#### REVIEW



### Resonant soft X-ray scattering in polymer science

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#### Abstract

Resonant soft X-ray scattering (RSoXS) is an emerging, powerful technique to probe the nano-to-mesoscale structure of polymers and other molecules. It joins together small-angle X-ray scattering (a statistical nanoprobe) with X-ray spectroscopy that brings with it unique chemical and bond-orientation sensitivity. Through over a decade of discovery and development, RSoXS is moving from a niche technique applied to organic electronic thin films to a mature tool applicable to a plethora of polymeric and molecular systems, encompassing new modalities, analyses, and simulation methods. This development promises to deliver increasingly quantitative answers to challenging questions in polymer science as well as expand its usefulness to complementary fields. This review presents a full synopsis of the technique, including background on the theoretical underpinnings, measurement best practices, and examples of recent RSoXS applications and discoveries provided here to accelerate the transition to a broader range of soft matter and polymeric fields.

#### K E Y W O R D S

NEXAFS spectroscopy, resonant soft X-ray scattering, small angle scattering, chemical and orientational nanostructure, polymer and small molecule materials

### **1** | INTRODUCTION

Resonant soft X-ray scattering (RSoXS) is a powerful but complex combination of scattering and spectroscopy which is simultaneously sensitive to the nanoscale structure, molecular orientation, and chemistry of polymeric materials. While sharing much with traditional anomalous X-ray scattering at hard X-ray energies (X-rays with energies generally greater than 6 keV), soft X-ray scattering (<3 keV) has become more accessible as synchrotron X-ray sources have made high-quality polarization-controlled X-rays across this energy range more accessible. As RSoXS is the combination of spectroscopy and scattering, it is important that both of these aspects are well accounted for in the theoretical background, experimental practices and analysis. It is common for experimenters well experienced with (usually non-resonant) X-ray scattering to approach RSoXS as a scattering technique with added spectroscopic sensitivities. Meanwhile those experienced with spectroscopic methods approach RSoXS as spectroscopy resolved at a nanoscopic spatial scale. While both of these views are valid, we want to encourage a united view which benefits from best practices of both scattering<sup>1,2</sup> and spectroscopy<sup>3,4</sup> and can provide more information than either alone. We will often rely on the extensive libraries of previous work in these fields, focusing on thoroughly covering the intersectional aspects.

In comparison to nonresonant scattering which is available even in common laboratory instruments, RSoXS is performed with considerably lower X-ray energies, or longer

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photon wavelengths. The benefit of using to these longer wavelengths is that for soft materials, X-ray absorption edges or low-Z materials (carbon, nitrogen, and oxygen) are preset, which enable organic chemically sensitivity.

Although it is performed in the soft X-ray region, there are absorption edges of many elements, and for reasons both historical and practical, the soft in RSoXS also denotes characterization of soft matter systems. It is an elastic photon-in, photon-out scattering technique, that varies from other resonant X-ray scattering methods such as Resonant Elastic X-ray Scattering (REXS) anomalous small angle X-ray scattering (ASAXS), and diffractionbased resonant tools by its focus on the often-avoided carbon K absorption edge, and by its focus on the examination of soft matter systems that generally exhibit non-Bragg or diffuse scattering. We will discuss how this focus leads to considerable experimental and analytical differences from these other techniques in Section 3. RSoXS has developed since the initial RSoXS experiments 15 years ago on polymers<sup>5-8</sup> into a widely used nanoscale characterization tool for organic electronics, where its sensitivity to the nano-to-mesoscale matches well to the structural features that govern device dynamics, its quantitative nature allows for domain purity analysis, and orientation sensitivity matches well the anisotropic electronic properties of many semiconductive polymers. It is rapidly expanding beyond just organic electronics, however, and we will review the recent applications in a range of fields where RSoXS is a window into the functional size scale.

The unique chemical and orientational sensitivities of RSoXS arise from the energy- and polarization-dependent X-ray interaction with molecules and is best understood by examining the related absorption spectroscopy. Following this logic, in Section 2, we present the theoretical background of RSoXS including a brief review of the complementary techniques of absorption spectroscopy and microscopy. While there are several excellent treatments of X-ray scattering,<sup>1,2</sup> and X-ray absorption spectroscopy,<sup>3,4</sup> including several reviews of RSoXS in various subfields of soft matter,<sup>9-11</sup> here we develop a basic physical intuition of the technique's fundamental mechanisms. As part of this, we will cover the theory behind an analytical approach using quantitative contrast variation and point out the current limitations of analytical treatments of RSoXS, where we discuss the importance of numerical approaches using modern high-performance computing.

In Section 3, we address the practicalities of conducting an RSoXS experiment to measure a sample. We cover the applicability of RSoXS in comparison to complementary measurement techniques, sample requirements, and limitations. We will then address best practices on planning an experiment, preparation, acquisition of RSoXS data, and review the levels of analysis and their applicability and limitations. Subsequently in Section 4, we will see how RSoXS has been applied in various fields including where the technique started with organic electronics and block copolymers (BCP's), to more advanced uses in determining membrane structure, directed self-assembly (DSA) of buried polymer structures, the various uses of polarization to determine molecular orientation, and the recently emerging applications revealing liquid crystalline (LC) phases and examining biological assemblies.

As an outlook to the future of RSoXS, Section 5 will cover recent advances, which shift the use of RSoXS from qualitative to quantitative structural characterization. This includes experimentation at multiple absorption edges and in new environmental cells allowing direct measurement of aqueous nanostructures in situ as well as advances of both analytical and computational analysis techniques.

We have strived to present a synoptic view of the background, practicalities, and applications of RSoXS in a narrative order, but the reader is encouraged to absorb the content in whatever order makes sense to them and skip back and forth as most usefully meets their needs.

#### 2 | RSoXS AND SPECTROSCOPY

#### 2.1 | Molecular orbital transitions

The "resonance" in RSoXS stems from varying photon absorption and thus can be treated in a similar manner to other photon spectroscopies, perhaps most familiar, that of visible light. For most soft matter and polymeric systems, the interaction can be reduced to the electric field of the photon E interacting with a bound electron on a molecule. RSoXS is only concerned with the elastic scattering, meaning the incoming and scattered X-ray has the same energy. However, we must consider the general interaction at a molecular level, which initially involves an electronic excitation. The final outcome of these interactions is a chain of these transitions, which eventually result in a measurable absorption or scattering event. Although we might only be interested in the scattering events, we need first to consider the fundamental transitions in general. The transition rate  $\Gamma$  of from initial  $\Psi_a$ to final  $\Psi_b$  state can be approximated by Fermi's golden rule<sup>12</sup> as the product of the matrix element  $\langle \Psi_b | \vec{E} \cdot \vec{r} | \Psi_a \rangle$  squared and the density of states  $\rho_{ab}$ 

$$\Gamma_{a\to b}(\omega) = \frac{2\pi}{\hbar} \left| \left\langle \Psi_b \middle| \vec{E} \cdot \vec{r} \middle| \Psi_a \right\rangle \right|^2 \rho_{ab}(\omega), \tag{1}$$

where the matrix element is characterized by the dipole operator moving the electron along  $\vec{r}$  from initial to final

