivity observed in the blocky PEKK copolymers compared to their random analogues.¹³

7.1.3 Synthesis and Characterization of Halogenated PEEK with Microstructural Control: Thermal and Morphological Effects of Halogen Identity¹⁵

Christopher R. Kasprzak, Erin R. Crater, Brendan M. Shumberger, Lindsey J. Anderson, Hannah D. Cornell, Mark S. McCrary, T. Daniel Crawford, Robert B. Moore

Background

In this study, post-polymerization halogenation reactions were performed to functionalize poly(ether ether ketone) (PEEK), a high-performance semicrystalline thermoplastic. Bromination and iodination reactions were performed on PEEK to yield brominated PEEK copolymers and iodinated PEEK copolymers. Each halogenation reaction was performed in both the homogeneous solution and the heterogeneous gel state to yield random and blocky copolymers, respectively. Similar to the post-polymerization functionalization of PEKK discussed above, randomly halogenated PEEK is synthesized by fully dissolving PEEK in a good solvent, dichloroacetic acid,⁶ followed by adding the functionalizing reagents in the homogeneous solution state. In this case, each polymer chain has equal opportunity for functionalization (**Figure 7.8a**) resulting in a random distribution of halogens along the backbone of PEEK. In contrast, blocky halogenated PEEK is synthesized by first preparing a gel through the TIPS process with PEEK and a solvent, such as dichloroacetic acid (DCA). Next, the same chemistry is performed in the heterogeneous gel state, where the polymer chains in the semicrystalline lamella have less access to the reagents. In this case, the functionalizing reagents preferentially react with the amorphous polymer chains of the semicrystalline gel network due to steric exclusion from the crystalline lamella, yielding a blocky distribution. Details about the bromination

reactions can be found in the work by Kasprzak, Anderson, and Moore,¹⁶ and the iodination reaction procedures can be found in Kasprzak 2022.¹⁵

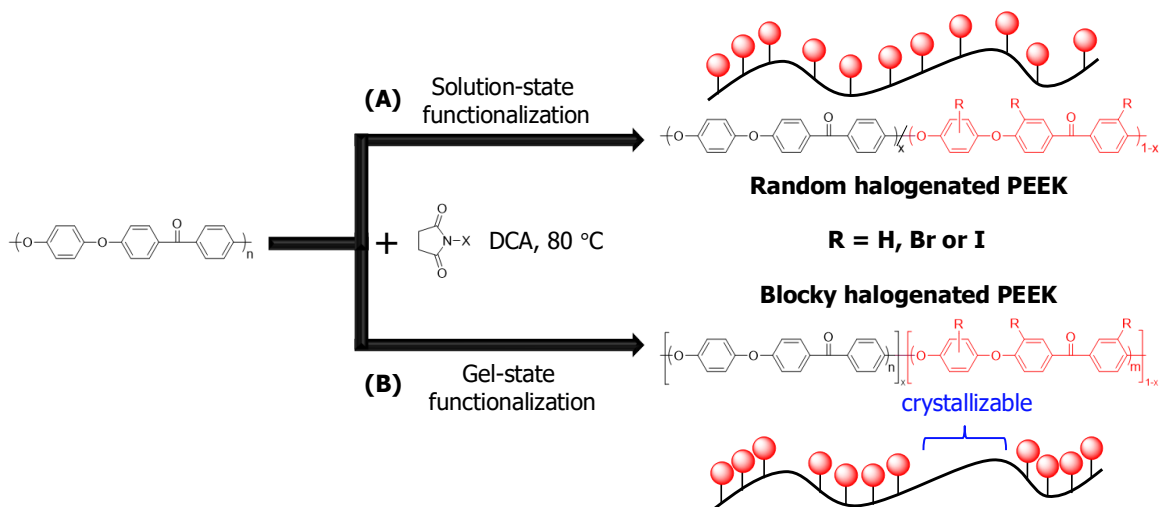


Figure 7.8. Schematic showing the post-polymerization halogenation (bromination and iodination) routes of poly(ether ether ketone) (PEEK). **a)** Bromination and iodination of PEEK in the homogeneous solution state results in a random copolymer. **b)** Bromination and iodination of PEEK in the heterogeneous, semicrystalline gel state results in a blocky copolymer.

Experimental

To prepare quenched films of halogenated PEEK, the polymers were melt pressed between two aluminum plates layered with Kapton films using a heated Carver hydraulic press. Steel shims were utilized to control the film thickness to approximately 100 μm . Samples were heated for 2 minutes at 375 °C in the Carver hydraulic press prior to pressing. Next, the melted samples were subjected to several press-release-press cycles in which the press cycles afforded 10 tons of force onto the samples. The aluminum plates and sandwiched polymer film were immediately transferred into an ice-bath to yield amorphous, ductile films. Samples were subsequently dried at 100 °C in a vacuum overnight. Annealing of quenched films was performed by placing the quenched films in an oven at 250 °C for 2 h.

Ultra-small-angle X-ray scattering (USAXS) and small-angle X-ray scattering (SAXS) experiments were performed at the Advanced Photon Source beamline 9ID-C at Argonne National Laboratory.²³⁻²⁴ The USAXS instrument was configured in standard mode with an X-ray energy of 21 keV ($\lambda = 0.5895 \text{ \AA}$), X-ray photon flux of ca. $10^{13} \text{ mm}^{-2}\text{s}^{-1}$, and a combined q range of 0.0001–1.3 $\text{\AA}^{-1}$ ($q = 4\pi/\lambda\sin(\theta)$, where λ is the wavelength and θ is one-half of the scattering angle). USAXS and SAXS profiles were reduced using the Irena²⁵ and Nika²⁶ packages for IgorPro, respectively. The USAXS and SAXS profiles were acquired sequentially and merged into a single data set using the Irena package.²⁵ Wide-angle X-ray diffraction (WAXD) experiments were performed at the Materials Characterization Lab (MCL) at Virginia Tech on a Xeuss 3.0 SAXS/WAXS beamline equipped with a GeniX 3D Cu HFVLF microfocus x-ray source utilizing Cu K- α radiation ($\lambda = 0.154 \text{ nm}$). The sample-to-detector distance was 46.3 mm and the q -range was calibrated using a lanthanum hexaboride standard. Measurements were collected at room temperature with 30 min exposure times using a Dectris EIGER 4M detector. Data reduction was performed using XSACT software provided by Xenocs. The WAXS profiles were vertically shifted to facilitate comparison. The USAXS/SAXS profiles are plotted as vertically offset absolute intensity vs. the scattering vector q , and the diffraction profiles are plotted as relative intensity vs. the scattering angle 2θ .

Results and Discussion

USAXS/SAXS/WAXS experiments were used to study the effects of the degree of halogenation (e.g., mol% functionalization), halogen identity (e.g., bromine vs. iodine), copolymer microstructure (e.g., random vs. blocky), and processing conditions (e.g., melt-quenched vs. annealed) on the semicrystalline morphology of PEEK. The merged

USAXS/SAXS scattering profiles of all annealed halogenated PEEK copolymer samples are shown **Figure 7.9**. The noise in the data observed in several of the samples around $q = 0.01 \text{ \AA}^{-1}$ is due to the relatively low scattering intensity of the sample in that q region. When the scattering intensity of the sample is essentially the same as the scattering intensity of the background, the final, background subtracted data (shown in **Figure 7.9**) can appear noisy in that q region.

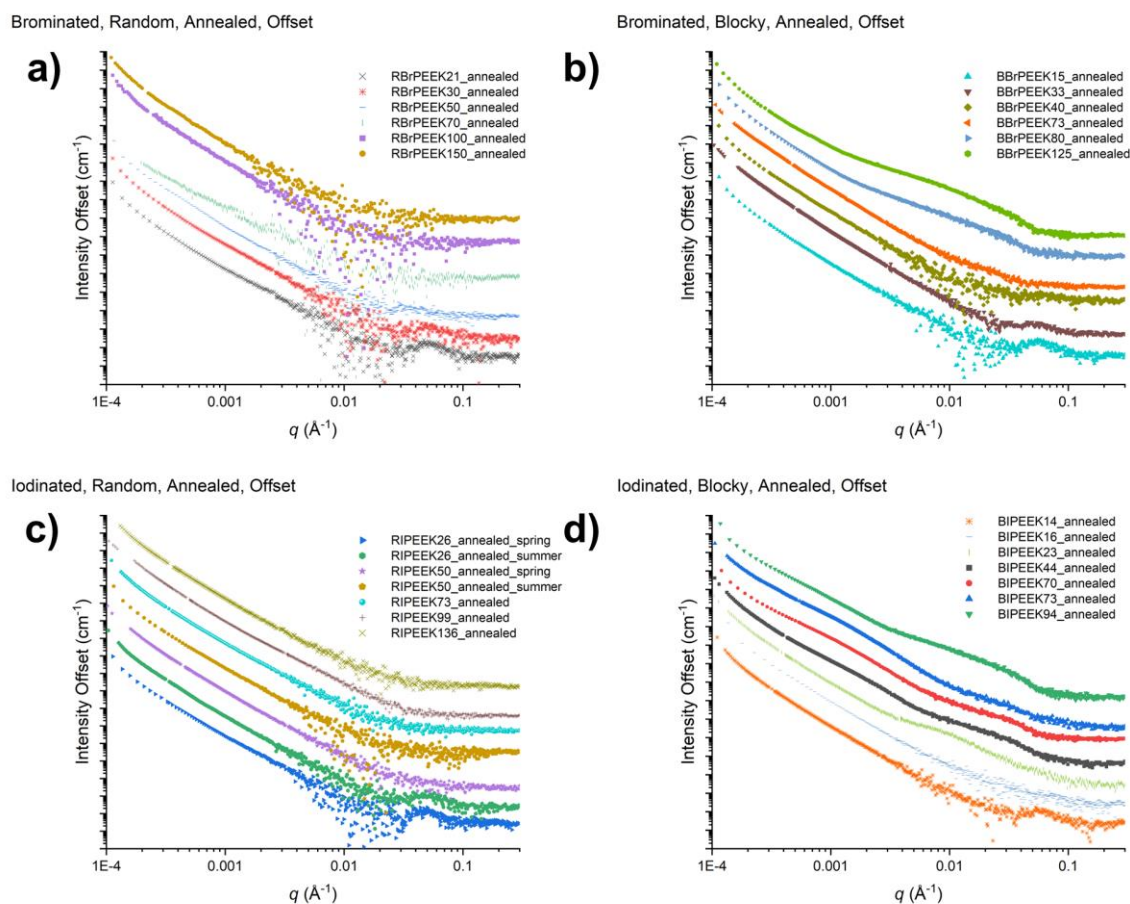


Figure 7.9. Merged USAXS/SAXS profiles of PEEK copolymers with various degrees of halogenation, annealed at 250°C for 2 hours. **a)** Randomly brominated PEEK copolymers, **b)** blocky brominated PEEK copolymers, **c)** randomly iodinated PEEK copolymers, **d)** blocky iodinated PEEK copolymers. The USAXS/SAXS profiles are vertically offset for visualization purposes.

First, the morphologies of the annealed halogenated PEEK copolymer films will be discussed. The merged USAXS/SAXS profiles of the annealed, randomly brominated PEEK samples are shown in **Figure 7.9a**. A scattering maximum centered around $q = 0.05 \text{ \AA}^{-1}$ is observed in RBrPEKK21 and RBrPEKK30, which is assigned to the intercrystalline long period and has been observed for pristine PEEK.²⁷ For randomly brominated PEKK at and above 50 mol% bromination, the USAXS/SAXS profile is characterized by a featureless power law region (**Figure 7.9a**), which is expected for an amorphous morphology that is homogeneous on the nanometer length scale. USAXS/SAXS profiles of the annealed blocky brominated PEEK copolymers are shown in **Figure 7.9b**. At low mol% bromination, BBrPEEK15 and BBrPEEK33 reveal a similar intercrystalline long period SAXS feature around $q = 0.05 \text{ \AA}^{-1}$. However, at higher degrees of bromination, the SAXS feature in the blocky copolymers appears to broaden and shift to lower q . The shift of this feature to lower q suggests that the interdomain distances associated with the crystallinity are increasing in size. As will be discussed below from the USAXS/SAXS profiles of melt-quenched sample, this broad feature is absent in the same films in their amorphous state, confirming that the source of the broad feature is the crystalline component.

The USAXS/SAXS profiles of the randomly iodinated, annealed PEEK copolymers are shown in **Figure 7.9c**. Similarly to the randomly brominated PEEK copolymers, shown in **Figure 7.9a**, the randomly iodinated PEEK copolymers display the signature intercrystalline long period peak for semicrystalline polymers at low degrees of iodination (RIPEEK26 and RIPEEK50, **Figure 7.9c**). At higher degrees of iodination, the scattering profiles of the randomly iodinated PEEK copolymers are characterized by a featureless

power law region, which is consistent with a mostly amorphous and homogeneous morphology on the nanometer length scale. Shown in **Figure 7.9d** are the blocky iodinated annealed USAXS/SAXS profiles. Similar to the blocky brominated samples, the low mol% BIPEEK14 displayed an intercrystalline long period peak, and this feature appears to shift to lower q and broaden with increasing mol% iodination. One fascinating result is the presence of an additional peak at low q (ca. $0.001 \text{ \AA}^{-1}$) in the high mol% iodinated PEEK samples (BIPEEK70 and BIPEEK73, **Figure 7.9d**). As will be shown below, the broad, low q feature around $0.001 \text{ \AA}^{-1}$ features remain present in melt-quenched films of the same copolymers, indicating that the scattering feature is associated with phase separation that is separate from crystallization.

In order to probe the origins of this novel scattering feature observed at low q , the same USAXS/SAXS experiments of all copolymers were performed on quenched films of the same materials. By melt-quenching the polymer films, the contributions of crystallinity to the scattering profile are minimized. To confirm that the iodinated copolymer films were fully quenched, wide-angle X-ray scattering experiments were conducted, and the results are shown in **Figure 7.10a**. Each profile is characterized by a broad amorphous scattering halo and absent from crystalline reflections. This result confirms that the processing

conditions were sufficient to erase crystallinity from the samples. A representative quenched film of the blocky brominated films is shown in **Figures 7.11 and 7.12**.

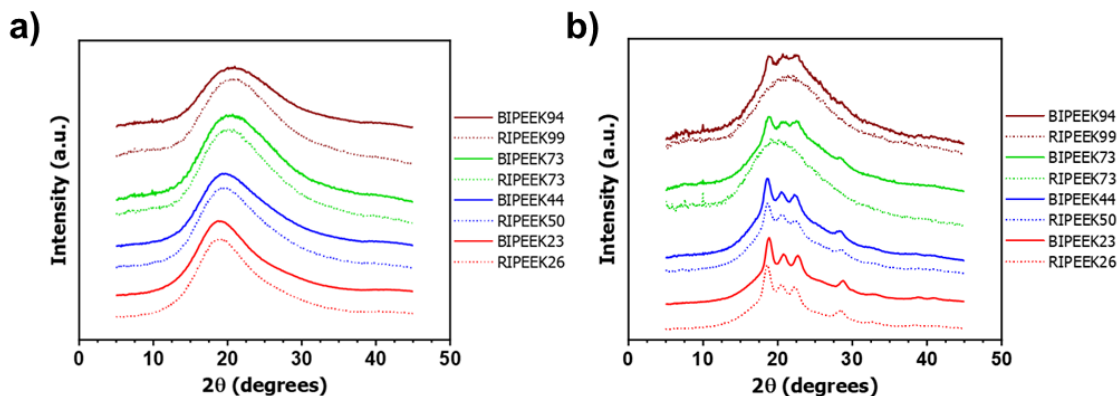


Figure 7.10. WAXS profiles of **a)** melt-quenched iodinated PEEK copolymers and **b)** annealed iodinated PEEK copolymers. All WAXS profiles are vertically offset for visualization purposes.¹⁵

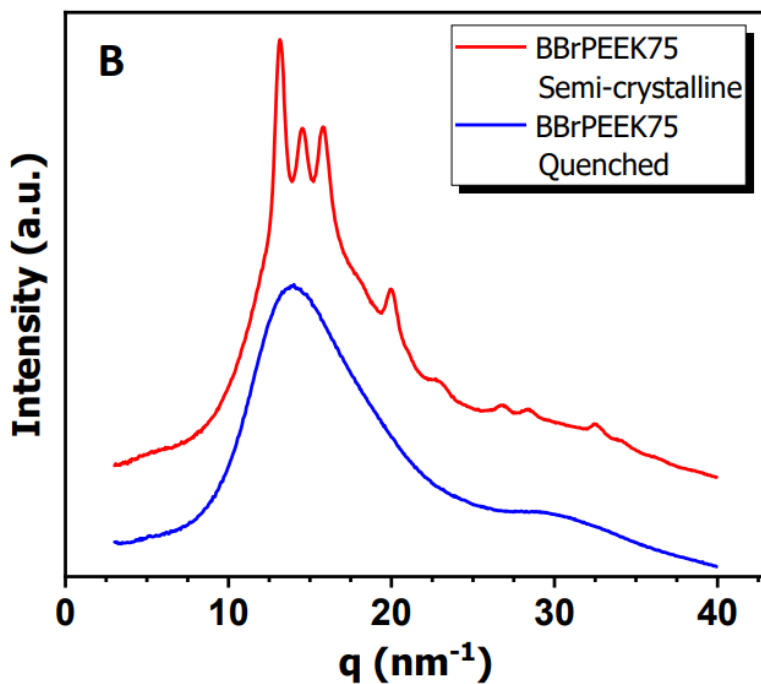


Figure 7.11. WAXS profiles of melt-quenched BBrPEEK75 and annealed BBrPEEK75. WAXS profiles are vertically offset for visualization purposes.¹⁶

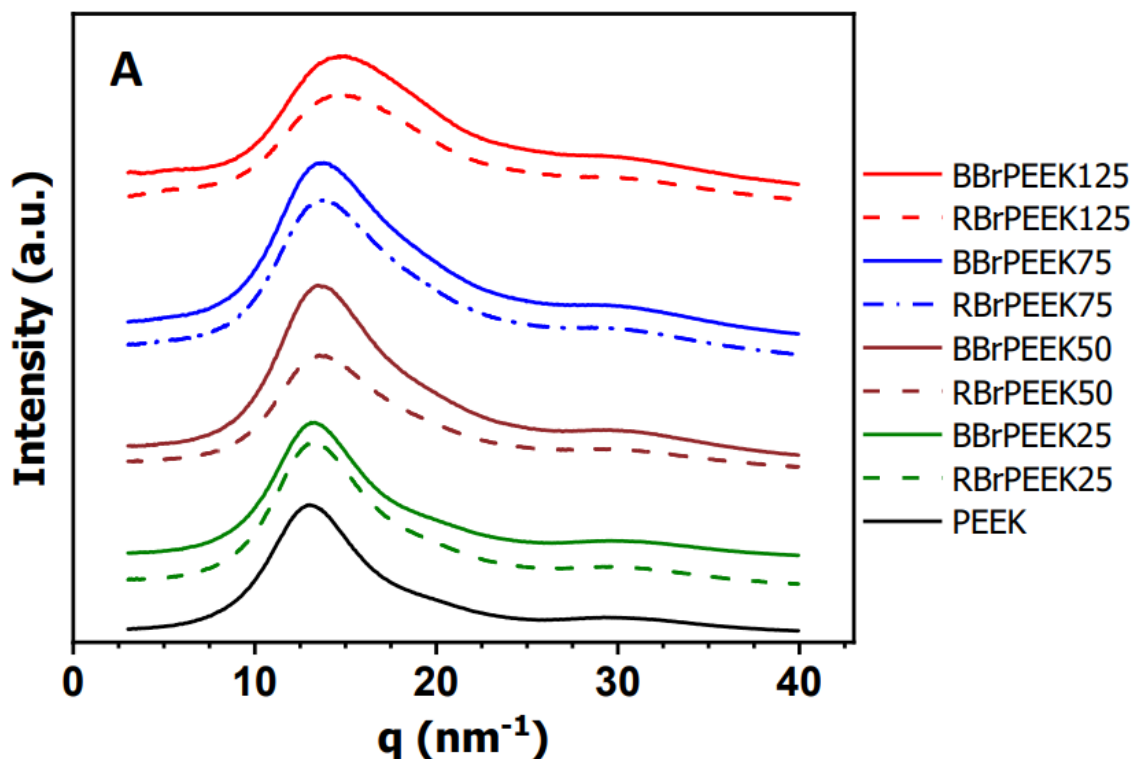


Figure 7.12. WAXS profiles of melt-quenched brominated PEEK copolymers and annealed brominated PEEK copolymers. All WAXS profiles are vertically offset for visualization purposes.¹⁶

Once the melt-quenching procedure had been confirmed, USAXS/SAXS experiments were conducted on all melt-quenched materials, and the results are shown in **Figure 7.13**. The quenched films for all random and blocky brominated films (shown in **Figure 7.13 a,b**), as well as the random iodinated films (shown in **Figure 7.13c**) reveal a featureless, power-law scattering behavior consistent with a homogeneous morphology on the nanometer length scale. This is expected, as the melt-quenching procedure was expected to erase the crystalline contributions to the profile. However, the melt-quenched profile for the blocky iodinated copolymers reveals features at low q that persist, despite the absence of crystallinity (**Figure 7.13d**). We hypothesize that the low q feature observed

in BIPEEK70 and BIPEEK73 may be due to phase separation of iodinated segments within the amorphous phase that could be occurring at high degree of iodination.