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**FIGURE 1** Schematic of resonant X-ray absorption in comparison to nonresonant X-rays and visible light, showing which occupied and unoccupied states participate in the transition. (Right) Example unoccupied absorption spectrum from a polymer with resonant unoccupied states identified to molecular orbitals

state. The separation of these terms is quite important. The matrix element is a geometric quantification of the wavefunction overlap perturbed by the electric field of the photon, understood as the change in electron trajectory from one orbital to another when excited by photon polarization. This matrix element is dipolar, in that the polarization vector of the electromagnetic wave must point in the right direction to move the electron from one state to the other. The density of states is the probability of finding an unoccupied  $\Psi_b$  and occupied  $\Psi_a$  where the difference in energy between the states is exactly  $E = \hbar \omega$ , the energy of the incident photon ( $\omega$  is the oscillation angular frequency of the electromagnetic wave). Predicting  $\Gamma_{a\to b}$  involves calculations of both of these terms, including the orbital, the wavefunctions  $\Psi$ , and their energies and occupation states for which a common approach is to use density functional theory (DFT).<sup>13</sup>

Figure 1 displays a schematic of possible transitions for nonresonant X-rays, visible light, and resonant X-rays. For nonresonant X-rays,  $\Psi_a$  is any electron in the material and  $\Psi_b$  is the free electron state. Traditionally, these are "hard" X-rays with energies above all atomic electron binding energies, so Equation (1) reduces to the scalar electron density of a material  $\Gamma = \frac{2\pi}{h} \rho_e$ . Nonresonant X-rays are also at lower energies where they have too little energy to excite core electrons but too much energy to excite those electrons into a bound orbital, instead exciting those electrons to ionized free states. In this case, the effective  $\rho_e$  is reduced compared to high-energy X-rays, but importantly still constant in the nonresonant energy range. It is often this latter nonresonant case that is used in RSoXS experiments to compare to resonance. The terms in  $\Gamma_{a\to b}$  for visible light are by comparison much more complex. Because E is small, below the energy needed to ionize or excite an electron all the way to an unbound state, the occupied  $\Psi_a$  and unoccupied  $\Psi_b$  states

are both bound orbitals near the Fermi level of the molecule—important states for chemical reactions. Because of this low energy and the density of molecular orbitals around the Fermi level in many materials, multiple pairs of  $\Psi_a$  and  $\Psi_b$  can often exist and overlap, and both the initial and final orbits can have complicated geometric structure. This means both the matrix element and density terms are typically information dense and difficult to pick apart.

On the other hand, resonant X-rays excite an electron from a core orbital<sup>1</sup> to an unoccupied orbital. If  $\Psi_a$  is a core atomic orbital, it is energetically separated, sharply defined, and (in the case of K-edges such as carbon, nitrogen, oxygen primarily employed in RSoXS on polymers) spatially symmetric, so all geometric and energetic information, often called the "fine structure" observed in the absorption transitions is primarily attributed to the unoccupied  $\Psi_b$  orbital structure. Although at higher-lying energies resonances begin to heavily overlap, oftendistinct absorption lines within the fine structure can be associated with unique bonds within the molecule. This exclusive focus on unoccupied orbitals leads to the powerful bond sensitivity in both energy and orientation. Thus, RSoXS can provide chemical bond localized information similar to infrared spectroscopies, but with a wavelength (and therefore potential spatial resolution) several orders of magnitude smaller. This information is demonstrated in Figure 1 as absorption of a polymer with the bonds labeled.

#### 2.2 | Dielectric tensor

Although every resonant interaction is a local transition of an electron from one state to another, RSoXS as a scattering technique is the ensemble response of a material system for which it is useful to use the classical electromagnetic wave picture. In this view, an incoming oscillating electric field interacts with a material, inducing the electrons within the material to oscillate in response, forming an induced electric field called a polarization field  $\vec{P}$  within the material. Although the source of  $\vec{P}$  is many local orbital transitions, the ensemble can be handled as a single property of that material. In the dipole approximation, the magnitude, direction, and phase offset of  $\vec{P}$ in response to the driving electric field  $\vec{E}_o$  can be reduced to a complex tensor constant called the susceptibility of the material<sup>14</sup>  $\vec{\chi}(\omega)$ .

$$\vec{P}(\omega) = \epsilon_0 \, \overleftrightarrow{\chi}(\omega) \cdot \vec{E}_o. \tag{2}$$

For X-rays near resonance the fine structure from the fundamental dipole matrix elements of electron transitions are all encoded in  $\overleftrightarrow{\chi}(\omega)$  where the double arrow notates a matrix (3 × 3). We can further split out the components of  $\overleftrightarrow{\chi}$ , as the real component  $-2\overleftrightarrow{\delta}$ , and imaginary component,  $i2\overleftrightarrow{\beta}$  which we call the optical tensors of a material. We note that we have named delta and beta in this way because for isotropic and orthorhombic materials, there is a natural relationship between the susceptibility and the index of refraction *n*, such that

$$n = 1 - \delta + i\beta. \tag{3}$$

However, the relationship of the optical constants and index or refraction in a general anisotropic medium has not been well demonstrated in the soft X-ray regime, so care should be taken in expanding<sup>3</sup> to the tensor forms. At visible wavelengths the optical constants can be substantial, however at X-ray energies, even soft X-rays, the components of  $\vec{\delta}$  and  $\vec{\beta}$  are generally far less than 1 (even at a resonance typically only  $\approx 10^{-3}$ ). At the material level, these (tensor) optical constants are the quantities typically used to describe RSoXS interactions.

All of the molecular orbital mechanics, which occur within a molecule, are coarse grained into these material parameters, which can then be macroscopically measured. Although we do not present the full derivation, the imaginary component  $\beta(\omega)$  encodes all chains of transitions, which result in a phase shift, or damping of the induced polarization field. This is the absorption experimentally accessible through parameter, absorption spectroscopy measurements. The real part of the index  $\delta(\omega)$  will be discussed in later sections. We note here as a connection to traditional scattering theory, the scattering length density (SLD) can also be related to the optical constants in the isotropic form

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 $\delta = \frac{2\pi}{\omega^2} Re(SLD), \beta = \frac{2\pi}{\omega^2} Im(SLD). \tag{4}$ 

#### 2.3 | NEXAFS of polymers

X-ray absorption spectroscopy (measuring  $\stackrel{\leftrightarrow}{\beta}$  although most usually in an isotropic or uniaxial symmetry-not the full tensor) across an elemental absorption edge has several names including near edge X-ray absorption fine structure (NEXAFS) spectroscopy typically if the edge is in the low-energy X-ray range  $< \sim 2 \text{ keV}$  and X-ray absorption near-edge structure (XANES) for higher energy X-rays, although there is no physical difference in these techniques beyond the name. In soft materials and polymers, carbon is an abundant atom, for which the core absorption edge (called the carbon-K absorption edge) is at  $\approx 285 \,\text{eV}$  (the binding energy of the 1 s carbon electron) or  $\approx 4.5 \, \text{nm}$  wavelength. Although there are several lab-scale sources of carbon K-edge photons,<sup>15</sup> and promise of more,<sup>16-18</sup> until now most of the work has come from monochromatic synchrotron light.<sup>6,7,19–23</sup> The first polymer NEXAFS spectrum at the carbon edge was produced in 1981<sup>24</sup> and the technique has quickly developed for characterization of surface chemistry and orientation.<sup>25</sup> Figure 1 demonstrates the chemical sensitivity of the interaction, while Figure 2A<sup>26</sup> demonstrates the mechanics of orientational sensitivity as well as experimental realization. Absorption peaks at unique energies near the edge represent transitions into specific unoccupied molecular orbitals (bonds) yielding the chemical sensitivity, while angle-dependent absorption of polarized X-rays yields the orientational sensitivity, and the elements of the tensor.

As a quick summary of the possible symmetries of a material which will be used throughout this section. First, the simplest case is isotropic symmetry, where there is no angular dependence of the interaction of a material with the vector that represents the electric field polarization direction. This can arise either because a material itself has similar bonds in most directions (as in a fullerene molecule) or when the ensemble of chromophores within the size scale of interest orient in every direction equally. Isotropically the optical constants reduce to scalars with one  $\delta$ , $\beta$  for a material uses uniaxial symmetry. In this approximation, there is one unique axis and all directions normal to this axis are planarly isotropic. Once again this can arise at a



**FIGURE 2** (A) NEXAFS spectra of an aligned polymer at varying incident angles and two resonances highlighted that have opposite angle dependence. A schematic is inset to illustrate how changing the experimental incident angle changes the polarization angle with respect to the two highlighted resonances' transition dipole moments (TDM's). Adapted from ref. 26 with permission. (2005) Wiley. (B) STXM images of aligned polymer showing the strength of molecular alignment (top) and direction of alignment (bottom) mapped across a thin film sample. Adapted from ref. 27 with permission. Copyright (2011) Wiley. (C) A three-dimensional reconstruction of polymer microspheres decorated with Fe<sub>3</sub>O<sub>4</sub> nanoparticles enabled by STXM laminography. Adapted from ref. 28 with permission. © (2020) American chemical society. NEXAFS, near edge X-ray absorption fine structure; STXM, scanning transmission X-ray microscopy

molecular level from the symmetry of a molecule, as in an aromatic ring, or at a coarse-grained level from uniaxial type of stacking of a material as in a liquid crystal. Here the optical constants have two independent components, one for the unique axis and one for perpendicular directions. Finally, there is biaxial symmetry, where either three components (for a material that is orthorhombic) or a full tensor (with six unique elements) for a triclinic material is needed to define the optical constants.

Although measuring an isotropic and uniaxial  $\beta$  are well-known,<sup>29,30</sup> methods to reliably measure a complete optical tensor have yet to be established. Progress in this effort is ongoing. NEXAFS spectroscopy is itself a broad field, which we cannot adequately cover here other than to point out many useful references for those interested in the details of X-ray absorption.<sup>25,31,32</sup> For our purposes, NEXAFS spectroscopy is the source of experimental values of  $\beta$  for materials, and directly used in the real-space complement of RSoXS, scanning transmission X-ray microscopy (STXM).

# 2.4 | STXM—the real space analog of RSoXS

There are a few different ways of measuring  $\vec{\beta}$  in effective microscopies. One can image the electrons ejected from a sample,<sup>33–35</sup> or use full field microscopy<sup>36</sup> but for soft

X-rays of organic materials, detector and optical technology as well as the materials' nonconductive properties has made STXM the most common way to image nanoscale soft matter structure. It is in many ways a complementary tool to RSoXS, using the same photon interactions but providing a real space image. It even shares many of the sample requirements of RSoXS, which are also similar to transmission electron microscopy (TEM). STXM has been used over the last 30 years to image the nanoscale properties of a myriad of materials, including polymers. We direct the reader to several reviews of the technique,<sup>37-41</sup> and here point out the ability to quantitatively measure the domain composition and orientation of polymer mixtures.<sup>27,42</sup> STXM shares the orientational sensitivity of RSoXS due to the same resonance mechanism. Figure 2B shows an excellent example of molecular orientational mapping of a polymer thin film by using X-ray resonance and rotating the polarization vector relative to the sample.<sup>27</sup> Using the spectral response and the uniaxial approximation the authors were able to solve for the out of plane component of alignment, which could not be measured directly. This enabled measurement both the alignment strength and direction at each pixel in the image. Recently STXM has further developed, combining with scanning probe microscopies in a multimodal measurement of nanoscale polymer density<sup>43</sup> and with a rotational stage even allow for the development of 3D laminography<sup>28</sup> shown in

Figure 2C, which is similar to 3D tomography but amenable to extended thin film samples. Although resolving structure in real space is powerful, the resolution of STXM is limited not by the wavelength used, but by the complex diffractive optics required. Thus the diffraction limit  $(\lambda/2 \approx 3 \,\text{nm}$  at the carbon edge) has not been achieved in STXM, and only resolutions of  $\approx$  30 nm have been demonstrated at the carbon edge.<sup>28</sup>

#### 2.5 From absorption to polarization

Scattering is not just the real space analogy of absorption however, as absorption only concerns the imaginary component  $\overline{\beta}$ . The real component of  $\overline{\delta}$ , is more difficult to measure directly. Because  $\overleftrightarrow{\chi}$  is the response of a material to an impulse (recall the dipole interaction from earlier) the Kramers-Kronig relations can be used to directly relate the real and imaginary components to each other, so after measuring  $\beta(\omega)$  one can solve for  $\delta(\omega)$ , and thus obtain the complete  $\stackrel{\leftrightarrow}{\chi}$  if we collect a wide enough spectrum of  $\beta(\omega)$  and use widely available tools.<sup>44,45</sup> Although, once again, the isotropic and uniaxial cases are well established, doing this for a full optical tensor is not common and it is not clear if the Kramers Kronig relations must hold for each tensor element independently in a medium with off diagonal elements. Often a wide enough spectrum for the calculation is not directly collected, but performed by splicing the tabulated nonresonant atomic spectrum<sup>46</sup> across a very large energy range with a measured  $\vec{\beta}(\omega)$  near the absorption edge described well elsewhere.<sup>45</sup> However, this approach only works if the chemical formula and densities of the material are known.  $\delta(\omega)$  along with  $\beta(\omega)$  can also be directly measured through resonant soft X-ray reflectivity (RSoXR) which can remove the need for knowledge of a material prior of the measurement<sup>47</sup> provided an extremely flat homogeneous thin film is available. Such measurements are time consuming to conduct at many energies and thus have only been accomplished in a few cases.<sup>47</sup> Once again to date only isotropic and recently uniaxially<sup>48</sup> symmetric systems have been demonstrated, and examples will be discussed in Section 4.