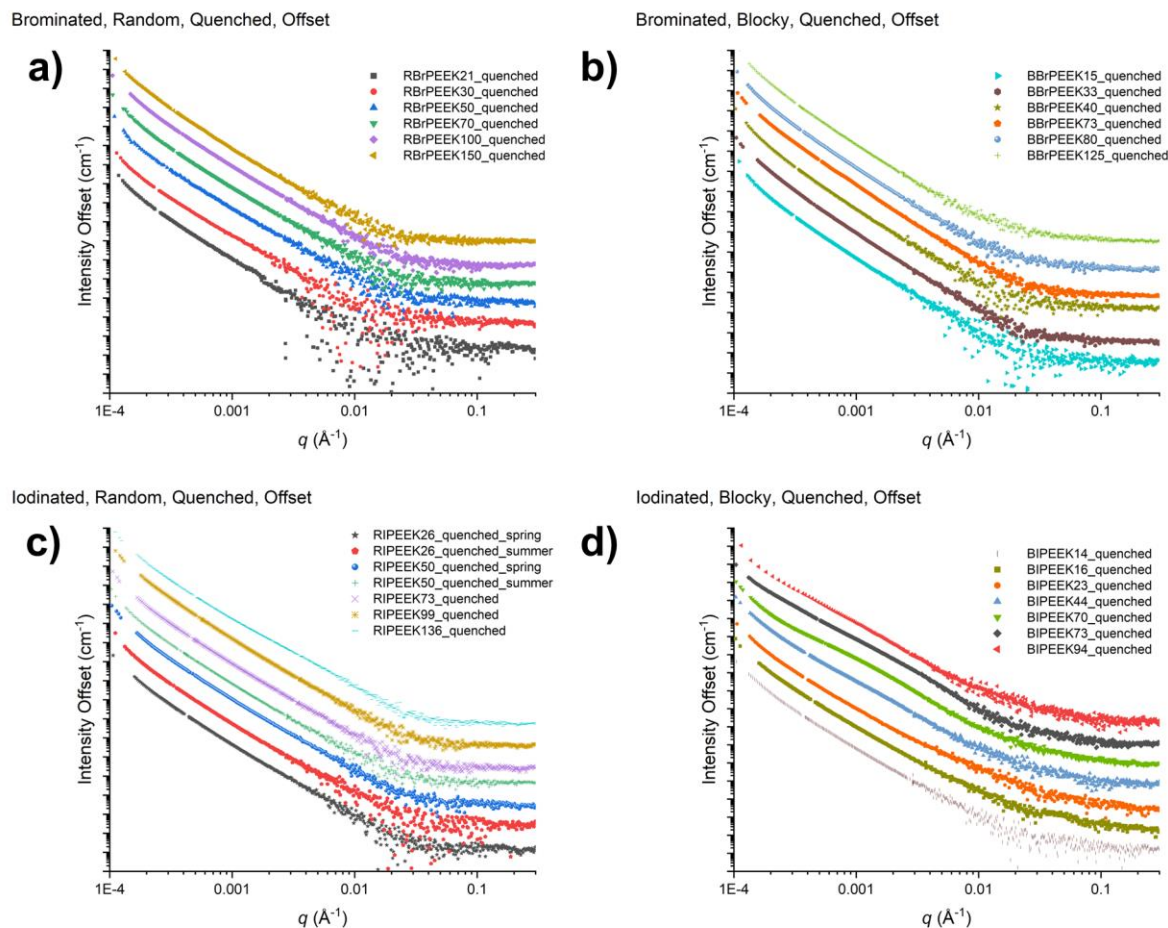


Figure 7.13. Merged USAXS/SAXS profiles of melt-quenched PEEK copolymers with various degrees of halogenation. **a)** Randomly brominated PEEK copolymers, **b)** blocky brominated PEEK copolymers, **c)** randomly iodinated PEEK copolymers, **d)** blocky iodinated PEEK copolymers. The USAXS/SAXS profiles are vertically offset for visualization purposes.

7.2. De novo Autogenic Engineered Living Functional Materials²⁸

Hoda M. Hammad, Seth Swarnadeep, Erin R. Crater, Robert B. Moore, Sanket Deshmukh, Avinash Manjula-Basavanna, Anna M. Duraj-Thatte

Background

In this work, the morphologies of aquaplastic materials created from excreted extracellular matrices from bacteria were studied through X-ray scattering experiments. In 2021, Duraj-Thatte and coworkers demonstrated that *Escherichia coli* bacteria could be genetically engineered to secrete a protein-based biofilm, which can be molded and dried into an “aquaplastic” that is biodegradable, with potential applications in replacing synthetic polymer materials.²⁹ *E. coli* bacteria are known to naturally excrete “curli fiber” proteins which are made up of CsgA repeating units. Once excreted, these fibers can self-assemble into amyloid nanofibers with a cross- β structure. The cross- β morphology has been well-studied in other materials and can be ascertained with X-ray scattering and diffraction techniques, as shown in **Figure 7.14**.³⁰ The two signature dimensions commonly obtained from wide-angle X-ray techniques are $d = 4.8 \text{ \AA}$ and $d = 10\text{-}11 \text{ \AA}$, which are associated with the distance between the stacked β -strands which participate in hydrogen bonding, and the distance between β -sheets, respectively.³⁰

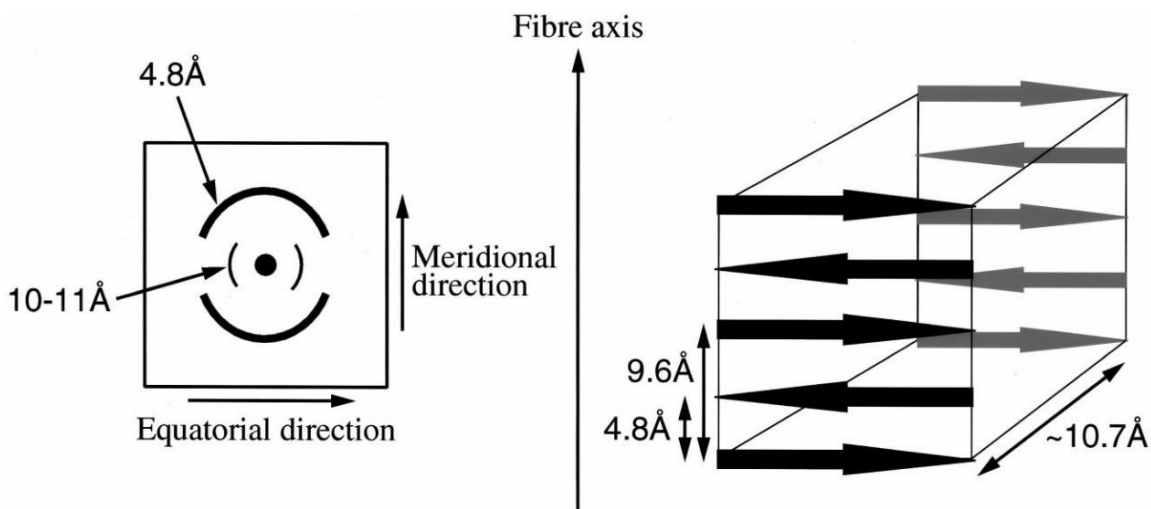


Figure 7.14. Schematic showing the characteristic dimensions of the cross- β structure of amyloid proteins using X-ray diffraction. Oriented fibers would produce the anisotropic 2D scattering pattern, but a random arrangement of fiber orientations would yield a symmetric, isotropic scattering pattern. Figure obtained from the work by Serpell.³⁰

In this novel work, bacteria other than *E. coli* capable of forming with the cross- β were identified using protein mining methods. Duraj-Thatte, Hoda Hammad, and coworkers cloned the genes identified in their mining studies into *E. coli* bacteria, which ultimately led to the excretion of these variant proteins and their assembly into fibers and aquaplastics. The goal of this work was to characterize the wide-angle reflections of the fibers to provide supporting evidence that the new aquaplastic materials exhibited the cross- β morphology.

Experimental

Aquaplastic samples were prepared and dried via lyophilization using the methods described in the published work.²⁸ The relatively small sample size of some of the aquaplastics required delicate sample handling and intentional care in securing it to the solid sample plate. The small and delicate samples were placed on the solid sample holder and characterized using the strategy shown in **Figure 7.15**.

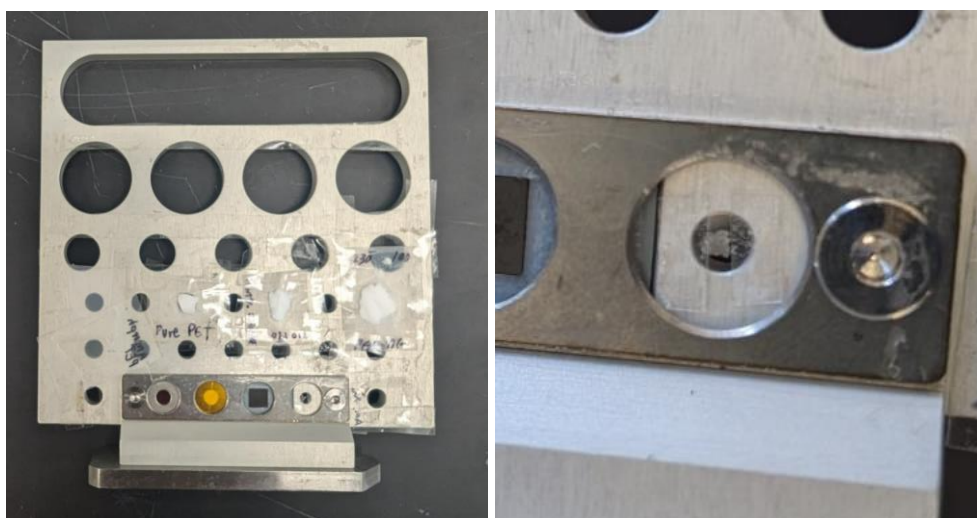
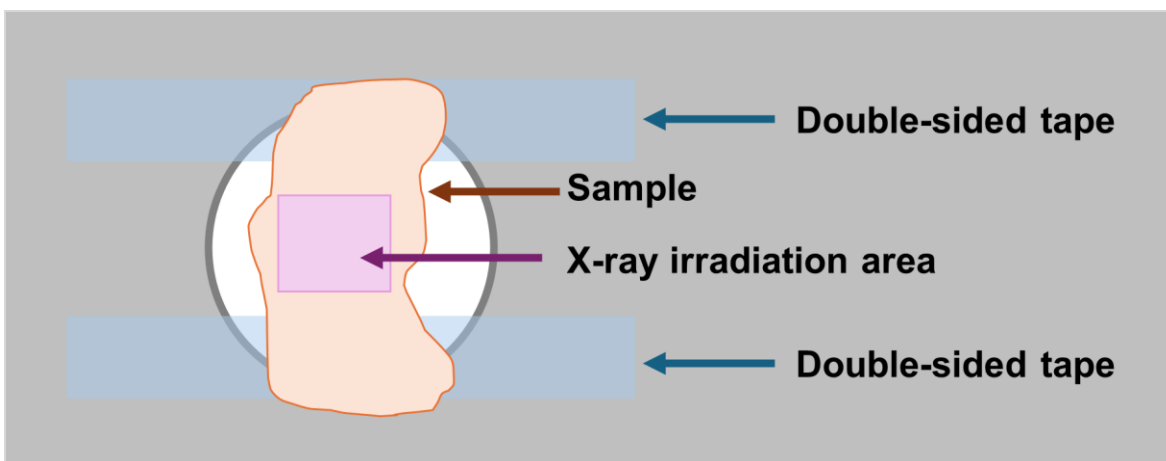


Figure 7.15. Drawing showing the strategy for performing X-ray scattering experiments on extremely delicate and small solid samples, along with the solid sample holder showing the use of double-sided tape in a small sample holder.

Small, mid, and wide-angle X-ray scattering (SAXS/MAXS/WAXS) experiments on the aquaplastics were performed using a Xenocs Xeuss 3.0 SAXS/WAXS equipped with a GeniX 3D Cu HFVLF microfocus X-ray source utilizing Cu K_{α} radiation ($\lambda = 0.154$ nm). The sample-to-detector distance was 42 mm for WAXS, 370 mm for MAXS, and 900 mm for SAXS, and the q -range was calibrated using a lanthanum hexaboride standard (WAXS) and a silver behenate standard (SAXS and MAXS). Due to the small sample width, a high-

resolution beam size was used (0.4 mm x 0.4 mm) to ensure that the beam size remained smaller than the sample area. Two-dimensional scattering patterns were obtained using a Dectris EIGER 4M detector with an exposure time of 30 minutes for WAXS, 2 hours for SAXS, and 1 hour for MAXS. Data reduction was performed using XSACT software provided by Xenocs.

Results and Discussion

As noted previously, protein mining methods identified CgA-like proteins that were predicted to form the characteristic cross- β fiber morphology. Their predicted structures from AlphaFold2 are shown in **Figure 7.16**, where the characteristic cross- β fiber morphology can be observed for each variant. As noted in **Table 7.1**, their predicted structures vary in the number of repeating CsgA units.

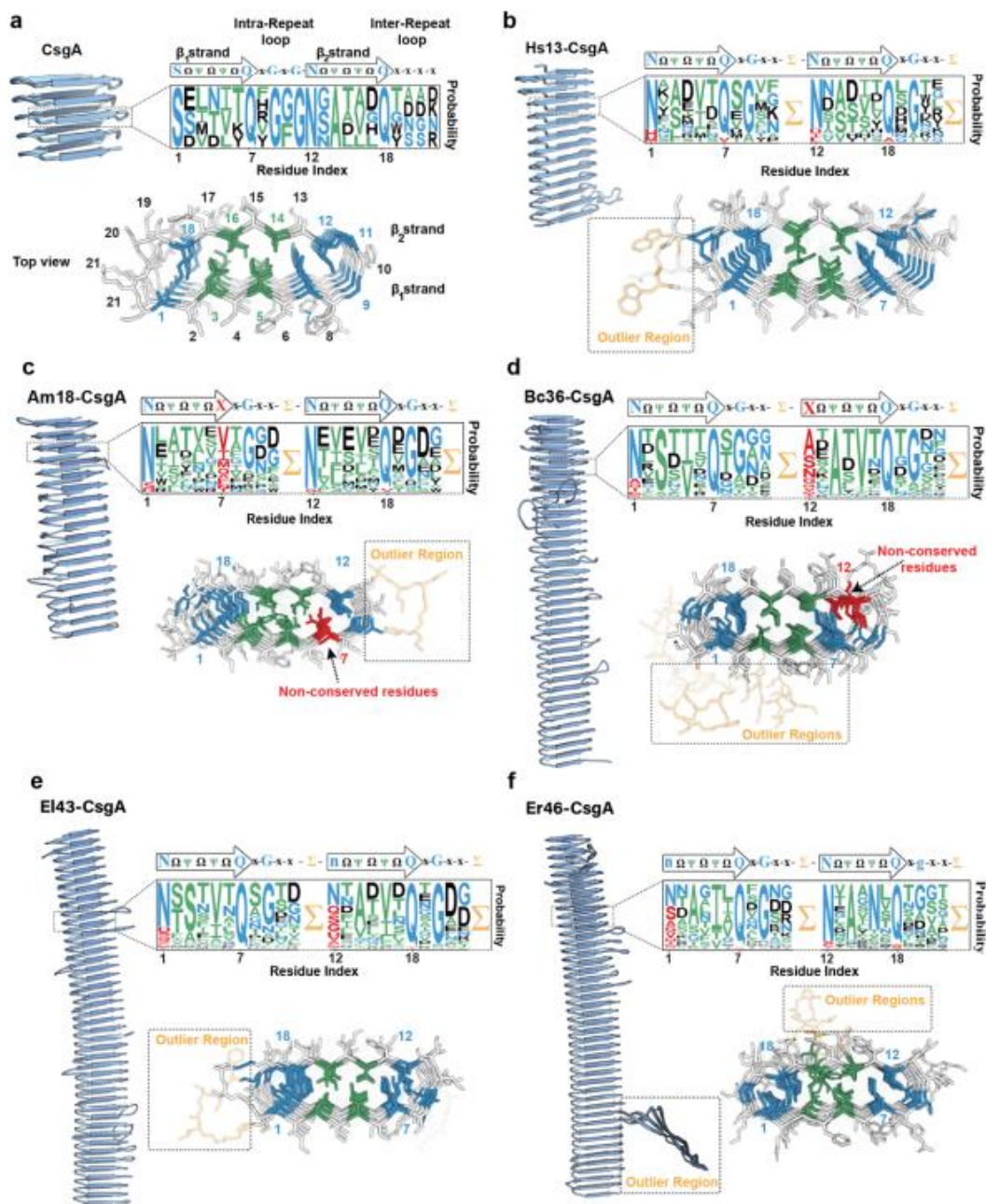


Figure 7.16. Structures of the proteins predicted by the protein mining program, AlphaFold2. These include **a**) CsgA, **b**) Hs13-CsgA, **c**) Am18-CsgA, **d**) Bc36-CsgA, **e**) El43-CsgA, and **f**) Er46-CsgA.