#### 2.6 | RSoXS as a reciprocal space measure of a sample

All photon scattering is the result of spatial variations of  $\vec{\chi}(\vec{r})$  across a sample. This is essentially, what is measured in microscopy, which again only measures the imaginary component directly but at a local level and to

date with limited spatial resolution. A scattering event of an individual photon is the coherent process of an absorption of the original wave  $\vec{E}_{o}$  producing an induced wave  $\overrightarrow{P}$  in the materials defined in Equation (2) which as it oscillates, reradiates a scattered wave  $\vec{E}_s$ . If the populations of chromophores interacting with an incoming electromagnetic wave have a spatial variation, then the induced polarization from these populations interfere constructively or destructively depending on phase and magnitude of that variation forming an angular pattern of scattered waves which encodes the local variations of  $\overrightarrow{\gamma}$ . If a sample has no spatial variations, there will be no interference, and no scattering pattern will occur. At a resonance,  $\stackrel{\leftrightarrow}{\chi}$  is most accurately described as a tensor, meaning rotations of otherwise identical molecules in different regions will also result in variations of P, causing a scattering pattern. The Born Approximation of scattering assumes only a single scattering event per photon in a sample (i.e., the sample thickness is less than one scattering-length). In this case, the scattered intensity far from the sample<sup>30</sup> is proportional to the Fourier transform of the real-space distribution

$$\begin{split} I\left(\overrightarrow{q}\right) &= \left|\frac{4\pi^{2}}{\omega^{2}}(\mathbb{I}-\widehat{r}\widehat{r})\cdot\mathcal{F}\left[\overrightarrow{P}\left(\overrightarrow{r}\right)\right]\right|^{2} \\ &= \left|8\,\pi^{2}(\mathbb{I}-\widehat{r}\widehat{r})\cdot\mathcal{F}\left(\frac{-\overrightarrow{\delta}\left(\overrightarrow{r},\omega\right)+i\overrightarrow{\beta}\left(\overrightarrow{r},\omega\right)}{\omega^{2}}\cdot\overrightarrow{E}_{o}(\omega)\right)\right|^{2} \end{split}$$
(5)

where  $I\left( \overrightarrow{q} \right)$  is the scattered intensity in the  $\widehat{r}$  direction and  $\vec{q}$  is the momentum transfer or the change of momentum from the incoming wave to the outgoing wave  $\vec{q} = \vec{k}_{out} - \vec{k}_{in}$ , ( $\vec{k}$  is the Poynting vector [momentum] of a photon).  $\mathcal F$  indicates the Fourier transform from real space  $(\vec{r})$  across the illuminated sample to reciprocal momentum space  $(\vec{q})$ . I in the polarization correction factor is the identity matrix.<sup>14,49</sup>

We can relate  $|\vec{q}| = q$  to the experimental scattering angle  $\theta$  via  $q = \frac{2\omega}{c} \sin \frac{\theta}{2}$ . Where c is the speed of light in vacuum. Thus,  $I(\vec{q})$  is effectively the angular distribution of scattering intensity with major quantities described schematically with respect to the experimental setup in Figure 3C.  $\vec{P}(\vec{q})$  can be replaced in the second part of Equation (5) by the optical tensors dotted to the electric field. This is the general Born Approximation of scattering, showing that the spatial frequencies of



**FIGURE 3** Examples of qualitative binary contrast RSoXS analysis and experimental setup. (A) Binary contrasts between polymer, fullerene, and vacuum. The arrow indicates the recommended resonant photon energy, which maximizes contrast between materials while minimizing competing signals and beam damage. (B) Contrast across a larger energy range, putting the absorption edge in context. (C) Schematic of RSoXS transmission experiment demonstrating how  $\vec{q}$  primarily probes the in-plane structure of the film. (D) Chemical structure of the polymer and fullerene and a schematic showing the competing structures of film roughness and internal film structure. (Right) Resonant and nonresonant scattering, showing the enhancement of contrast between materials at an absorption edge and reduction of vacuum contrasts. RSoXS, resonant soft X-ray scattering

nanoscale materials fluctuations are revealed in the angular intensity variation of scattering pattern in the far field.

Ideally, one desires to invert this measured Fourier transform to achieve the real space map of  $\overleftrightarrow{\chi}(\vec{r})$  and the nanostructure it encodes. Unfortunately, the intensity measured is the magnitude squared of the electric field far from the sample, so all phase information  $\mathcal{F}[\vec{P}(\vec{r})]$  is lost. There are methods to directly recover phase information, and so solve for the real space distribution functions, but those require small coherent X-ray beams and more flux on the sample, which has not been achieved in RSoXS of soft materials before damaging them. The reader is directed elsewhere for those discussions.<sup>40,50</sup>

It is important to note that Equation (5) reduces in nonresonant form, where *n* is a constant proportional to the effective electron density  $\rho_e$ , to

$$I(\omega, q) \propto \left| \frac{\widetilde{\rho_e}(\vec{q})}{\omega^2} \right|^2, \tag{6}$$

or the magnitude squared Fourier transform of the electron density variations. This is traditional nonresonant scattering and has been extensively used to classify polymeric systems.<sup>1,2,51</sup> We cover common X-ray scattering analysis procedures in Section 3. Our purpose here is to show how RSoXS analysis can differ from this classical view of X-ray scattering.