Table 7.1. Proteins predicted from AlphaFold2 and their predicted number of CsgA repeating units, shown visually in **Figure 7.16**.

Sample Name	Predicted Number of CsgA Repeat Units
CsgA	5
Hs13-CsgA	13
Am18-CsgA	18
Bc36-CsgA	36
El43-CsgA	43
Er46-CsgA	46

The aquaplastic form of the samples were selected for investigation as opposed to the crude products for two reasons. First, the aquaplastics were dry, thus eliminating the background scattering contributions from water, which also scatters at wide angles. Second, the aquaplastic formation process involved purification of some of the materials used during the fabrication procedure, which increased our confidence in the data being observed reflecting the true morphology of the fibers.

A representative 2D WAXS image of the aquaplastic is shown in **Figure 7.17**. The profile reveals two isotropic halos, and their isotropic behavior indicates that no orientation of the atomic planes was observed. This was expected, as the aquaplastic formation process did not involve drawing or orienting the material. The vertically offset reduced and background-subtracted WAXS profiles of the series is shown in **Figure 7.18**. Quantitative analysis of the wide-angle X-ray scattering (WAXS) data revealed the characteristic *d*-spacing (interplanar spacing) values of 0.98 nm and 0.46 nm, corresponding to inter- β -sheet and inter- β -strand distances, respectively. This is again consistent with that of CsgA, indicating the cross- β architecture of CsgA homologs (**Figure 7.14**).³⁰⁻³¹

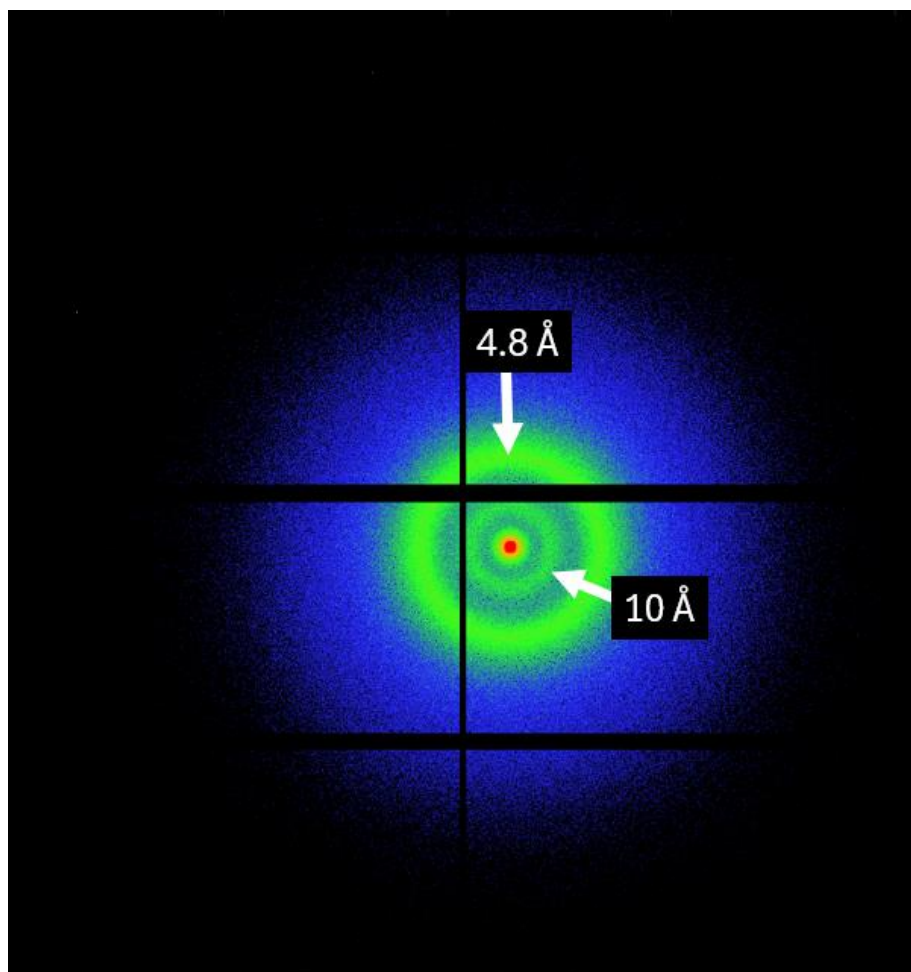


Figure 7.17. Representative 2D WAXS image from the aquaplastics. The isotropic scattering profile indicates that the physical origins of the scattering profile are randomly oriented in all directions.

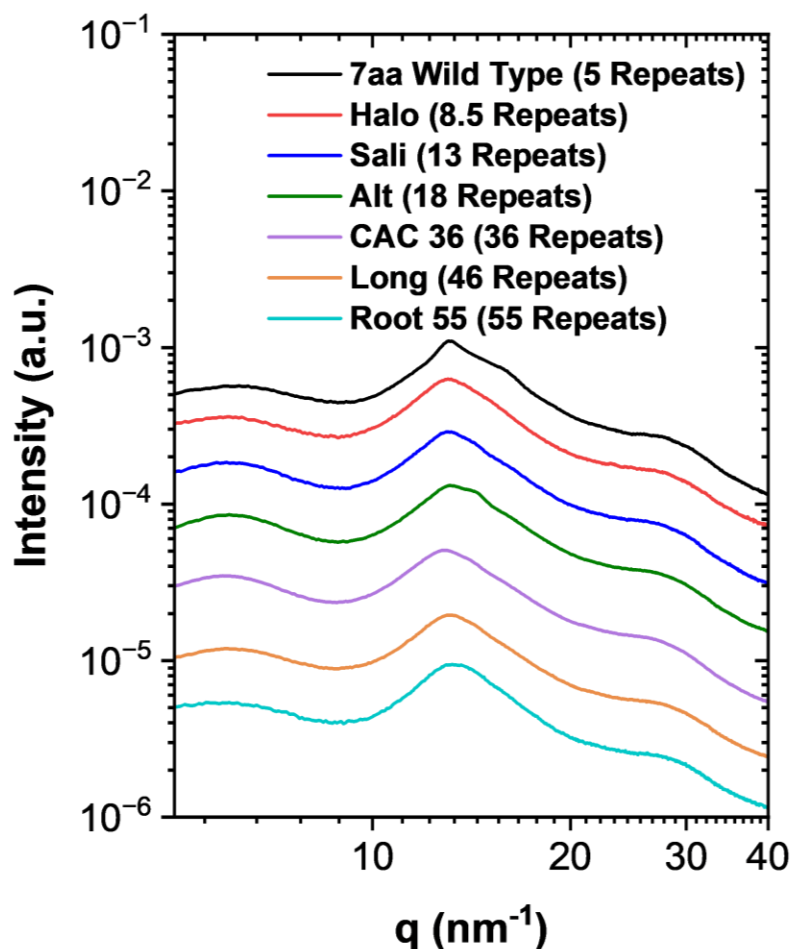


Figure 7.18. Background subtracted WAXS profiles of the aquaplastics in this study. The profiles are vertically offset for visualization purposes.

In addition to WAXS experiments, SAXS experiments were also performed. The full merged SAXS/MAXS/WAXS profiles of the aquaplastics are shown in **Figure 7.19**. Interestingly, an additional feature appears in all of the aquaplastics at low q in the vicinity of $q = 1 \text{ nm}^{-1}$. Using Bragg's law, this feature corresponds to roughly 6 nm, though the peak position shifts between the different samples. While most of the studies utilizing X-ray techniques of protein involve collecting wide-angle data, there are some studies that report scattering features at a similar q range. Tursi and coworkers reported a SAXS feature with a peak position of 1.5 nm^{-1} ,³² and attributed this feature to “an ordered columnar array”

associated with an inter-DNA spacing in curli fiber-DNA assemblies. Therefore, this feature, being present in each aquaplastic in our system may be due to the long-range ordering of the fibers within the aquaplastic. Further studies should be performed to better understand the origins of this scattering feature and the differences between the different aquaplastics. One study that would yield profound insights into this feature could involve studying the effects of processing conditions of the gel/aquaplastic on the peak position and breadth. The longer-range organization of these fibers leading to this feature would likely be highly sensitive to processing conditions. Additionally, experiments on the pure fibers or solutions, prior to forming aquaplastics, would yield fascinating insights; if the SAXS feature is absent, then the feature's assignment to the organization of fibers within the aquaplastic would be further supported. Last, an impactful finding from this study is that very small solid samples ($\sim 2 \times 2$ mm) can be characterized via lab-scale X-ray scattering experiments through the use of double-sided tape and careful sample positioning. The ability to fully capture the scattering of these samples over a broad angular range will allow for new discoveries of materials that have previously been undercharacterized due to insufficient yields.

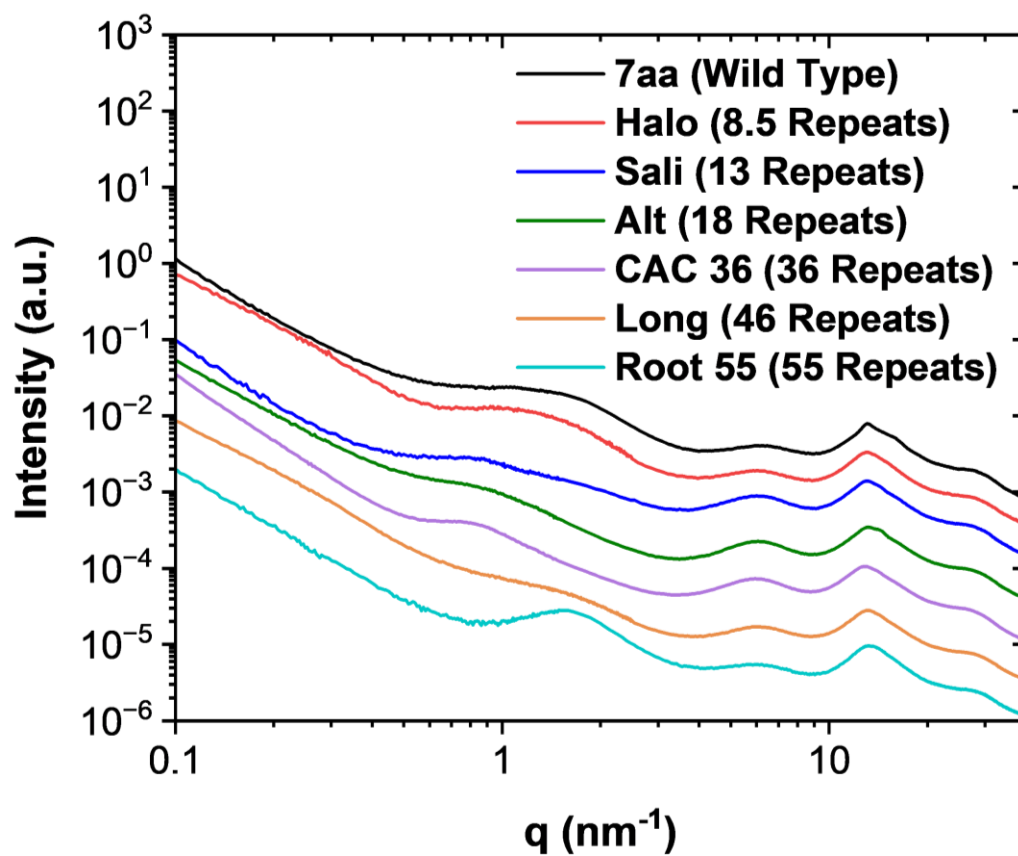


Figure 7.19. Merged SAXS/MAXS/WAXS profiles of the aquaplastics.

7.3 1, 4-cineole: a bio-derived solvent for highly stable graphene nanoplatelet suspensions and well-dispersed UHMWPE nanocomposite fibers³³

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Advanced Composites and Hybrid Materials **2024**, 7 (5), 160.

Background

This work focuses on the preparation and characterization semicrystalline, ultra-high molecular weight polyethylene (UHMWPE) fibers imbued with graphene nanoplatelets (GnP) with 1,4-cineole as a renewable solvent.³³ Dispersions of GnP in 1,4-cineole were prepared through ultrasonication and shear mixing, and the dispersions were subsequently combined with UHMWPE. The fibers were prepared by spinning the UHMWPE/1,4-cineole/GnP dispersion using a custom gel spinning extruder, and the draw ratio of the fibers was fixed at 5:1. The effects of GnP concentration in wt.% was studied on the mechanical and morphological properties of the fibers.

Experimental

Samples were prepared for SAXS experiments by threading a bundle of fibers through a 1.0 mm outer diameter quartz capillary. A drawing of the samples on the stage is shown in **Figure 7.20**. Small-angle X-ray scattering (SAXS) experiments on a bundle of fibers were performed using a Xenocs Xeuss 3.0 SAXS/WAXS equipped with a GeniX 3D Cu HFVLF microfocus X-ray source utilizing Cu K α radiation ($\lambda = 0.154$ nm). The sample-to-detector distance was 900 mm, and the q -range was calibrated using a silver behenate standard. Due to the small sample width, a high-resolution beam size was used (0.4 mm x 0.4 mm). Two-dimensional scattering patterns were obtained using a Dectris EIGER 4M

detector with an exposure time of 2 hours. Data reduction was performed using XSACT software provided by Xenocs. Herman's orientation parameter was calculated using the Irena software package.³⁴⁻³⁵

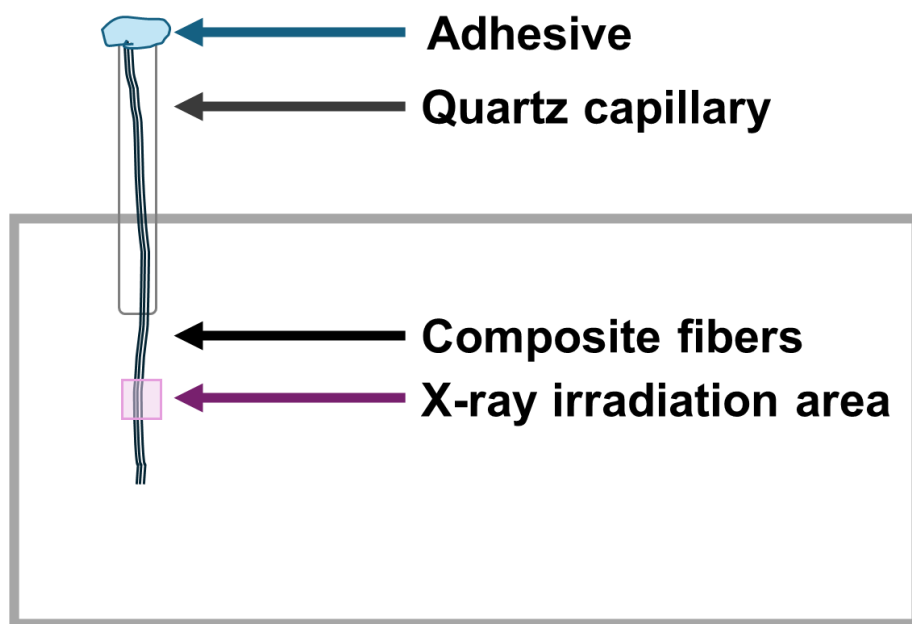


Figure 7.20. Drawing of the sample geometry for SAXS analysis. Fibers were adhered to a quartz capillary to keep them from splaying, and the bottom of the quartz capillary was broken to yield the fibers without a quartz background.

Results and Discussion

The crystalline phases are organized into nanoscale and mesoscale structures that can be probed via WAXS and SAXS. During the gel spinning of UHMWPE, lamellar crystals are formed and oriented loosely towards the fiber axis during crystallization upon gel spinning.³⁶⁻³⁷ Heated drawing of the fibers highly orients these crystals along the fiber axis and the lamellar crystals are converted into extended chain crystals with increasing draw ratio.³⁸⁻³⁹ Ultimately, the crystallites are completely extended into fibrillar crystals, but the intermediate composition is referred to as “shish-kebab”, owing to combination of

extended crystals (shishes) skewering regions of folded-chain crystals (kebabs). This shish-kebab structure is identifiable by the presence of a meridional streak and equatorial lobes in the 2D SAXS patterns, wherein the meridional streak is associated with the extended chain shish crystals and the equatorial lobes are associated with the lamellar kebab crystals.⁴⁰ With and without GnPs, the sample fibers exhibited these general scattering features, shown in **Figure 7.21**, which is consistent with UHMWPE fibers drawn to a similar degree.³⁹

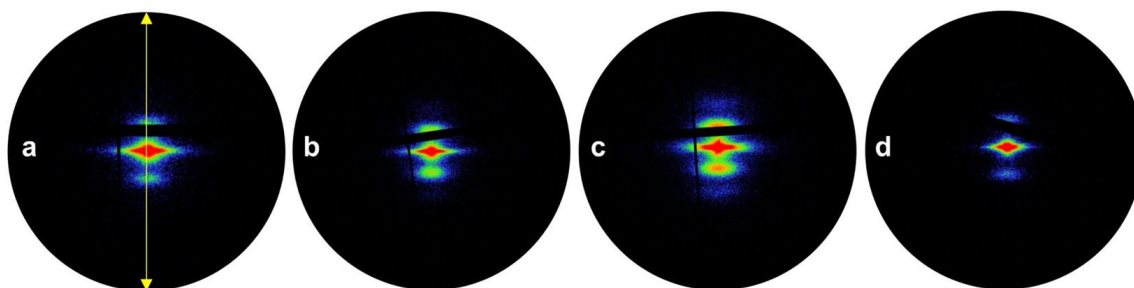


Figure 7.21. 2D SAXS patterns of the UHMWPE fibers containing graphene nanoplatelets (GnP) at **a)** 0 wt.%, **b)** 0.01 wt.% **c)** 0.1 wt.%, and **d)** 1 wt.%. The 2D scattering patterns are rotated to align the fiber axis vertically, along the axis indicated by the yellow arrows.

The 2D SAXS patterns can be used to quantitatively measure the average axial dimensions of these crystallites based on the characteristics of the equatorial streak and meridional lobes, which arises from the electron density differences between the lamellar crystallites and other polyethylene phases. The average center-to-center spacing of adjacent lamellar crystals, referred to as the long period, can be measured via Bragg's law of the peak position of the lamellar lobe from the 1D intensity curve along the fiber axis direction. The thickness of this lamellar crystal can be assessed by a 1D correlation function of the electron density distribution,⁴¹ which can be used to identify the long and short

periodicity of the lamellar structure in the fibers. The lamellar crystals are composed of orthorhombic and monoclinic crystallites, so the short period is taken to be the lamellar thickness. The difference between the long period and short period is composed of the intercalated crystallites, tie molecules, and the amorphous phase. The dimensions for the neat and nanocomposite samples are shown in **Figure 7.22**.

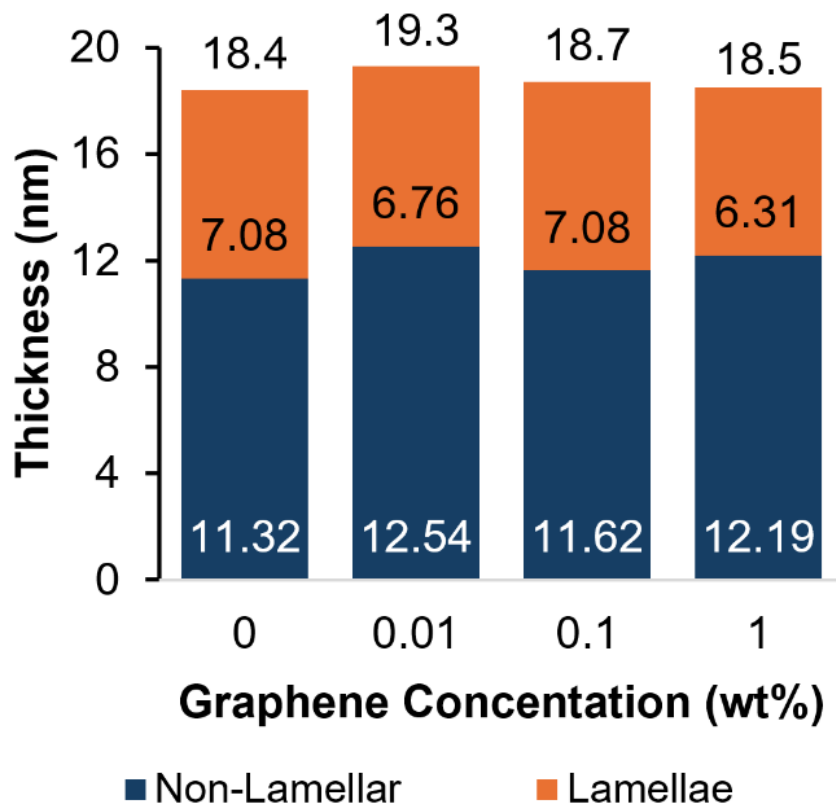


Figure 7.22. Crystalline lamellar thickness and non-lamellar component thickness of each fiber.

The long period of the neat UHMWPE fibers spun using 1,4-cineole are similar to that of fibers using conventional spin solvents and drawn to a similar degree.³⁹⁻⁴⁰ From 0 wt% to 0.1 wt% the short period is in keeping with the linear density of the fibers, but the short period shrinks at 1 wt% GnP concentration. It is expected that the lamellar thickness and long period would increase with increasing draw down at a low total draw ratio because

the amorphous molecules extend and strain-crystallize into the lamellar structure, which also extends.³⁹ However, the high concentration of GnPs prevents this anticipated extension resulting in a smaller than expected long and short periods.

The average orientation of the crystallites is approximated by calculating Herman's orientation factor (HOF) of the major orthorhombic reflection (110), and the values are shown in **Table 7.2**. The neat UHMWPE fibers exhibited significant orientation after drawing with a HOF of 0.83, which is consistent with other fibers spun under similar conditions albeit slightly lower.⁴²⁻⁴³ The incorporation of GnPs negatively affected crystallite orientation. HOF decreased with increasing GnP concentration up to 0.1 wt% where it plateaued to 1 wt%, as shown in **Table 7.2**. Future work in this research area could involve studying the fibers under tension during the scattering experiments using the Linkam tensile stage (**Figure 7.23**).

Table 7.2. Herman's orientation factor for the fibers determined from the 2D SAXS patterns.

Sample	Herman's Orientational Factor (HOF)
0 wt.% GnP UHMWPE	0.83
0.01 wt.% GnP UHMWPE	0.74
0.1 wt.% GnP UHMWPE	0.68
1 wt.% GnP UHMWPE	0.69



Figure 7.23. Photograph of the Linkam tensile stage.

7.4 Vat photopolymerization of olefinic elastomers from sulfonated ethylene-propylene-diene monomer (EPDM) latexes⁴⁴

Jianheng Wen, Garvit Nayyar, Erin R. Crater, Ren H. Bean, Rui Zhang, Robert B. Moore,

Timothy E. Long

Additive Manufacturing **2024**, 91, 104359.

Background

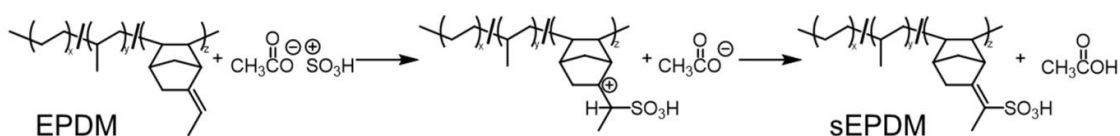


Figure 7.24. Reaction conditions for the sulfonation of EPDM with acetyl sulfate. ⁴⁴

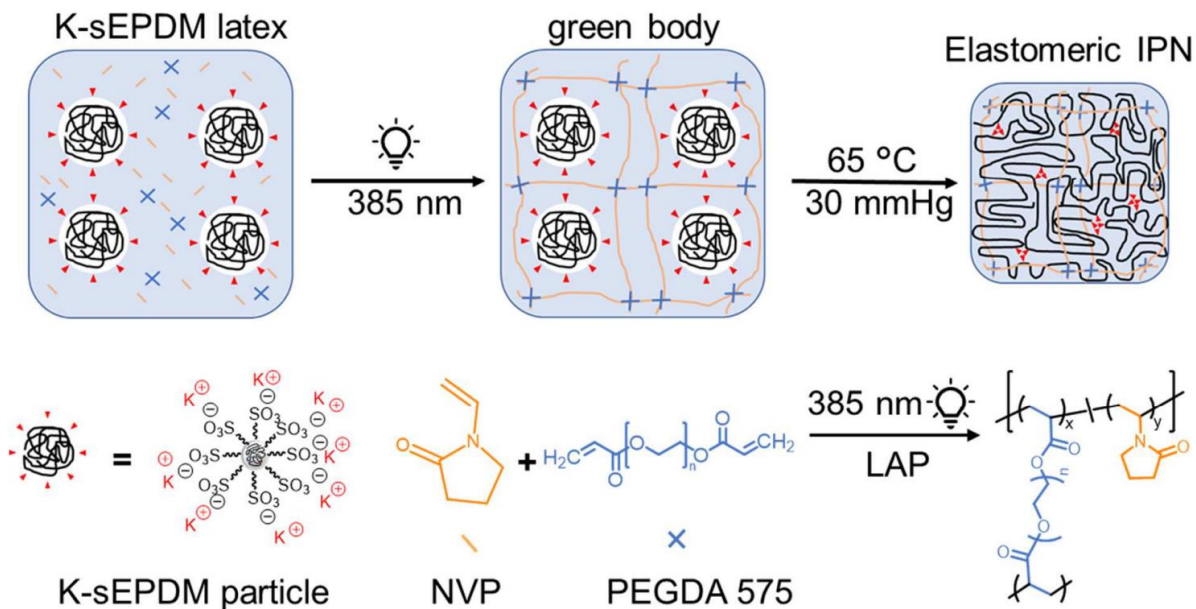


Figure 7.25. Schematic showing the chemical composition of photocurable latexes with water-soluble scaffold precursors and UV curing scheme with subsequent post-processing removing water. ⁴⁴

Experimental

Small, and mid-angle X-ray scattering (SAXS/MAXS) experiments were performed on a Xenocs Xeuss 3.0 SAXS/WAXS equipped with a GeniX 3D Cu HFVLF microfocus x-ray source utilizing Cu K α radiation ($\lambda = 0.154$ nm). The sample-to-detector distance was 370 mm for MAXS and 900 mm for SAXS, and the q -range was calibrated using a silver behenate standard. Two-dimensional scattering patterns were obtained using a Dectris EIGER 4M detector with various exposure times (SAXS: 2 hours, MAXS: 1 hour). Data reduction was performed using XSACT software provided by Xenocs.

Results and Discussion

Small-angle X-ray scattering (SAXS) experiments were conducted to confirm the presence of a phase separated morphology within the IPN elastomer. SAXS profiles of the pure K-sEPDM, the pure scaffold, and the printed and post-processed K-sEPDM latexes with varying amounts of scaffold are shown in **Figure 7.26**. The SAXS profile of the NVP scaffold is essentially featureless, which suggested an amorphous polymer with a homogeneous morphology, as expected. The SAXS profile of pure K-sEPDM revealed an intense scattering feature centered at around $q = 1.4 \text{ nm}^{-1}$ indicating the presence of a phase separated morphology within the ion-containing rubber. This characteristic scattering peak, which is often described as the “ionomer peak,” arises from the spatial correlations of ionic aggregates in a polymer matrix, as discussed in Chapter 3.^{21, 45} As shown in **Figure 7.26**, the ionomer peak remains in all printed K-sEPDM samples with varying scaffold content, showing that physical crosslinks from metal sulfonate associations are formed in the final IPN structure. In the K-sEPDM latexes, the position of this feature shifts to slightly lower q , indicating that the average center-to-center distance between ionic aggregates increased

in the IPN elastomers. This subtle shifting suggests the formation of an interpenetrating network, as diffusion and chain entanglements presumably increase the separation of the ionic aggregates. At low q ($q < 1 \text{ nm}^{-1}$), the significant increase in scattering intensity suggests long-range heterogeneity in the IPN, consistent with dimensional heterogeneity of the scaffold formed around the ca. 100 nm K-sEPDM latex particles in the photocured green body. Future work could study the size distributions of the latex particles throughout the manufacturing process through USAXS techniques.

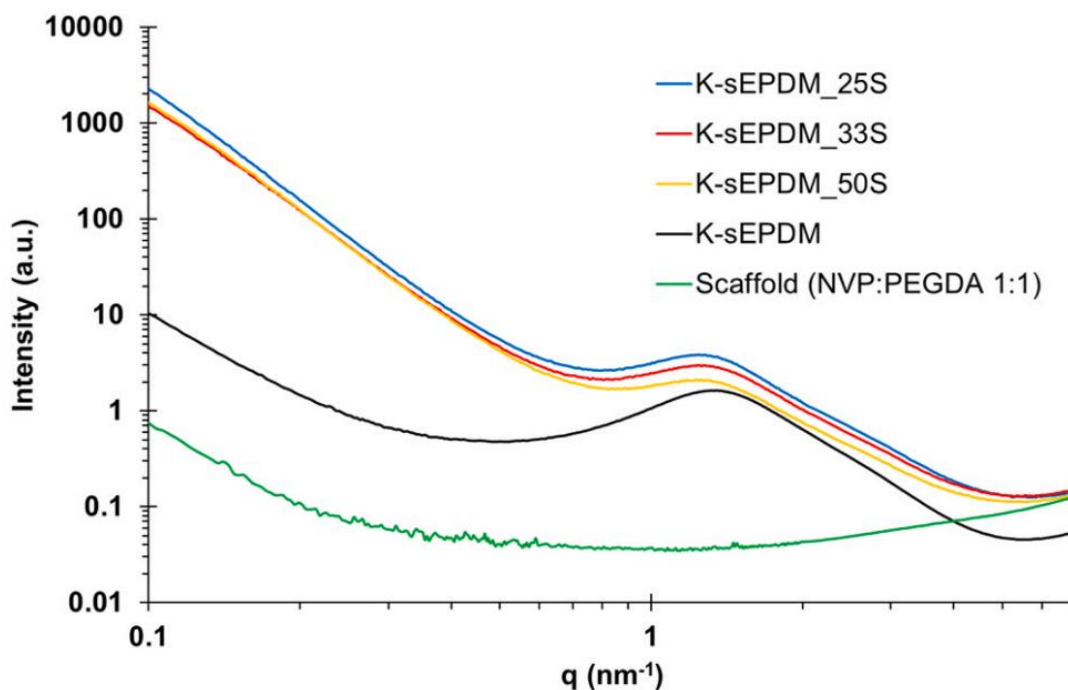


Figure 7.26. Merged SAXS/MAXS profiles of the samples from this study.⁴⁴

7.5 Polyphenylene sulfide for high-rate composite manufacturing: Impacts of processing parameters on chain architecture, rheology, and crystallinity⁴⁶

Lina N. Ghanbari, Erin R. Crater, Nicholas R. Enos, Olivia D. McNair, Robert B. Moore, Jeffrey S. Wiggins

Polymer Degradation and Stability **2023**, 218, 110580.

Background

In this study, the morphology poly(phenylene sulfide) (PPS) (**Figure 7.27**) was studied after processing it for various temperatures and times near and above the melting point. Structure-property relationships were drawn that allow for an understanding of how the thermal processing history of PPS materials influences the semicrystalline morphology and the physical properties of thermally treated films. Three processing temperatures were studied: 300 °C, 320 °C, or 340 °C, and 3 processing times were studied: 0, 30 and 60 minutes. SAXS/WAXS experiments were conducted to better understand how the thermal treatment influenced the degree of crystallinity and the lamellar thickness of PPS crystallites within the processed films.

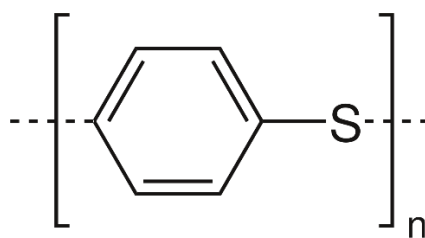


Figure 7.27. Chemical structure poly(phenylene sulfide) (PPS).

Experimental

Samples for scattering analysis were prepared *via* DSC in Tzero aluminum DSC pans. Samples were prepared identically to DSC analysis, where thermal history was first erased, then the samples were subjected to the process temperature (300 °C, 320 °C, or 340

°C) for 0, 30 or 60 minutes, and finally cooled to 50 °C at 10 °C/min. The samples were removed from the DSC pans using a thin razor blade for scattering analysis at room temperature. Small, mid, and wide-angle X-ray scattering (SAXS/MAXS/WAXS) experiments were performed on a Xenocs Xeuss 3.0 SAXS/WAXS equipped with a GeniX 3D Cu HFVLF microfocus X-ray source utilizing Cu K α radiation ($\lambda = 0.154$ nm). The sample-to-detector distance was 43 mm for WAXS, 370 mm for MAXS, and 900 mm for SAXS, and the q-range was calibrated using lanthanum hexaboride and silver behenate standards. Two-dimensional scattering patterns were obtained using a Dectris EIGER 4M detector with various exposure times (SAXS: 3 hours, MAXS: 2 hours, WAXS: 1 hour). Data reduction via azimuthal integration was performed using XSACT software provided by Xenocs, and the 1D profiles were corrected for sample thickness, background, transmission, and absolute intensity. The SAXS and MAXS profiles were merged into one dataset (hereafter referred to as “SAXS” profiles) and plotted on an absolute intensity scale vs. the scattering vector, q. The WAXS profiles are plotted separately as relative intensity vs. the scattering angle 2θ . The scattering profiles were analyzed via the 1D correlation function in SasView.

Results and Discussion

Given the profound effects of melt processing on the physical properties of PPS as revealed by rheology and DSC, the semicrystalline morphologies were expected to also show a strong dependence on the processing history. To investigate the effects of melt processing on the semicrystalline morphologies of PPS, SAXS and WAXS experiments were conducted on recrystallized samples previously processed at 300 °C, 320 °C, and 340°C in air for 0, 30, and 60 minutes. The 2D scattering SAXS, MAXS, and WAXS

profiles are shown in **Figure 7.28-7.30**. All profiles are isotropic indicating a random orientation of PPS crystallites in the films, as expected.

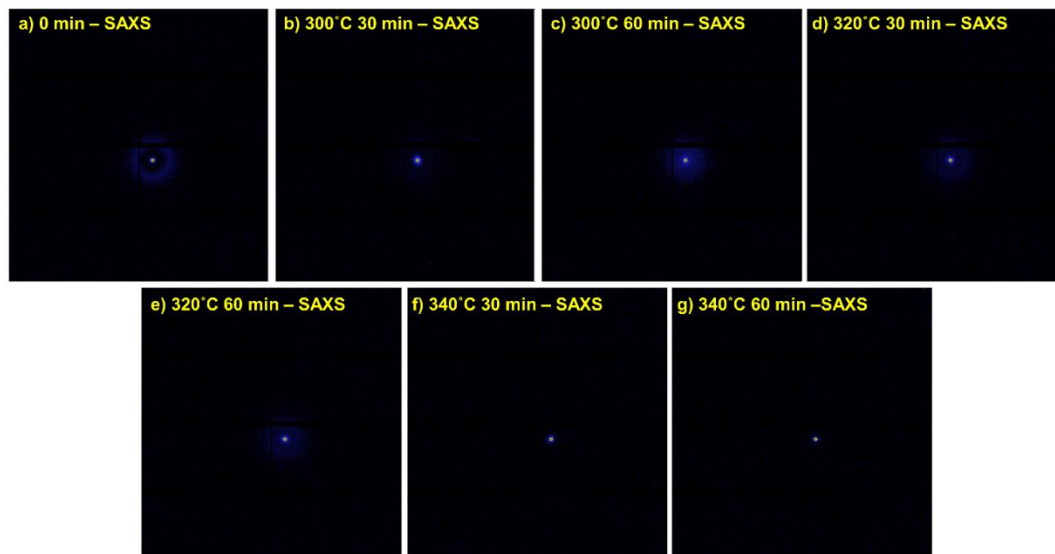


Figure 7.28. 2-D SAXS images of a) neat PPS, PPS held at 300 °C for b) 30 and b) 60 minutes, PPS held at 320 °C for d) 30 and e) 60 minutes, and PPS held at 340 °C for f) 30 and g) 60 minutes.