#### 2.7 | Scattering contrast

One of the most important methods to predicting and understanding scattering in a heterogenous system is the contrast between different materials. In any structure measurement, contrast quantifies how differently the probe interacts with one material in a sample versus another. In RSoXS it is often defined as squared difference in index of refraction between two materials (the origin and consequences of which we will explore below) but more generally contrast is how well a technique measures some structure. The higher the contrast, the easier the corresponding physical feature is resolved from everything else. This is fundamentally a separation of where a material is (spatial variation) from how well we see it. Expressing this in an equation, a measurement  $M(\omega, \vec{r})$  is split into terms which are a function of some spectral parameter which we call the contrast of a material  $c_i(\omega)$  and terms which are a function of only the

spatial distribution of the material usually called the structure of the material  $V_i(\vec{r})$ :

$$M(\omega, \vec{r}) = \sum_{i} c_{i}(\omega) V_{i}(\vec{r}).$$
<sup>(7)</sup>

Here  $V_i(\vec{r})$  is the spatial distribution of one material in the system-the local volume fraction of a molecule in the sample. The sum is over all unique materials that make up the sample. The aim of microscopy is to measure  $V_i(\vec{r})$ , which is to specify the 3D distribution of each material in the sample, while spectroscopy aims to measure the fundamental spectroscopic properties  $c_i(\omega)$ of the materials.  $M(\omega, \vec{r})$  contains both but splitting it out is not trivial. Through decomposition techniques such as principal component analysis or non-negative matrix decomposition, given enough measurements M spanning wide enough ranges of  $\omega$  and  $\vec{r}$ , independent sets of  $c_i$  and  $V_i$  can be simultaneously found. This concept is commonly used for hyperspectral imaging (image at many wavelengths) or variable deuteration in neutron scattering. It is particularly powerful for RSoXS, which will be discussed in this subsection.

### 2.7.1 | Isotropic symmetry and binary contrast

RSoXS contrast variation has historically not been used for quantitative analysis but only to qualitatively simplify structural analyses by tuning to the correct energy or collecting spectra of scattering patterns. The most common usage assumes that there are only two materials present in the sample (a binary sample) and those materials are oriented isotropically (no polarization dependence) enabling a scalar treatment of  $\overleftrightarrow{\chi}$ . In an isotropic treatment the majority of the RSoXS literature is formulated in terms of the refractive index *n*, and we will adopt that convention. In this case it is common to apply the concept in Equation (7) to scattering from Equation (5) (in the Section 2.7.3 we will show how this is derived) giving

$$I\left(\omega,\vec{q}\right) \propto = \frac{\left|\Delta n(\omega)\right|^2}{\omega^4} S\left(\vec{q}\right)^2,\tag{8}$$

where  $|\Delta n_{AB}|^2 = (\delta_A - \delta_B)^2 + (\beta_A - \beta_B)^2$  is the squared difference in refractive index between material *A* and *B*, analogous to electron density in nonresonant scattering.  $S(\vec{q})$  is the Fourier transform (from  $\vec{r}$  to  $\vec{q}$  space) of  $V(\vec{r})$  the structure function of the material, containing the ensemble spatial information of a material. In this binary isotropic system, the contrast function is then

$$c(\omega) = \frac{|\Delta n(\omega)|^2}{\omega^4}.$$
 (9)

Notice the symmetry in both  $\Delta n$  as well as  $S(\vec{r})$  where each material is interchangeable resulting in the important Babinet's principle for binary systems. This is a direct consequence of the property of Fourier transforms allowing us to add any spatial constant to the real space side and obtain the same  $I(\vec{q} \neq 0)$ , a property, which will come in quite useful throughout this section.

#### 2.7.2 | Informal contrast in complex systems

The most basic use of binary contrast is to employ a photon energy where  $c(\omega)$  is high to enhance the scattering signal of the structure of interest (e.g., polymer domains) that are difficult or impossible to distinguish at nonresonant energies. Although the assumptions are not always explicit, this approach is valid so long as a system can be adequately approximated by those two isotropic materials. This is useful in many polymeric systems where the components have similar electron densities. Although if there are more materials, the concepts of binary contrast do not quantitatively apply (addressed in the following sections) often plotting each of the binary contrasts in a complex system can still qualitatively inform the source of scattering at any given energy. If one binary contrast is signifyingly higher than others at a particular energy, then a scattering feature whose intensity is enhanced at that energy is likely to arise from spatial variations of those materials. We want to stress that although this is not a quantitative analysis technique, it is a powerful and extremely successful informal tool in predicting experimental parameters and qualitatively explaining scattering features and is by far the most common use of contrast in the field. This concept is demonstrated for a polymer-fullerene blend in Figure 3 where the contrast function between materials is labeled "Material." Here, the material contrast varies by more than two orders of magnitude as the photon energy increases approaching the first resonance of carbon absorption edge at 284 eV. This means that the scattering signal from molecular domains will increase by that same amount in an experiment while photon energy is varied, enabling many uses in the nanoscale structural determination of organic electronic materials.<sup>9–11,52–55</sup>

Even though there may only be two isotropic materials in a sample, surface roughness or voids in the sample may also be present (usually at least roughness). Due to the thin film nature of most RSoXS measurements, this is more important than techniques, which measure thicker samples, where the relative contribution of surface roughness is lower. Scattering from these features is between a material and vacuum, which should be treated as a third material (and contrast) in the system (where  $\delta_{vac} = \beta_{vac} = 0$ ). Vacuum contrast with a material has its own unique energy dependence, and this contrast with either the polymer or fullerene is exhibited in Figure 3A, B along with binary contrast between materials. Vacuum contrast typically is high far from the absorption edge but is suppressed approaching it, although it is also enhanced dramatically in resonant peaks through absorption edges. Figure 3 therefore displays how qualitatively monitoring intensity changes of a scattering feature while tuning the photon energy can help identify the source of that feature.

One might attempt to isolate an individual contrasts and to minimize all others in this binary contrast view, but because the contrasts are coupled, this can never be done well at a single energy. We are limited to the incidental arrangement of optical constants in the system, and all combinations must be considered. For instance, as demonstrated in Figure 3A often the maximum material contrast also has maximized vacuum contrast. One must always rely upon other factors to fully discount these other scattering sources, including the structure factor intensity (i.e., knowing the surface roughness is low) and or structure factor shape (i.e., measuring the surface roughness separately and knowing it has a characteristic feature size that is far different that being examined) to justify the assignment of scattering intensity to one contrast or another.

A related qualitative use of contrast is index matching: to minimize some otherwise large obscuring scattering features to pick out other signals. If we can pick energy where either refractive indices are very close to another material or vacuum, often called an index-matching point, then that material will resemble vacuum and so its scattering can be reduced, allowing another material of interest to dominate the scattering pattern.<sup>55,56</sup> An important caveat in considerations of index-matching which makes resonant soft X-rays more complex than nonresonant X-rays and neutrons is both  $\delta$  and  $\beta$  contribute similarly across an absorption edge, so contrast has two components. Index matching is not just a matter of making the  $\delta_A \cong \delta_B$  but the  $\beta$  components must also match. In other techniques, changes in  $\beta$ across an edge are often much smaller in magnitude and can be safely ignored.