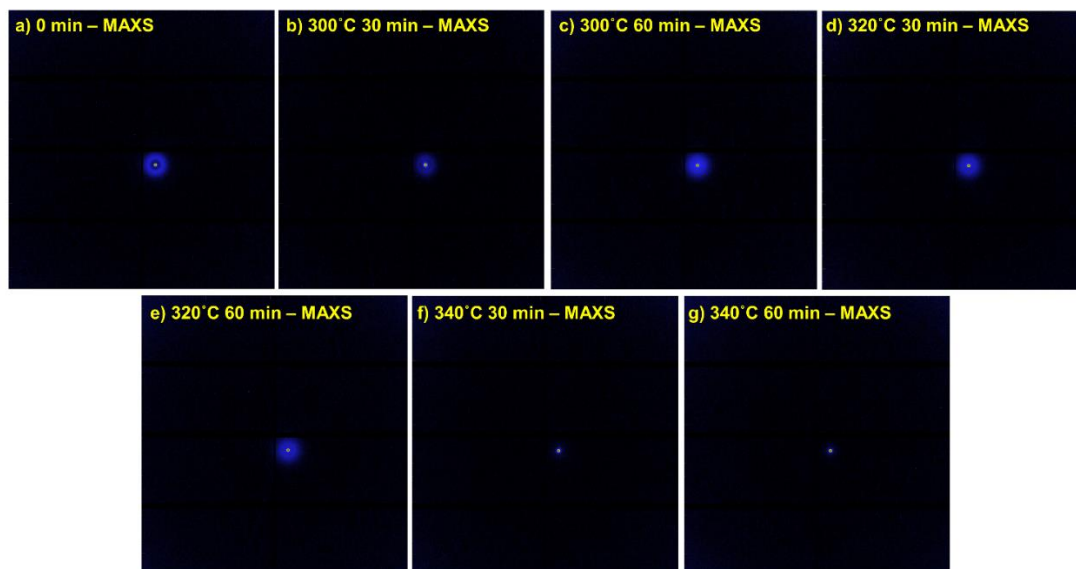


Figure 7.29. 2-D MAXS images of a) neat PPS, PPS held at 300 °C for b) 30 and b) 60 minutes, PPS held at 320 °C for d) 30 and e) 60 minutes, and PPS held at 340 °C for f) 30 and g) 60 minutes.

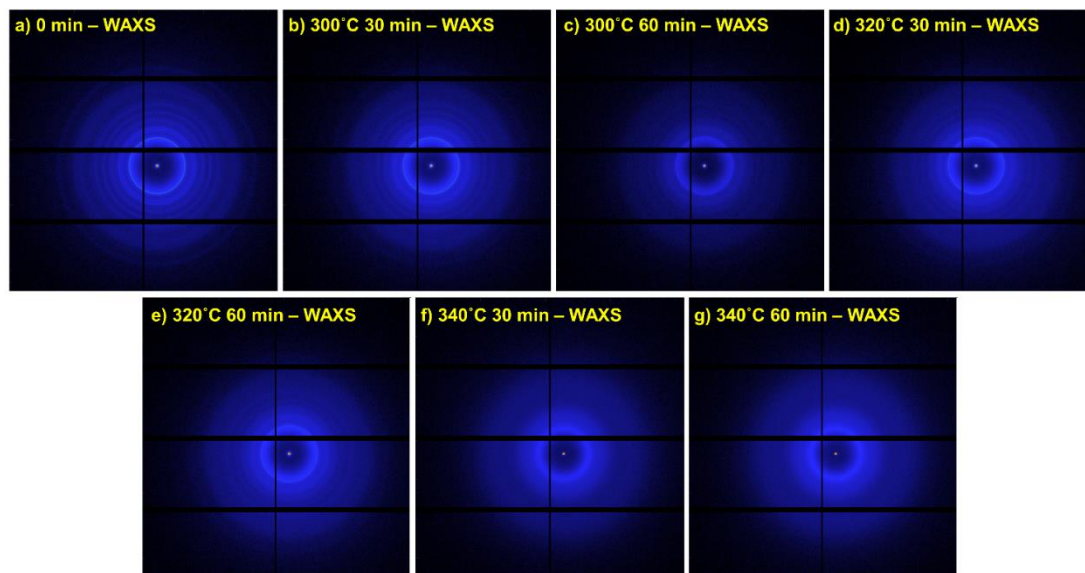


Figure 7.30. 2-D WAXS images of a) neat PPS, PPS held at 300 °C for b) 30 and b) 60 minutes, PPS held at 320 °C for d) 30 and e) 60 minutes, and PPS held at 340 °C for f) 30 and g) 60 minutes.

The 1D WAXS profiles are shown in **Figure 7.31 a-c**. The diffraction pattern of neat PPS reveals characteristic reflections of the orthorhombic unit cell reported for semicrystalline PPS.⁴⁷⁻⁴⁸ Moreover, the same crystalline reflections are observed in the melt processed samples, revealing that the unit cell structure is preserved upon recrystallizing samples from the processing temperature. Retention of the unit cell structure has also been observed in recrystallized samples from melt processed PEKK. Therefore, it can be concluded that the long chain branches and crosslinks formed during melt processing do not alter the unit cell structure within PPS crystallites. Despite the retention of the unit cell structure, the overall intensity of the crystalline reflections dramatically

decreases with increasing processing temperature. For example, the reflection centered at $2\theta = 20.5^\circ$ corresponding to the (200) and (111) family of planes decreases in prominence as the processing time is increased, indicating a reduction in crystallinity (**Figure 7.31a**). For the samples processed to 340°C , the crystalline reflections are virtually absent at 30 min and 60 min (**Figure 7.31c**), further showing that the crosslinks and branching formed at elevated processing temperatures significantly reduces the polymer's crystallizability. The quantitative degree of crystallinity determined from analysis on this WAXS data supports the trend observed from the DSC measurements that crystallinity decreases with increasing processing temperature and decreases more rapidly at higher processing temperatures (**Figure 7.32**).⁴⁶

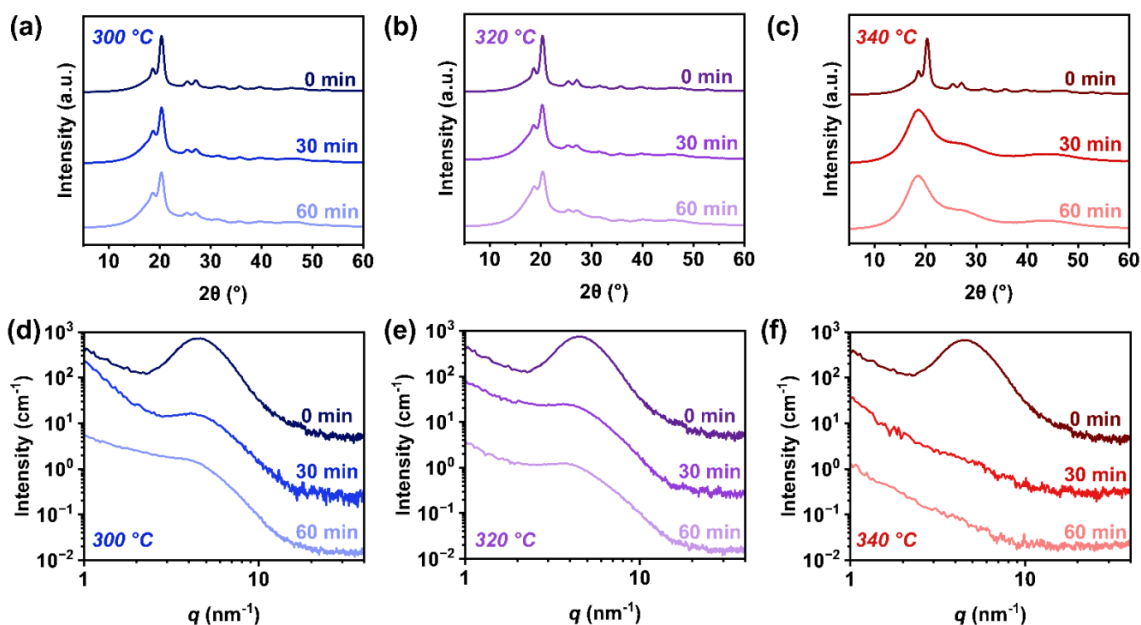


Figure 7.31. 1D SAXS profiles for PPS processed to a) 300°C , b) 320°C , and c) 340°C for the specified amount of time, and 1D WAXS profiles for PPS processed to a) 300°C , b) 320°C , and c) 340°C for the specified amount of time. All samples were recrystallized upon cooling from the specified temperature. SAXS intensities have been vertically offset for visualization purposes.

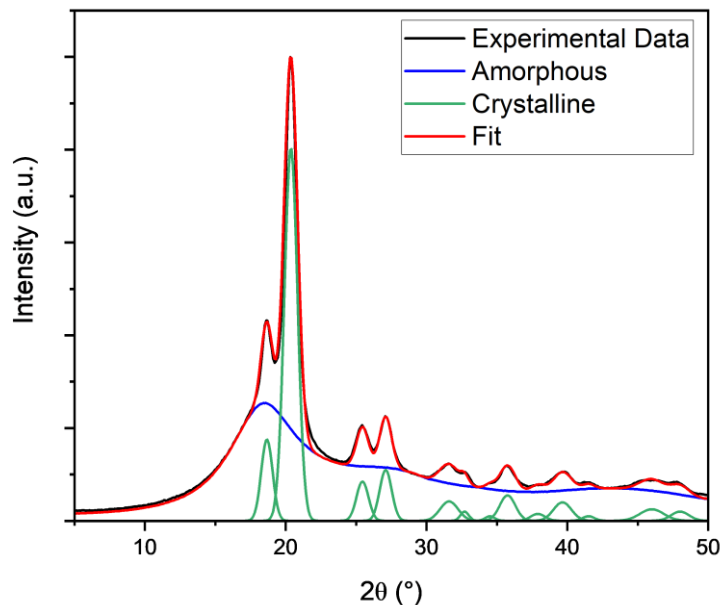


Figure 7.32. Representative data showing the method used to determine the degree of crystallinity from the WAXS data.

The 1D SAXS profiles are shown in **Figure 7.31 d-f**. The scattering pattern for neat PPS (listed as 0 min in all profiles), reveals a strong peak centered at $q = 4.5 \text{ nm}^{-1}$, corresponding to the interlamellar long period. With increasing processing time, this feature dramatically broadens into a knee-like feature due to the loss of long-range spatial order in the PPS crystallites. SAXS patterns of samples processed at 340°C for 30 and 60 minutes (**Figure 7.31f**) are featureless, consistent with a mostly amorphous morphology.

The 1D correlation function analysis was used to determine the lamellar thickness of neat PPS as 3.2 nm (**Figure 7.33a**) which is consistent with previous reports of melt crystallized PPS.⁴⁹ From the same analysis, PPS processed for 30 minutes at 300°C resulted in a smaller lamellar thickness of 2.6 nm (**Figure 7.33b**). Consistent with the DSC analysis that showed lower melting temperatures of crystallites in melt processed PPS, this

scattering analysis provides additional evidence that branching and crosslinking results in thinner crystals.⁵⁰ Due to the lack of crystalline order in the other melt processed samples giving rise to the knee-like SAXs pattern, analysis from the 1D correlation function was not applicable. Overall, WAXS and SAXS supports that melt processing reduces the overall crystallinity and results in thinner crystallites compared to neat PPS.

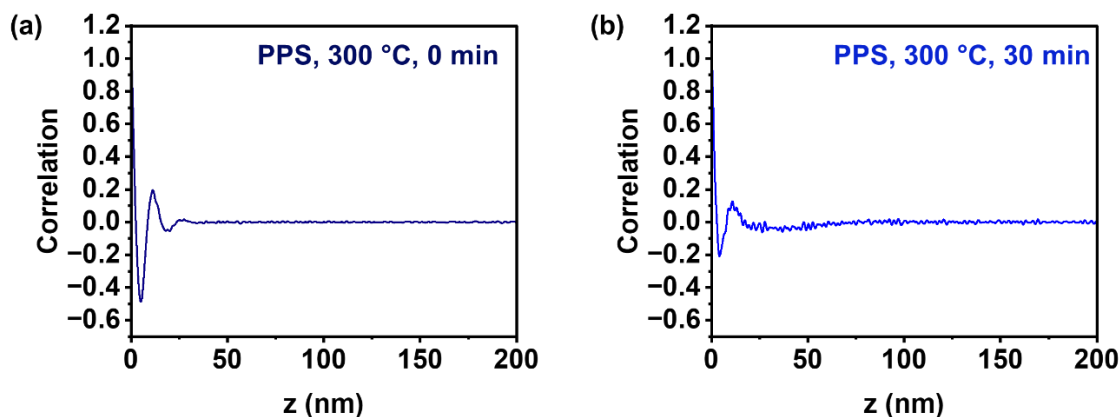


Figure 7.33. 1D autocorrelation function fitted curves for PPS held at 300 °C for a) 0 min, and b) 30 min.

7.6 Broadband achromatic quarter-waveplate using 2D hybrid copper halide single crystals⁵¹

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Journal of the American Chemical Society **2023**, 145 (32), 18007-18014.

Experimental

Grazing-incidence mid-angle X-ray scattering (GI-MAXS) experiments were performed on a Xenocs Xeuss 3.0 SAXS/WAXS equipped with a GeniX 3D Cu HFVLF microfocus X-ray source utilizing Cu K α radiation ($\lambda = 0.154$ nm). The sample-to-detector distance was 370 mm for MAXS, calibrated using a silver behenate standard, and the incident angle was 0.2°. Two-dimensional scattering patterns were obtained using a Dectris EIGER 4M detector and processed using the XSACT software package.

Results and Discussion

To investigate the interlayer packing of the hybrid copper halide (HCH) crystals (shown in **Figure 7.34**) with different thicknesses, we performed GI-WAXS experiments on crystals with thicknesses ranging from 3 μm to 164 μm , which are shown in **Figure 7.35** and monitored the diffraction peak of the (0 0 2) plane and the (0 0 4) plane. The diffraction peaks of the thinnest HCH crystal with a thickness of 3 μm (**Figure 7.35e**) are more elaborate, sharper, and showed less out-of-plane order than the thickest crystal (**Figure 7.35g**), which showed significant streaking of the (0 0 2) reflection along q_{xy} .

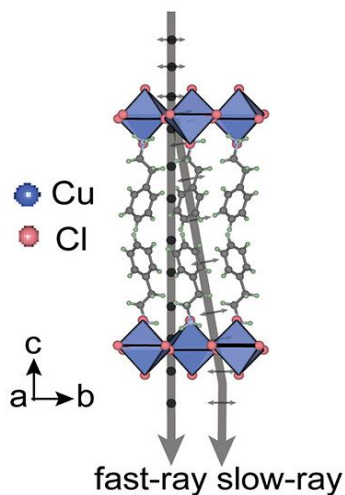


Figure 7.34. Crystal structure of an HCH crystal with a schematic illustration of birefringence with gray arrows.

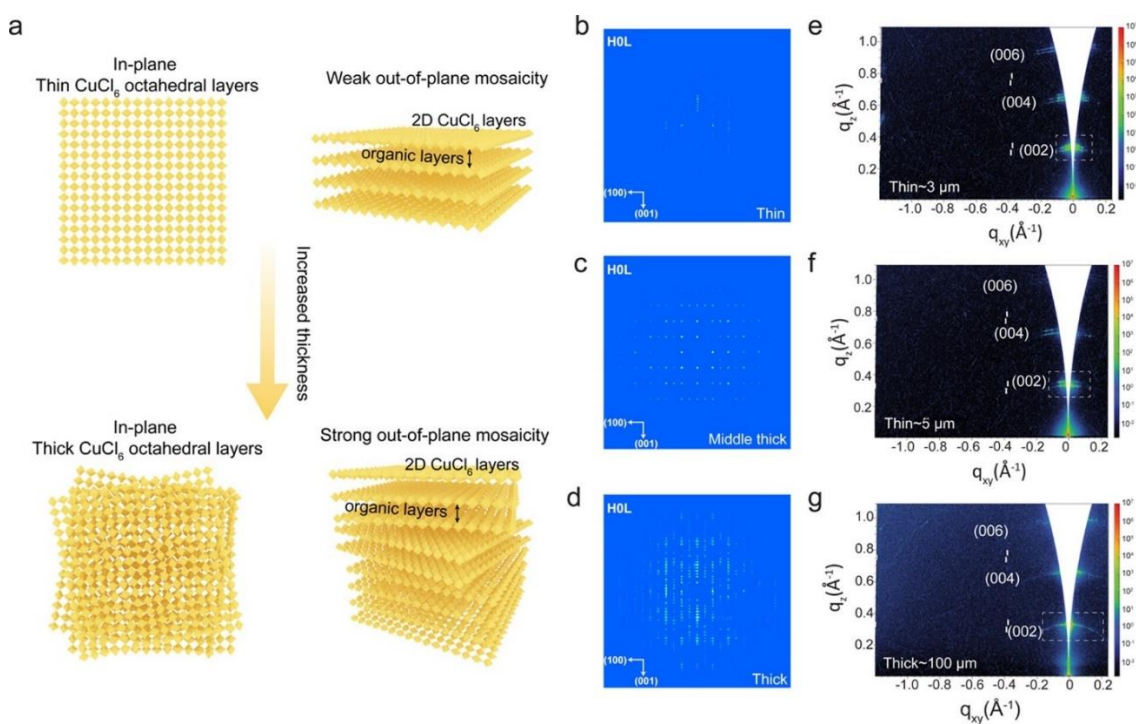


Figure 7.35. a) Schematic diagram that shows the formation of out-of-plane mosaicity between thin and thick single crystals. SCXRD unwrapped images generated from the (100) and (001) crystallographic axes of (b) thin HCH crystal, (c) middle-thick HCH crystal, and (d) thick HCH crystal. GI-WAXS measurements for the HCH crystals with varied thicknesses (e), 3 μm , (f) 5 μm , and (g) 164 μm .

Future experiments could explore the temperature-dependent scattering behavior of these and other HCH crystals using the Linkam-GI stage combination, shown in **Figure 7.36**, which would allow the temperature-dependent morphology of the crystals to be correlated with their morphologies at specific temperatures.



Figure 7.36. Photograph of the Linkam temperature stage attached to the grazing incidence stage on the Xenocs Xeuss 3.0 SAXS/WAXS system at Virginia Tech.

7.7 Effect of Polymer-Grafted Reduced Graphene Oxide on Properties of Single-Layer Graphene Composite Thin Films

Connor S. Thompson, Zacary L. Croft, Erin R. Crater, Oscar Valenzuela, Nuwayo Eric Munyaneza, Robert B. Moore, Gabriel Zeltzer, and Guoliang Liu

Experimental

A thin layer of graphene oxide powder was packed into a 1 mm thick metal washer with Scotch® Magic™ tape windows on either side. The films were taped on the solid plate as received, with the top and bottom frame of the film taped onto the solid sample holder with double sided tape. Wide-angle X-ray scattering (WAXS) experiments were performed using a Xenocs Xeuss 3.0 SAXS/WAXS equipped with a GeniX 3D Cu HFVLF microfocus X-ray source utilizing Cu K α radiation ($\lambda = 0.154$ nm). The sample-to-detector distance was 43 mm for WAXS and the q -range was calibrated using a lanthanum hexaboride standard. Two-dimensional scattering patterns were obtained using a Dectris EIGER 4M detector for 30 minutes. Data reduction was performed using XSACT software provided by Xenocs, and the 1D profiles were corrected for background and transmission. All scattering intensities are reported on an absolute intensity scale. The WAXS profiles are plotted as relative intensity vs. the scattering angle 2θ in degrees.

Results and Discussion

Wide-angle x-ray scattering (WAXS) experiments were performed to investigate the morphology of the randomly mixed and grafted rGO/PEI composites. The WAXS patterns of pure PEI and rGO controls are shown in **Figure 7.37**. As shown in **Figure 7.37**, poly(etherimide) (PEI) displays a broad, amorphous halo that is indicative of an amorphous morphology. This result is consistent with the literature as it is well known that PEI does not crystallize under these conditions. Next, the morphology of the as-received rGO

powder was characterized. As shown in **Figure 7.38**, rGO displays strong diffraction peaks centered at around $2\theta \approx 25^\circ$ and 42° . The diffraction peak at $25^\circ 2\theta$ is well-documented for rGO, and has been assigned to the (002) family of planes representing the interlayer spacing of rGO platelets.⁵⁴⁻⁵⁵ The diffraction peak centered around $42^\circ 2\theta$ has also been previously document and been assigned to the (100) family of planes of the hexagonal carbon structure.⁵⁶⁻⁵⁷ It is important to note that the characteristic diffraction peak of non-reduced GO at $11^\circ 2\theta$ was not observed in the diffraction pattern of the as-received powder, which confirms that the graphene oxide powder was completely in the reduced form.⁵⁴

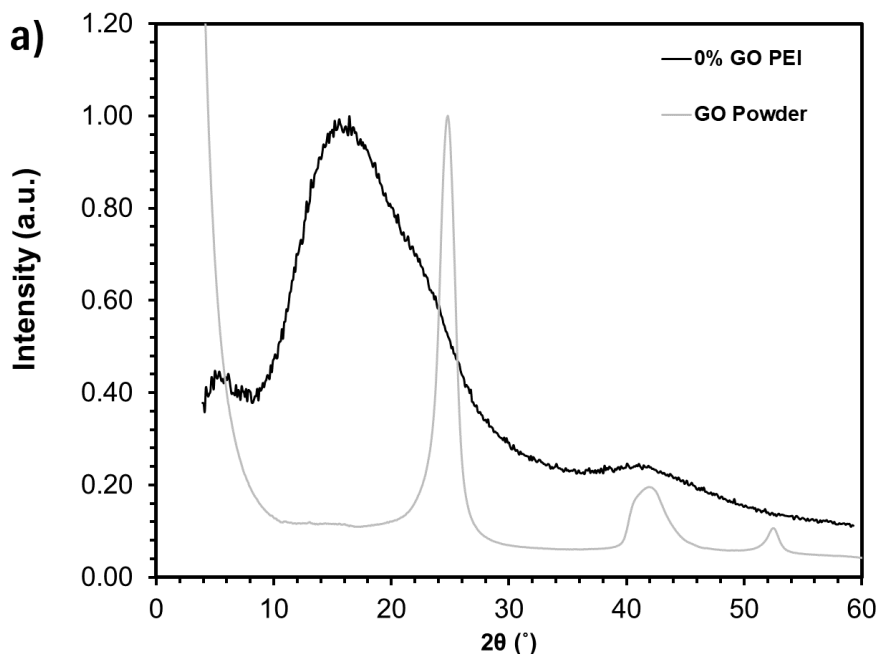


Figure 7.37. Wide-angle X-ray scattering (WAXS) patterns of the as-received rGO powder and the PEI control (0% rGO).

The WAXS patterns of the randomly mixed composites at a range of rGO concentrations are shown in **Figure 7.38a**. The characteristic diffraction peaks of rGO in the composites become obvious at relatively high concentrations (≥ 12 wt.% rGO). As

expected, the (002) and (100) reflections of rGO become increasingly more intense as the concentration of rGO in the composite is increased. A similar trend is observed in the grafted rGO/PEI composites (**Figure 7.38b**), as the diffraction peaks of rGO increase in intensity with increasing content of grafted rGO. Interestingly, at similar weight percents of rGO in PEI, the (002) diffraction peak of rGO appears to be sharper in the randomly mixed composites compared to the grafted rGO composites. This may suggest that the rGO is more ordered in the randomly mixed composites, as opposed to the grafted composites in which the covalent attachment of PEI chains may disrupt some of the stacking of the rGO platelets. Overall, these WAXS experiments show that the rGO platelets remain present in the randomly mixed and grafted composites, and their characteristic diffraction peaks increase as their concentration in PEI increases.

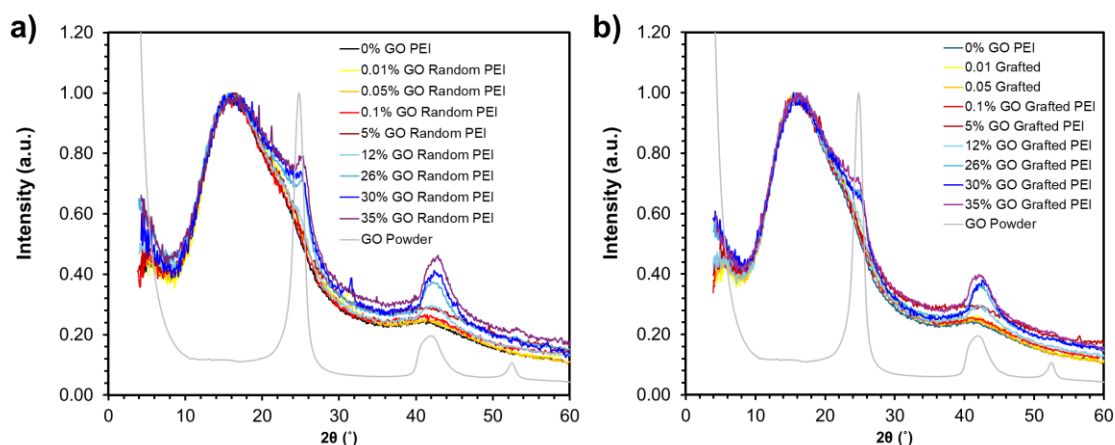


Figure 7.38. Wide-angle X-ray scattering (WAXS) patterns of **(a)** the randomly mixed rGO/PEI composites, and **(b)** the grafted rGO/PEI composites.

7.8 Using Redox-Switchable Polymerization Catalysis to Synthesize a Chemically Recyclable Thermoplastic Elastomer⁵⁸

Jiangwei Liu, Sarah E. Blosch, Anastasia S. Volokhova, Erin R. Crater, Connor F. Gallin, Robert B. Moore, John B. Matson, Jeffery A. Byers

Angewandte Chemie International Edition **2024**, 63 (6), e202317699.

Background

Experimental

Samples for small-angle X-ray scattering were prepared by dissolving the polymers (~30 mg) in 1 mL of CHCl₃ at room temperature, filtering the polymer solution through a 0.45 μ m syringe, and drop-casting onto a polyimide substrate. The solution was allowed to dry at room temperature overnight, and the films were subsequently annealed at 100°C for 2 hours, which is an ideal crystallization condition for the PLLA and PDLA end blocks.⁵⁹ The final sample thicknesses were between 0.100 – 0.150 mm.

Small, mid, and wide-angle X-ray scattering (SAXS/MAXS/WAXS) experiments were performed on a Xenocs Xeuss 3.0 SAXS/WAXS equipped with a GeniX 3D Cu HFVLF microfocus X-ray source utilizing Cu K α radiation (λ = 0.154 nm). The sample-to-detector distance was 43 mm for WAXS, 370 mm for MAXS, and 900 mm for SAXS, and the q-range was calibrated using lanthanum hexaboride and silver behenate standards. Two-dimensional scattering patterns were obtained using a Dectris EIGER 4M detector with various exposure times (SAXS: 2 hours, MAXS: 1 hours, WAXS: 0.5 hour). Data reduction via azimuthal integration was performed using XSACT software provided by Xenocs, and the 1D profiles were corrected for sample thickness, background, transmission, and absolute intensity. The SAXS, MAXS, and WAXS profiles were merged into a single dataset and plotted on an absolute intensity scale vs. the scattering vector, q .

Results and Discussion

The merged small, mid, and wide-angle X-ray scattering (SAXS/MAXS/WAXS) profiles are shown in **Figure 7.39**. In the wide-angle region ($q > 5 \text{ nm}^{-1}$), strong diffraction peaks are present in both samples, which arise from the intracrystalline reflections of the crystalline PLLA or PDLA segments.⁵⁹ In the small-angle region ($q < 1 \text{ nm}^{-1}$), a strong scattering feature centered at $q \sim 0.3 \text{ nm}^{-1}$ is present in both samples. This knee-like feature has been assigned to the intracrystalline long period of PLLA and PDLA, related to the averaged distance between PLLA or PDLA crystallites.⁶⁰ It appears that the D stereochemistry of the end blocks resulted in greater degrees of crystallinity and greater crystalline order as compared to the L stereochemistry; however, it is unclear whether this is due to the difference in stereochemistry or to minor discrepancies in block lengths or dispersities between the samples.

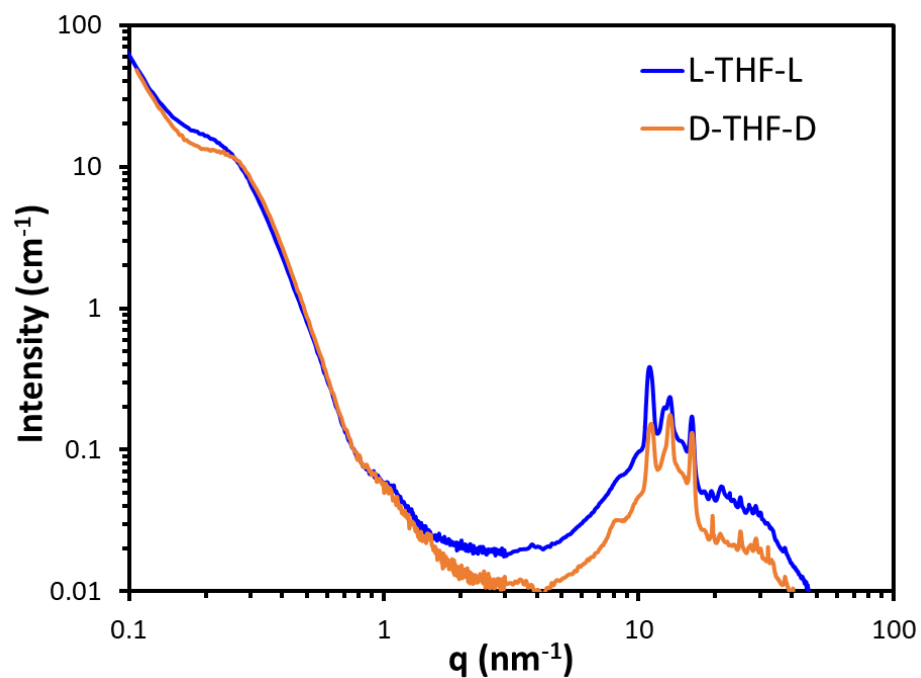


Figure 7.39. Merged SAXS/MAXS/WAXS profiles of PLLA-PTHF-PLLA and PDLA-PTHF-PDLA triblock copolymer films. All films were annealed at 100°C for 2 hours prior to measurements, and the data was collected at room temperature.

7.9 Cellulose-Based Sustainable Nanocomposites with Tunable Opacity

Justin Anderson, Mica Pitcher, Erin C. Jackson, Tyler Sequine, Yimin Yao, Robert B. Moore, Michael J. Bortner, Amir Sheikhi

Background

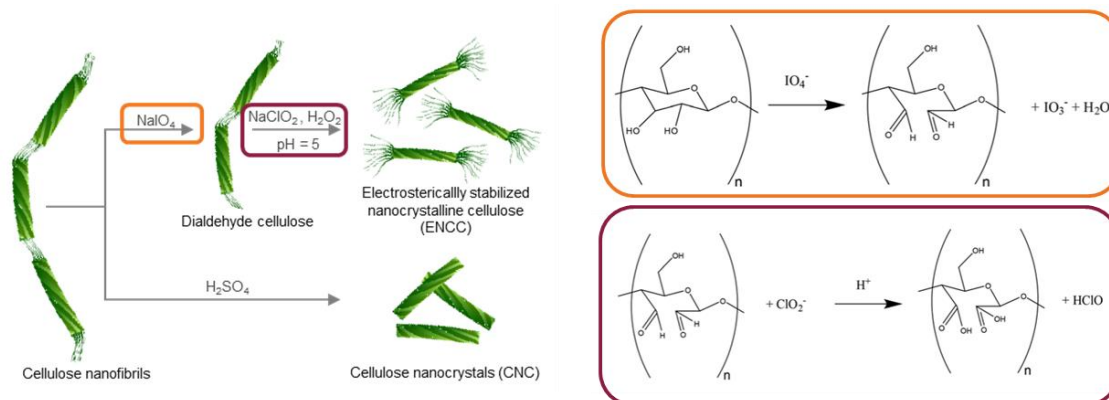


Figure 7.40. Synthetic routes to cellulose nanocrystals and electrosterically stabilized nanocrystalline cellulose.

Experimental

The ambient-environment samples for X-ray scattering analysis were prepared by mounting the films onto the solid sample plate with tape. The hydrated samples were prepared by soaking the films in deionized water for at least 24 hours, followed by cutting the film into small pieces and mounting into a sealed sample cell with polyimide windows and a rubber O-ring to ensure the samples remained wet. Extra-small, small and mid-angle X-ray scattering (WAXS) experiments were performed using a Xenocs Xeuss 3.0 SAXS/WAXS equipped with a GeniX 3D Cu HFVLF microfocus X-ray source utilizing Cu K α radiation ($\lambda = 0.154$ nm). The sample-to-detector distance was 1.8 m for ESAXS, 900 mm for SAXS, and 370 mm for MAXS, and the q -range was calibrated using a silver behenate standard. Two-dimensional scattering patterns were obtained using a Dectris EIGER 4M detector with various exposure times (ESAXS: 4 hours, SAXS: 2 hour, MAXS:

1 hour). Data reduction was performed using XSACT software provided by Xenocs, and the 1D profiles were corrected for background and transmission. All scattering intensities are reported on an absolute intensity scale. The ESAXS, SAXS, and MAXS profiles were merged into a single dataset and are hereafter referred to as “ESAXS” profiles.

Results and Discussion

The merged ESAXS/SAXS/MAXS profiles of the neat TPU, 8% CNC/TPU, and 8% ENCC/TPU films are shown in **Figure 7.41**. Through X-ray scattering experiments on the wet and ambient films, subtle shifts in the scattering profiles can be observed, further helping to clarify any morphological changes that may be occurring during hydration. X-ray scattering experiments were conducted to characterize the morphology of the composite films. In these tests, the scale size being measured is on the order of nanometers to hundreds of nanometers. This range covers both the ENCC body and hairs which are both approximately 100nm each.⁶¹ The ESAXS profile of neat TPU in the ambient and wet states are shown in **Figure 7.41a**. A broad scattering peak is observed in both the wet and dry states, centered around $q \sim 0.4 \text{ nm}^{-1}$. This feature is attributed to the phase-separated morphology of the hard/soft segments of the TPU and has been well-studied in TPUs.⁶² As shown in **Figure 7.41a**, the peak position and intensity do not significantly change upon hydration, which is as expected for this relatively hydrophobic material. Next, the morphology of the 8% CNC/TPU composite was characterized in the ambient and wet states.

As shown in **Figure 7.41b**, the ESAXS pattern of the CNC/TPU composite reveals an additional scattering feature centered around $q \sim 0.05 \text{ nm}^{-1}$. This feature is attributed to a characteristic dimension of the CNC particles. Fitting this broad scattering feature with a

Guinier feature yielded a shape-independent size⁶³ of the ESAXS feature being equal to $R_g = 120$ nm, which is consistent with the length of the CNC body. This scattering feature does not significantly change in intensity upon hydration (**Figure 7.41b**). The ESAXS pattern of the 8% ENCC/TPU composite is shown in **Figure 7.41c**. In the ambient state, the ENCC/TPU composite shows a distinct scattering feature centered around $q \sim 0.06$ nm⁻¹, yielding a size of $R_g \sim 150$ nm, whereas in the hydrated state, the feature shifts to lower q , yielding a size of $R_g \sim 240$ nm. As neither the neat TPU nor CNC-TPU show this shift, it is likely that this scale shift is due to the “hairs” interacting with the introduced water. This points towards the hair swelling theory, but with the possibility that the water is still creating some voids in the TPU matrix that could be interacting with light.

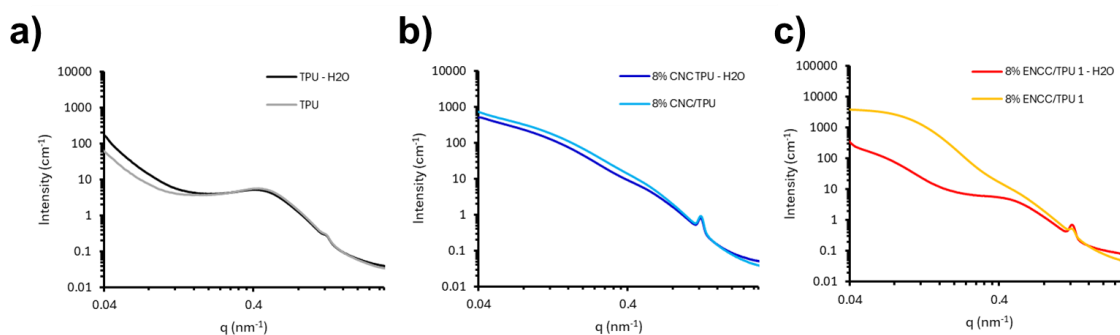


Figure 7.41. Merged SAXS/MAXS patterns of dry and hydrated samples of **a)** TPU, **b)** 8% CNC/TPU, and **c)** 8% ENCC/TPU.