To summarize, binary contrast is a useful tool in RSoXS analysis, both in preparing for experiments and doing initial analysis to understand when a scattering feature corresponds to structure between certain materials. However, it has limited uses as systems gain complexity, and although we can in some ways reduce a complex system into a sum containing terms resembling binary contrasts, we will show there are simpler way of approaching these problems. While in a simple twocomponent system, it is informative to think in terms of structure between pairs of materials, formalizing the idea into individual material structure and correlations between materials can lead to an analysis that is both conceptually simpler and quantitative.

## 2.7.3 | Quantitative contrast in multicomponent systems

In general, any complex system of multiple isotropic materials can be split up into the different contribution of the structure of each material and contrasts of those materials. Because this has not been thoroughly treated elsewhere in RSoXS relevant terms, we will be more detailed in our description of this important concept. This serves three purposes. First to highlight where in the derivations key assumptions are made. Second, we hope to encourage this more complete treatment of RSoXS in future analysis, given the distinct advantages over viewing all scattering in terms of simpler binary contrasts. Finally showing an outline of the steps taken in the isotropic case is an important starting point in the hope to inspire future work beyond this review completing a polarization-sensitive treatment.

We start back with the Born approximation in Equation (5) (focusing on the last equality), where we write the isotropic version of this equation and leave off the scaling factors and polarization correction factors:

$$I\left(\omega, \vec{q}\right) \propto \left|\frac{\tilde{n}\left(\omega, \vec{q}\right)}{\omega^2}\right|^2.$$
 (10)

Here we have used the fact that we can add a constant (in this case 1) to a Fourier transform (indicated here by ~) to combine from  $\delta$  and  $\beta$  into *n*. If  $n(\omega, \vec{r})$  is parameterized as the autocorrelation function, then the phase component is removed at this point.<sup>57</sup> Assuming that we account for the entire scattering volume, including all materials and vacuum, we can explicitly break  $I(\omega, \vec{q})$  into separate terms of the material spectroscopic and structure functions as we described in Equation (7):

$$I(\omega, \vec{q}) \propto \left| \frac{\widetilde{n}(\omega, \vec{q})}{\omega^2} \right|^2 = \sum_a \sum_b \frac{n_a(\omega) n_b^*(\omega)}{\omega^4} S_a(\vec{q}) S_b(\vec{q}).$$
(11)

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By starting with the autocorrelation of n, rather than n itself, S are all real and so the cross terms ( $S_aS_b$  and  $S_bS_a$ ) can be combined. We split the sum into "primary" terms of shared indices and cross terms obtaining

$$I(\omega, \vec{q}) \propto \sum_{i} \frac{|n_{a}(\omega)|^{2}}{\omega^{4}} S_{i}(\vec{q})^{2} + 2\sum_{i} \sum_{j>i} \left(\frac{n_{a}(\omega)n_{b}^{*}(\omega) + n_{a}^{*}(\omega)n_{b}(\omega)}{\omega^{4}}\right) S_{i}(\vec{q}) S_{j}(\vec{q})$$
(12)

Offsetting the indices of refraction by a constant again subtracting vacuum index of refraction (n = 1) from each and simplifying and combining terms we can obtain the following result

$$I(\omega, \vec{q}) \propto \sum_{i} \frac{\delta_{i}(\omega)^{2} + \beta_{i}(\omega)^{2}}{\omega^{4}} S_{i}(\vec{q})^{2} + 2\sum_{i} \sum_{j>i} \frac{\delta_{i}(\omega)\delta_{j}(\omega) + \beta_{i}(\omega)\beta_{j}(\omega)}{\omega^{4}} S_{i}(\vec{q})S_{j}(\vec{q}),$$
(13)

where *i*, *j* are over all non-vacuum materials. The vacuum terms go to zero with this approach making each primary term contain properties of a single material, while the cross terms are properties of each pair of materials.

Because we could have subtracted any optical constants, the same  $I(\omega, \vec{q})$  can be split into different contrasts and structure factors where different terms are canceled out. A common practice is to choose a material to offset all optical constants rather than vacuum as we have chosen, changing all contrast factors to resemble binary contrast functions with that chosen material.<sup>57,58</sup> In this way, in a system of two materials (again, discounting vacuum) one can obtain Equation (8). Downside of this choice in complex systems are the unnecessary complication of terms, making the primary terms dependent on properties of two materials and the cross terms properties of three, as well as the necessity of retaining vacuum primary and cross terms. Because in RSoXS, samples are often thin films (again, different from techniques such as neutron scattering where scattering volumes are macroscopic) vacuum contribution to scattering can be considerable, suggesting that the form of Equation (13) is the better choice in many instances.

The primary term structure functions  $S_i^2$  can be split into the familiar structure or form factors from classical scattering theory, representing the scattering pattern as if it were of that material alone, isolated in vacuum. The 26424169, 2022, 7, Downloaded from https://onlinelibary.wiley.com/doi/10.1002/pa.20210414 by National Institute Of Standard, Wiley Online Library on [14/10/2021]. See the Terms and Conditions (https://onlinelibary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

cross-term structure functions  $S_iS_j$  on the other hand quantify the interference effects between those two materials or the spatial correlation of the materials within the system and as such, they can be negative. The magnitude of the cross terms must be less than or equal to the primary terms, so the total sum must be positive or zero.

Because we can make this split into spectral contrast functions and spatial structure functions, given enough  $\vec{q}$ ) measurements of  $I(\omega, \vec{q})$ , in principle, even making no assumptions and using Equation (13), each structure and contrast function can be found. An important point when solving this equation in practice is although an agnostic decomposition fit is possible, the identification of which basis set is fit (what offset of the optical constants is used) is impossible using only  $I(\omega, \vec{q})$ . By embedding any knowledge about the spectral or structural properties of any material and using these as essentially fixed eigenvalues or eigenvectors of the decomposition this ambiguity can be removed. The yet unfulfilled promise of this quantitative decomposition approach to RSoXS data analysis is that the chemical properties  $(\delta, \beta)$  of each component, its distribution within the system  $(S_i^2)$ , and the correlations between each pair of materials  $(S_iS_j)$  can each be isolated and measured. The decomposed structure functions could be quantitatively fit to classical scattering models, while measuring optical constants of a material distributed in a film could flip the paradigm from using spectroscopy as a fingerprint to understand RSoXS, to instead RSoXS revealing a material's in situ nanoscopic electronic structure directly. To date whether for the complexity of the mathematics or the lack of computational tools, quantitative contrast variation has only been conducted once using RSoXS on a polymer system.<sup>58</sup> Although this work did not conduct a full decomposition analysis, they did use quantitative contrast variation and absolute scattering intensity determination, which will be discussed in Section 5. Although the concept of binary contrast has been used effectively as a qualitative tool, quantitative decomposition rather than simple identification of scattering features promises to remove ambiguity and reveal subtler structure at the same time. A goal should be the development of accessible tools to allow routine quantitative contrast variation and decomposition.

It is informative to look to contrast variation techniques in other scattering fields for comparison. In neutron scattering, where the contrast stems from the nuclear interaction with neutrons, commonly contrast variation is accomplished by replacing hydrogens with deuterium either in the material or more often in the surrounding medium, until the desired level of contrast is achieved, either accentuating or minimizing the scattering contrast between different components. While the contrast can be changed with high fidelity, this technique requires that the structure factors of different samples with different isotope makeups do not change. Unfortunately, it has been shown that thermodynamic properties and even structure formation can be affected by deuteration or even placing polymer nanostructure in D<sub>2</sub>O.<sup>59,60</sup> The unique power available with resonant X-rays is the structure is identical and so unchanged during variation, and one need only change the incident X-ray energy to vary the contrast in situ.

#### 2.7.4 | Orientational self-contrast

One of the most unique powers of resonant X-rays comes into play when  $\stackrel{\leftrightarrow}{\chi}(\vec{r})$  can no longer be simplified into a scalar, meaning that the X-ray interaction is dependent on molecular orientation. The simplest approach is a uniaxial approximation, which reduces the tensor index of refraction to components of  $\vec{E}_{o}$  parallel and perpendicular to a unique molecular axis.<sup>30</sup> The uniaxial approximation closely matches both the molecular symmetry of many polymers, which might have one unique axis and rotational symmetry about that axis, or the LC like stacking which is common in polymers with side chains or aromatic centers where there is a preferential packing direction and more disorder in other directions. Whatever the source of the symmetry, these two principal indices of refraction for a uniaxial material are often then to simply treated as two different isotropic materials in the system to create orientational self-contrast. To a basic approximation this is true, and we will use a term orientational self-contrast informally, however as covered in the next section, there is no formal definition of contrast in anisotropic systems. Still, it is a powerful and useful concept. Regions of a material oriented parallel to the electric field can look effectively like a different material than regions oriented perpendicularly. This means that at energy where this orientational selfcontrast is significant; the orientational correlations within a single material at the nanoscale can be measured just as if they were domains of different materials. This is independent of the material's level of crystallinity. Although a crystalline domain has orientational correlations, it is not necessarily the only source of long-range structure and using orientational self-contrast, the molecular orientation correlation length (OCL) propagating through otherwise amorphous regions of a material can be measured.61-63

An important clarification of language, often we refer to these orientational correlations revealed by polarized RSoXS as orientational order, this should be understood to be quite distinct from the "order" in an the orientational order parameter, which is a measure of overall amount of orientation within a film. Orientational order discussed in RSoXS context comes from the scattering view of order as extended local spatial correlations. It is a measure of local molecular orientation correlated nanoscopically within a sample.

#### 2.7.5 | The breakdown of contrast

There are a few ways that when we consider an oriented material, the very concept of a contrast breaks down. The fundamental requirement for defining a contrast (as in something of the form of Equation (7)) is the separation of a material structure and contrast, such that the structure factor is independent of wavelength and contrast independent of location. The separation does not have to be linear as in Equations (7), (8), and (11), but in an anisotropic material, local orientation will have to appear both in the structure factor and the optical constants, so the two terms cannot be linearly independent. This is a grand challenge in the RSoXS community, to find such a resonant aligned structure factor definition that can be separated from the optical constants such that a contrastlike decomposition is possible. With extra knowledge about a system, such as crystallinity resulting in diffraction peaks, simplifying away from the material centric view to an atomic one, this has been dealt with which will be discussed below,<sup>64</sup> but to our knowledge no diffuse scattering equivalent has been found even in the most basic uniaxial approximation.

Part of the fundamental complication is depolarization in scattering, although in optics is known as modeconversion. If we look back at the origin of the induced polarization field this can be seen most easily.  $\vec{\chi}(\omega) \cdot \vec{E}_o$  is not a scalar operation when  $\stackrel{\leftrightarrow}{\chi}$  is not reducible to a constant, meaning the direction of  $\vec{P}$  is not necessarily in the same direction as  $\vec{E}_o$ . If we split a material into one unique (often referred to as parallel) and one mixed perpendicular components in a uniaxial approximation the problem comes for material oriented somewhere in between. The X-rays will excite both orbitals along the parallel axis and those perpendicular to the extraordinary axis, but the excited states themselves will be in their respective directions. We must remember that each excitation to a bound orbital is fundamentally in a fixed direction determined by the geometry of the moleculerecall Equation (1) and origin of the transition dipole. In simple terms, when an electron moves coherently from a ground state to an excited orbital and back to the core

once again, the direction of the decay determines the polarization of the outgoing wave.

Although it might seem counterintuitive, this happens in all materials, but it is only revealed in an anisotropic material. In an isotropic material, the states are the same in each direction, so the only thing determining the rate difference, (and so the final outgoing polarization of the scattered wave) is the geometrical dipole moment. However, if the states have angular dependence, then this changes the relative strength of excitations, changing the relative occupation rates of each direction, and rotating the emitted polarization. This anisotropy is encoded in the  $\chi$  tensors.

When scattered waves from differently oriented parts of the system have different polarizations, they cannot interfere and produce scattering patterns in the same way. The easiest way to treat this is each Cartesian component of the scattered wavefront interferes with itself separately. Generally, a split is made between the polarized component, those scattered waves matching the incident polarization, and the depolarized component, those scattered waves with orthogonal polarizations to the incident field. See<sup>30</sup> for the breakdown of this in the uniaxial example. Measuring any polarization component separately at every pixel of a detector is difficult with current technology, but it is possible in special geometries such as the Brewster's angle.<sup>65</sup> Depolarized scattering will generally be weaker than polarized scattering because each excitation was a dipole interaction. Although these depolarized fields can be calculated, they further complicate a clean split between structural and spectral aspects.

Because of the breakdown of contrast as a quantitative concept in any nanoscopic anisotropic system, and the lack of analytic treatments of polarized-RSoXS, the only approaches for rigorously dealing with anisotropic materials thus far is numerical forward simulations.<sup>30,66</sup> With modern high-performance computing resources, this is expected to be a standard way to analyze and fit anisotropic RSoXS spectral scattering sets in the future.

We want to be clear that an analytical contrast-like treatment of polarized X-ray scattering is not in principle impossible, but rather that there is no linear decomposition of spectral and spatial components as are in the familiar concept of contrast given in Equation (7). A nonlinear but still decomposable functional relationship should be possible and would be a welcome advance in RSOXS analysis. With this advance a truly agnostic decomposition of a system into a number of components, their chemical properties as well as nanoscale spatial and orientational structures could be measured and determined simultaneously.