7.10 References

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Appendix A. Characterization of the Morphology-Property Relationships of Perfluorosulfonic Acid Precursors

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A.1 Introduction

This study presents preliminary data characterizing the crystallization kinetics, morphology, and rheology of the thermoplastic sulfonyl fluoride precursors to perfluorosulfonic acid membranes. For the first time, Flash DSC is used to characterize PFSA precursors. In a 2004 study by Gilbert and Haworth,¹ the physical properties of N115F, the thermoplastic precursor to Nafion, were studied. A broad melting endotherm over the temperature range 150°C to 250°C was attributed to melting of imperfect PTFE-like crystallites with a range of thicknesses.

In a recent study,² several thermal properties (thermal degradation temperature, melt viscosity, and glass transition) of a Nafion precursor (970 EW) and an Aquivion precursor (870 EW) were reported. From oscillatory shear rheology experiments, the melting temperature of Aquivion was determined as 240°C, whereas the melting temperature of Nafion was determined as 200°C, as the crossover point between the storage and loss modulus curves. Aquivion was also shown to have a higher melt

viscosity than Nafion at all frequencies and shear rates tested. The authors did not discuss the morphological origins of the different rheological properties and did not explain the differences on the basis of either chemical structure of the ionic equivalent weight. Moreover, the precursors varied in both equivalent weight and side chain length, making direct comparisons difficult.

To the best of our knowledge, the crystallization kinetics of PFSA's or their precursors have not been directly studied. Taylor and coworkers studied the crystallization of poly(vinylidene fluoride) (PVDF) blends with a perfluorosulfonate ionomer.³ However, the authors were primarily interested in how the presence of a PFS-X ionomer influenced the crystallization kinetics of PVDF, and as such, they did not study the crystallization of the PFS-X itself. The authors observed that the crystallization rate of PVDF in the blend was significantly diminished as the size of the counterion on the PFSA was increased.³

A.2 Results and Discussion

The sulfonyl fluoride PFSA precursors in this study possessed a range of equivalent weights (determined based on the hydrolyzed EW) and two different sidechain lengths, C2 and long sidechain (**Figure A1** and **Table A1**). Using Equation 5.1, the number of TFE units per mole of sidechain were calculated. For a given sidechain length, the number of TFE units increases with the EW. At a similar EW, C2 precursors have a greater number of TFE units between sidechains due to the lower MW of the sidechain.

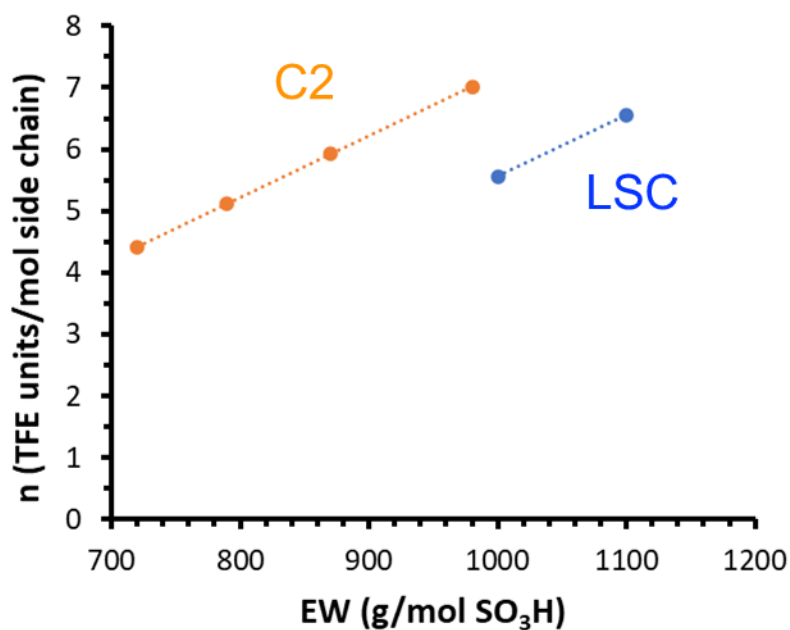


Figure A1. The number of TFE units per mole of sidechain vs. the EW for C2 and LSC PFSA.

Table A1. The number of TFE units per mole of sidechain vs. the EW for the PFSA precursors in this study.

PFSA	<i>n</i> (TFE units/mol sidechain)
720 EW C2	4.42
790 EW C2	5.12
870 EW C2	5.92
980 EW C2	7.017
1000 EW LSC	5.56
1100 EW LSC	6.56

Experiments using a standard DSC were performed to characterize the non-isothermal crystallization kinetics of the precursors. An example experiment is shown in **Figure A2**. As the cooling rate increases, the crystallization exotherm shifts to lower

temperatures. This experiment was performed for all precursors in this study and the onset of the crystallization temperature is plotted for each precursor in **Figure A3**. For a given sidechain length, the higher EW precursors (with a higher n) crystallize at higher temperatures, suggesting faster kinetics of crystallization. The data from the precursors is plotted together in **Figure A4**.

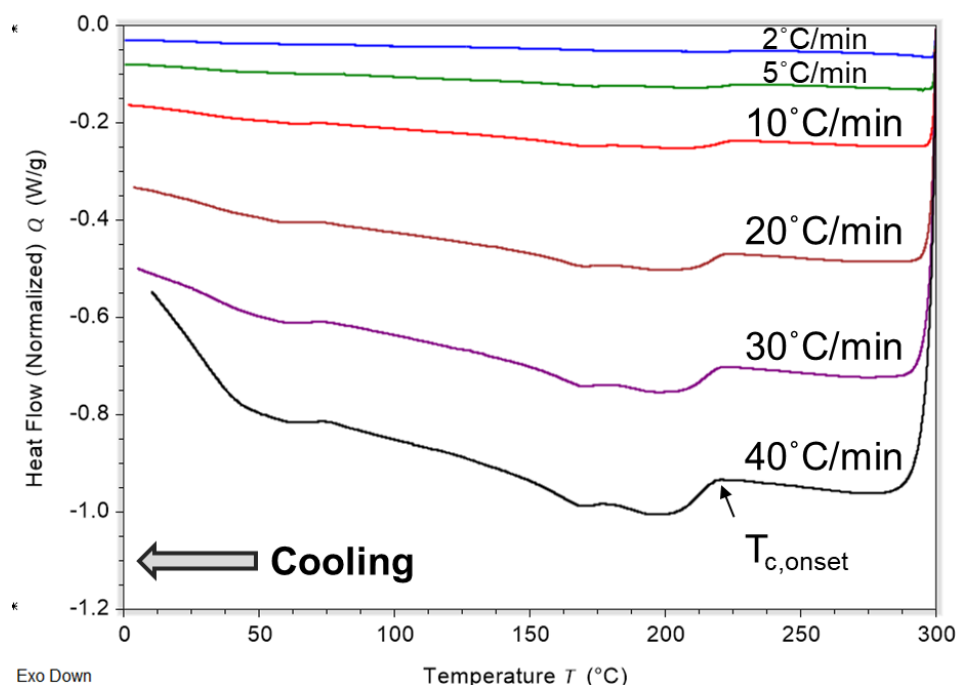


Figure A2. DSC cooling curves for the 980 EW C2 precursor from standard DSC.

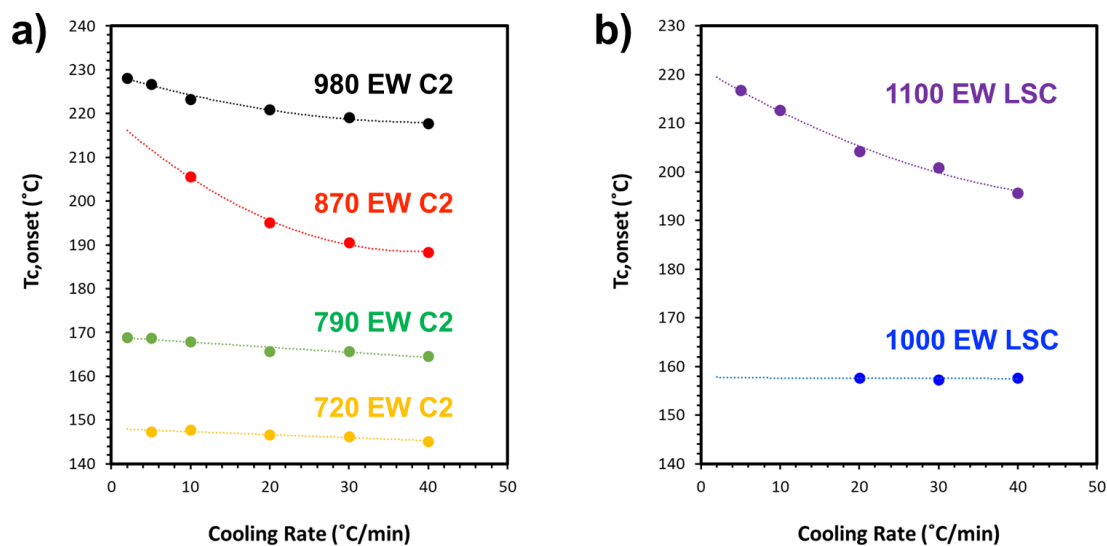


Figure A3. Onset of crystallization temperature plotted for the **a)** C2 precursor series and **b)** the LSC precursors.

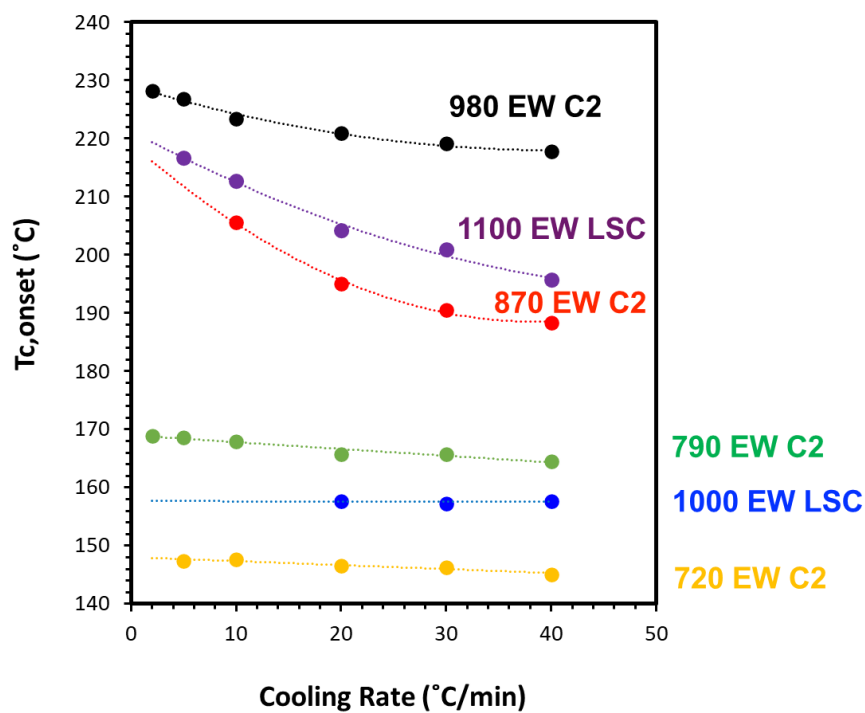


Figure A4. Onset of crystallization temperature plotted for each precursor as a function of the cooling rate. Data were collected on a standard DSC.

In order to study the influence of the number of crystallizable TFE units between sidechains on the nonisothermal crystallization kinetics of the precursors, the data can be presented as a function of the TFE units between moles of sidechains, n (**Figure A5**). For the C2 series, there is a clear trend ($R^2 = 0.9995$) between the onset of the crystallization temperature and the number of TFE units between sidechains. As the number of crystallizable segments increases, the precursor crystallizes at higher temperatures, indicating faster kinetics.

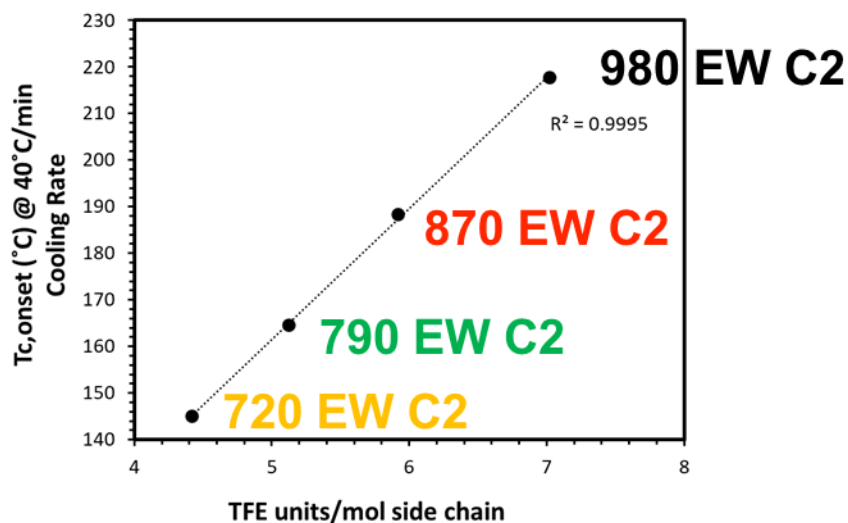


Figure A5. Onset of crystallization temperature plotted for each precursor as a function of the cooling rate. Data were collected on a standard DSC.

A similar data presentation is given for the LSC precursors, and is shown alongside the C2 series in **Figure A6**. Similar to the C2 series, LSC precursors with a higher value of n displayed higher onset of crystallization temperatures, suggesting faster kinetics. The trendlines suggest that for a given value of n , the C2 PFSA precursors crystallize at higher temperatures and thus have faster nonisothermal crystallization kinetics. More studies would need to be conducted on other LSC precursors with different EW to

confirm this. However, this result suggests that C2 precursors crystallize faster than LSC precursors at similar values of n .

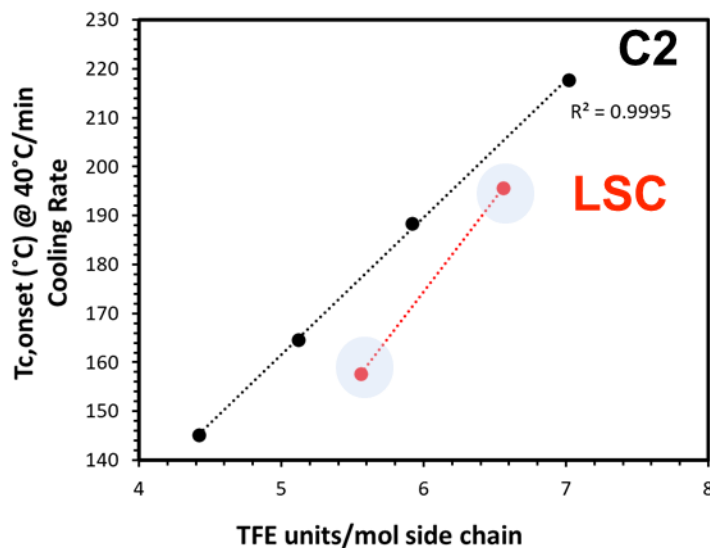


Figure A6. Onset of crystallization temperature plotted for each precursor as a function of the cooling rate. Data were collected on a standard DSC.

Flash DSC experiments were conducted on the 980 EW C2 precursor to allow for faster cooling rates and therefore better characterization of the crystallization kinetics. An interrupted isothermal crystallization (IIC) experiment was conducted which can allow for the determination of the crystallization half-time, $t_{1/2}$, which represents the time associated with crystallizing 50% of the maximum crystallinity for a given material.⁴ Additional information about this Flash DSC method to determine crystallization kinetics can be found in Pomatto and Moore's work.⁴ Data from a representative IIC experiment for the 980 EW C2 precursor is shown in **Figure A7**. As the time at the crystallization temperature increases, the resulting melting endotherm of the crystallites formed at that step increases in intensity. The fractional crystallinity can be estimated using the plot

shown in **Figure A8**. The crystallization half-time of the precursors is shown in **Figure A9**.

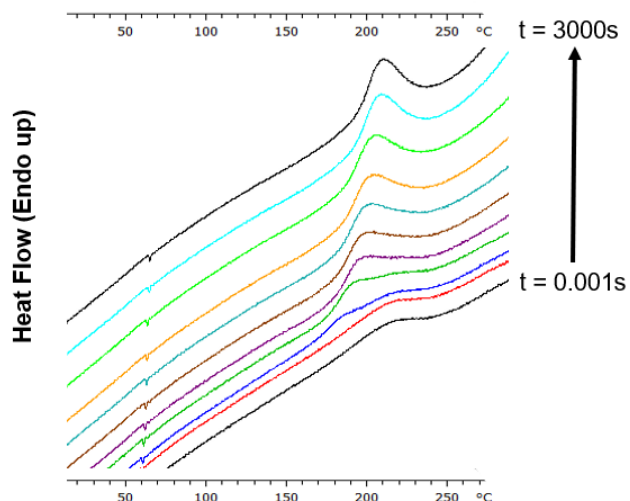


Figure A7. Data for the 980 EW C2 precursor collected from Flash DSC using the interrupted isothermal crystallization method for determining the crystallization half-time.

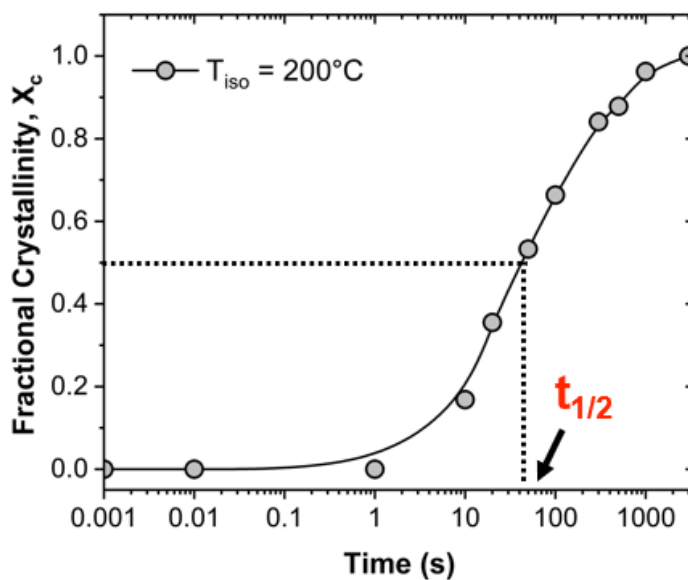


Figure A8. Crystallization half-time plot showing the origin of the crystallization half-time, $t_{1/2}$ for a given semicrystalline polymer.

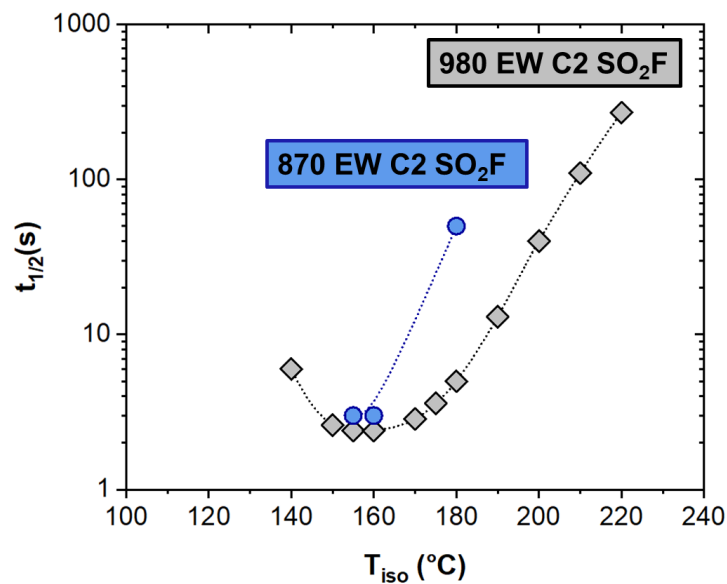


Figure A9. Crystallization half-time determined for the 980 EW C2 and the 870 EW C2 precursors from Flash DSC.

Another interesting result from the Flash DSC experiments was that the melting temperature of the PTFE crystallites in the precursor could be tuned by changing the isothermal crystallization temperature. This can clearly be seen in **Figure A10**, where increasing the isothermal crystallization temperature results in endothermic peaks at higher temperatures. The trend is easily visualized in **Figure A11**, which shows the clear relationship between the crystallization temperature and the melting temperature. This data suggests that, by carefully tuning the processing temperature of the thermoplastic precursor, PTFE crystallites with varying thicknesses and therefore melting points can be created. Further studies are needed to understand how higher melting point crystallites can change the physical and mechanical properties of the resulting films and membranes.

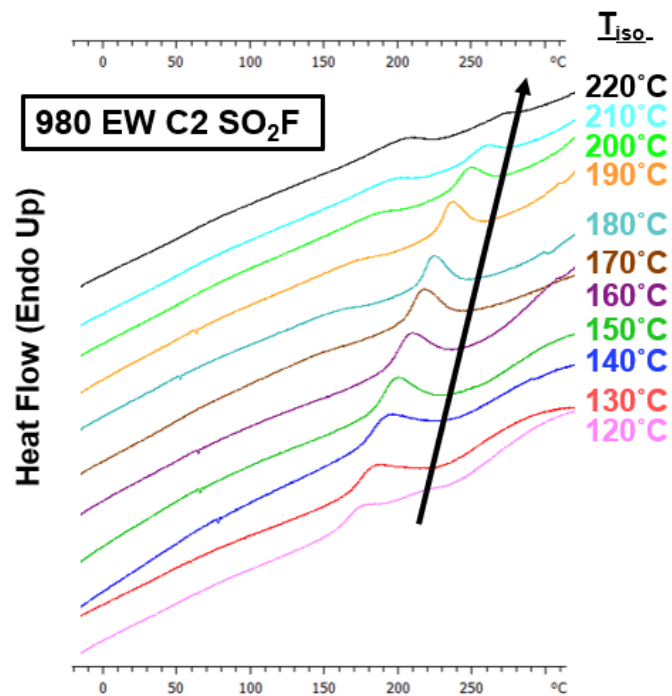


Figure A10. Data from Flash DSC showing the heating data of the 980 EW C2 as a function of the isothermal crystallization temperature.

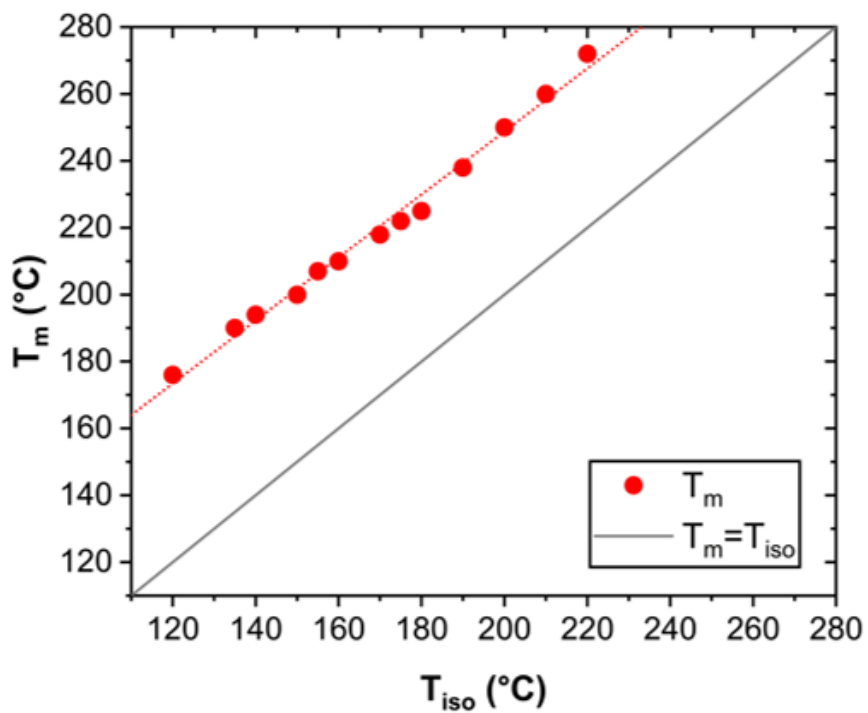


Figure A11. Melting temperature vs. the isothermal crystallization temperature for the 980 EW C2 precursor as determined by Flash DSC.

SAXS and WAXS experiments were conducted on melt-pressed films of the precursors, and the results are shown in **Figure A12** and **Figure A13**. For a given sidechain length, the intercrystalline long period shifts to higher intensity and lower q with increasing EW, likely due to the increase in the degree of crystallinity and therefore larger crystalline domain dimensions. In the WAXS region, the (100) crystalline reflection increases in intensity with increasing EW, as expected for a greater degree

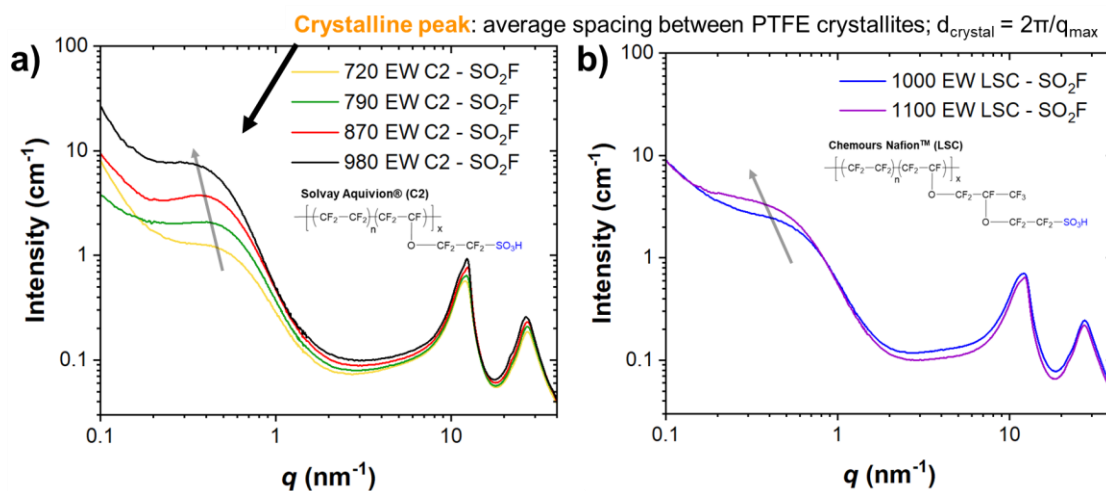


Figure A12. Merged SAXS/MAXS/WAXS profiles of melt-pressed PFSA precursors.

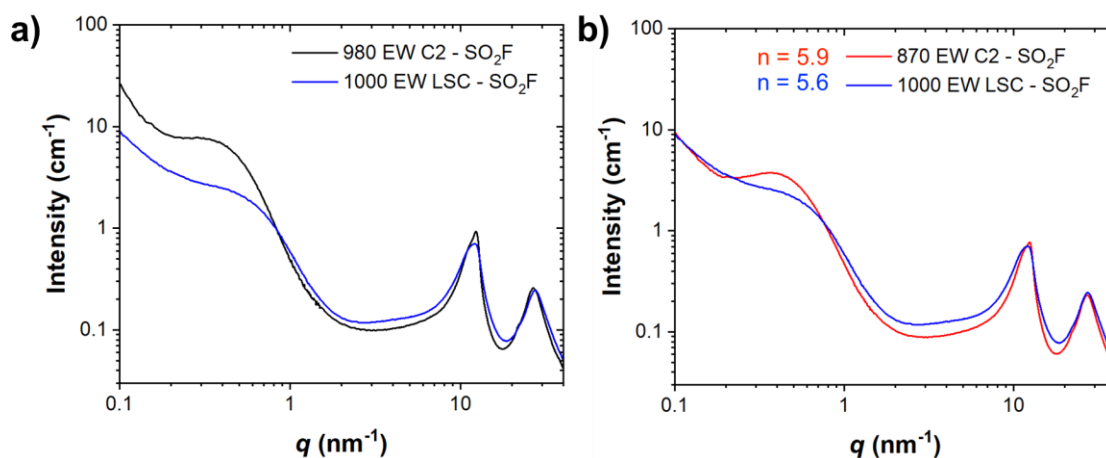


Figure A13. Merged SAXS/MAXS/WAXS profiles of melt-pressed PFSA precursors.

Variable-temperature oscillatory shear rheology experiments of the PFSA precursors were conducted to study the temperature-dependent rheological behavior of the precursors upon cooling. Example profiles from the experiments are shown in **Figure A14**. Upon cooling from 300 °C, the storage and loss modulus increase when crystallization occurs. The G'/G'' crossover, shown by the arrows, is related to the point where the polymer melt exhibits more solid-like behavior. Interestingly, as shown in **Figure A15**, this crossover point appears to have a linear dependence on the number of TFE units between sidechains, which is consistent with the nonisothermal DSC data discussed previously. Similarly, these preliminary experiments reveal a loose linear relationship between the rubber plateau modulus and n (**Figure A16**). The temperature-dependent complex viscosity of the precursors is shown in **Figure A17**.

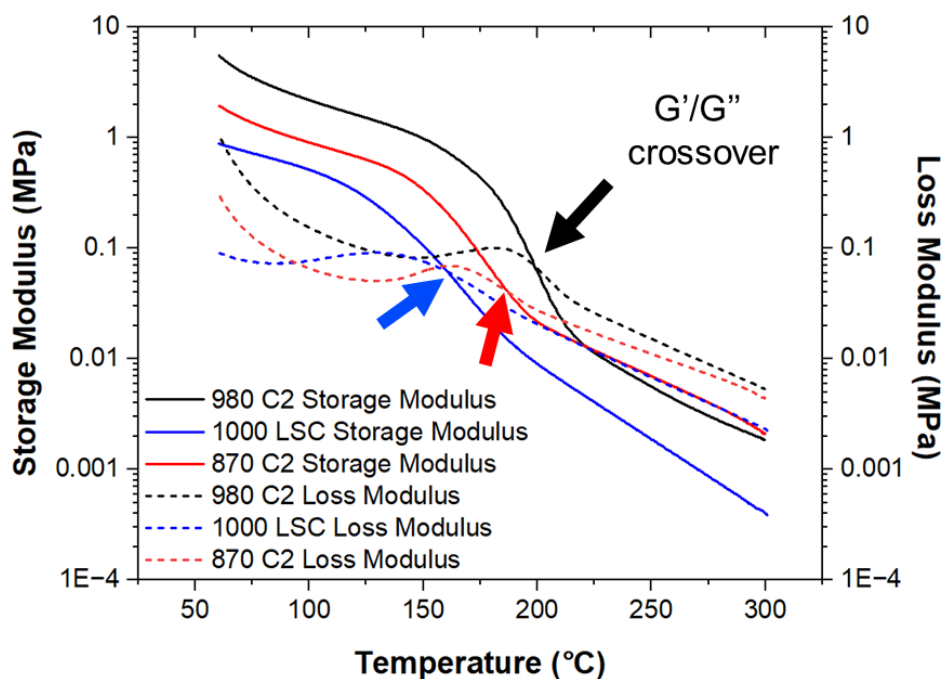


Figure A14. Oscillatory shear rheology experiments for the precursors to the PFSAAs shown.

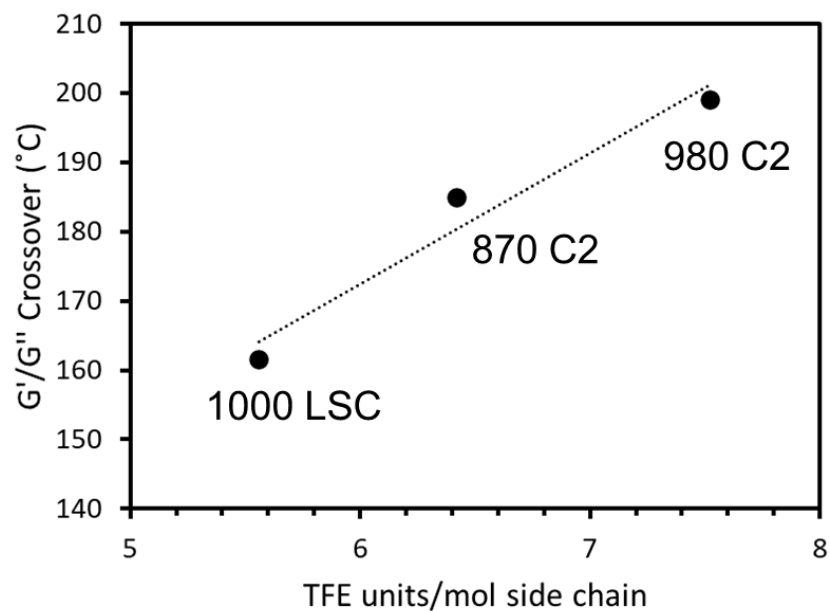


Figure A15. The G'/G'' crossover point for the PFSA precursors plotted as a function of the number of TFE units between sidechains (n).

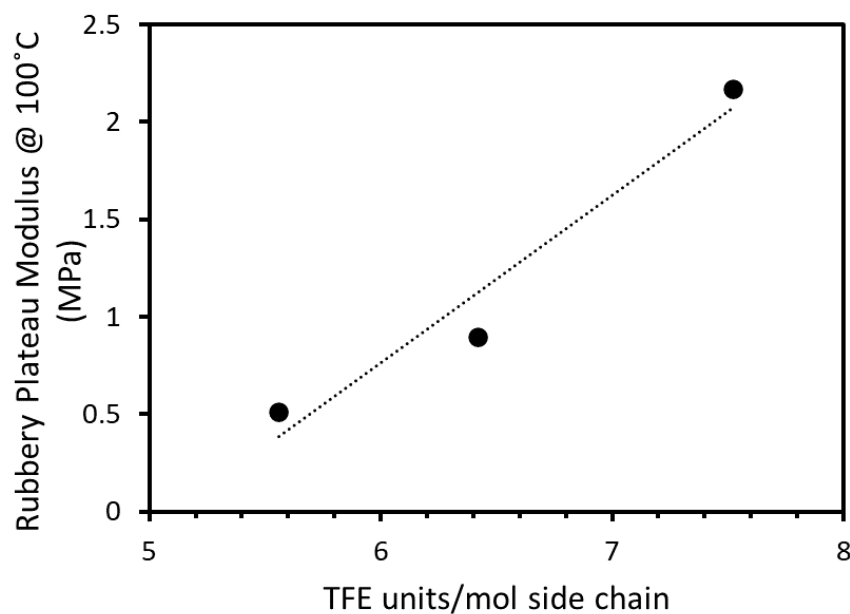


Figure A16. The rubbery plateau modulus for the PFSA precursors plotted as a function of the number of TFE units between sidechains (n).

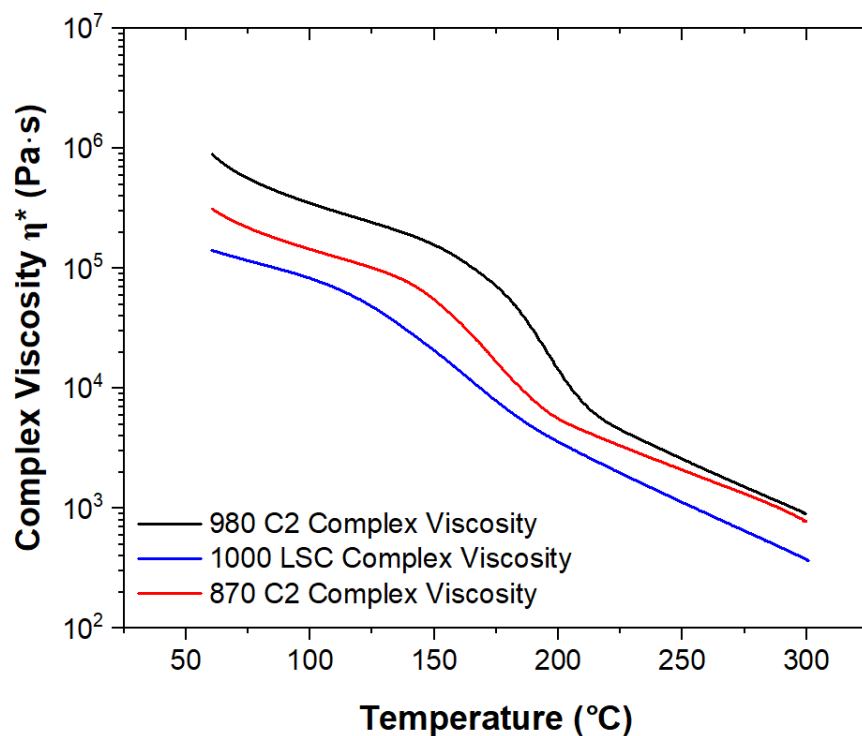


Figure A17. The complex modulus of the PFSA precursors obtained from variable-temperature oscillatory shear rheology experiments.

In summary, there appears to be a clear relationship between the amount of crystallizable TFE units between side chains, the nonisothermal crystallization kinetics, the crystalline morphology, and the melt rheology properties in PFSA precursors. Future experiments should explore these relationships more closely and their effect on the overall properties, both mechanical and electrochemical, in the hydrolyzed PFSA membranes. These results could help optimize the processing conditions of thermoplastic PFSA precursors by tuning the melting point and crystalline morphology, leading to more informed processing decisions.

A.3 References

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