#### 3 | RSoXS IN PRACTICE

Now that we have covered the theoretical underpinnings of RSoXS, it is important to address how the technique is accomplished in practice. This includes sample prep, experimental methods, and analysis best practices that exploit the power and avoid the complications of this unique scattering tool in the measurement of soft matter and polymeric systems. We will again in this section point the reader to well established resources for more general scattering and spectroscopy practices and cover only those unique intersectional aspects of RSoXS which are not well covered in these other sources.

## 3.1 | RSoXS compared to other resonant scattering techniques

RSoXS measurement of soft matter is distinguished in practice from otherwise similar resonant X-ray techniques primarily due to the different materials properties and scope of scientific questions as compared with hardcondensed matter. Resonant scattering on hardcondensed matter is often called REXS<sup>3</sup> or ASAXS or resonant diffraction<sup>67-70</sup> but sometimes when employed at lower energies is also called RSoXS.<sup>71-73</sup> Although these studies employ the same physics of scattering at an absorption edge, in practice little common language is used in RSoXS of soft materials. Employed in soft matter there is a nearly universal use of the index of refraction to explain and understand scattering, whereas for hardcondensed matter, scattering factors are generally preferred. This is primarily because REXS generally measures highly crystalline materials with the coherence lengths well above anything practically achievable in soft matter. Thus, the focus is to employ diffraction peaks and unit cell models to probe atomic placement. These crystalline lattices simplify the analysis considerably, and scattering factors are a practical treatment. For RSoXS of soft matter, on the other hand, it is almost always diffuse scattering or highly paracrystalline peaks, which are examined, so systems are almost always coarse grained on a material basis. Thus, rather than the placement of atoms in a unit cell, it is generally the placement of materials in nanodomains. This measurement challenge shares much more in practice with visible wavelengths, and thus the optical index of refraction is more useful. Another reason is the development of RSoXS from thin film spectroscopy and reflectivity, where the index of refraction is traditionally used. Another consequence of the relative level of disorder in soft matter systems is that where crystalline materials deal with conduction and valence bands, in soft matter it is more often

molecular orbitals (such as the lowest unoccupied molecular orbital—or LUMO) that are used. Band systems do not properly exist in these highly disordered materials. In many hard-condensed matter systems, both the magnetic and electric fields interact, and spin orbit coupling effects can play an important role, whereas in organic materials, composed of generally low-Z atoms such as carbon, oxygen, and nitrogen, this is not usually the case.

Perhaps most starkly, the use of resonance is often utilized completely differently between RSoXS and REXS experiments. In REXS, the structure is relatively well understood, and the details of spectral resonances are measured for their fundamental physical information about subtle shifts within unit cells, and orbital densities and electron transitions to test theoretical calculations. In contrast soft matter spectra are often used agnostically as fingerprints of different material identities in a highly heterogeneous systems. Furthermore, the measurement of soft matter means that in general, beam damage is much more of a concern, so experimental methods that minimize the flux density of X-rays through the sample are necessary.

One special example of resonant diffraction applied to soft matter is in multiwavelength anomalous diffraction (MAD),<sup>74,75</sup> which primarily targets protein crystallography. Here a focus on diffraction aligns analyses toward scattering factors, but importantly the absorption edges of interest are often high-Z elements that are synthetically added as tags such as bromine, selenium, or gold. Longer wavelengths are also being employed in some circumstances,<sup>76</sup> although not down to the soft X-ray range where UHV environments are needed. RSoXS applied to polymers and small molecules utilizes the intrinsic low-Z edges such as carbon, nitrogen, and oxygen, which requires very different experimental considerations. The sulfur edge is emerging as a strategic opportunity at the higher end of soft X-ray energies.

#### 3.2 | Measurement practicalities

#### 3.2.1 | Sample considerations

RSoXS can produce nanoscale structural information on any system with nanoscale chemical or orientational heterogeneities. At the carbon edge, this means heterogeneities from  $\approx 2$  nm to  $\approx 3$  µm can be seen directly in the scattering intensity (this can be extended considerably with additional knowledge about the system, as we discuss below) while at the sulfur edge, both limits are approximately an order of magnitude smaller, from  $\approx 0.3$ to  $\approx 300$  nm.

RSoXS samples generally must be thin films. As with other scattering techniques, an optimal thickness is the penetration depth of a material (where transmission  $I_t$ through thickness x of a material with penetration depth  $x_t$  compared to incident light  $I_0$  is approximately  $I_t = I_0 e^{-x/x_t}$ ), and about one order of magnitude above and below the penetration depth are generally the limits of being able to extract quantitative information, although qualitative information might be available beyond these limits. The penetration depth of materials can vary over the soft X-ray range, but sticking to the most commonly used carbon absorption edge for polymeric materials,  $\approx 100 \text{ nm}$  is a good estimate. This means samples (10-1000) nm thick is generally acceptable, although the data quality declines toward both extremes. At the thin side, beam damage becomes a major concern as increased exposure times are necessary, while at the thick side the thin film approximations begin to break down, absorption reduces the signal and fluorescence becomes a larger component of a measured signal. There is promise of work in a reflection geometry,<sup>56,77</sup> which would allow for at least the surfaces of bulk samples to be measured. The thickness requirement for transmission measurements extends to the film substrate as well. Thus, thin film samples are typically delaminated from their original substrate (often by employing a sacrificial watersoluble layer) and fixed to Si substrate window frames that hold a (typically 100 nm) SiN membrane. The specialized substrates can be purchased commercially ready to mount into RSoXS instruments.

The second practical requirement is RSoXS experiments must take place in high-vacuum environments. This is because the penetration of soft X-rays through air is short. Recent advances using enclosed sample environments developed originally for TEM, which has a similar requirement for thin films and a high-vacuum path for electrons, enable liquid scattering RSoXS, which opens up whole new classes of materials to be examined, including biological assemblies and in situ electrochemical processes.<sup>78</sup> Details of these exciting advances will be discussed in Section 5. Further use of sample environments promise to expand the applicability far beyond strictly thin film studies.

#### 3.2.2 | RSoXS instrumentation

Soft X-rays are generally created at synchrotron sources. These are large generally national facilities with proposal systems for experimental access.<sup>79,80</sup> The vast majority of polymeric RSoXS work has been done at two synchrotron beamlines: The 11.0.1.2 beamline at the Advanced Light Source (ALS)<sup>19</sup> and the recently opened SST-1 beamline



FIGURE 4 RSoXS Beamline schematics. (top) the instrument at ALS beamline 11.0.1.2 where X-rays are detected by the (A) CCD camera, (B) sample goniometer, (C) photodiode detector, (D) beamstop, (E) exit slits, and (F) sample location. Adapted from ref. 19 with permission. (2012) American Institute of Physics. (bottom) the instrument at NSLS-II beamline SST-1, with the incoming beam (B), TEM sample holder (C), and multi sample holder (D). Two cones representing the scattering at the wide angles (F) and small angle (H) sample locations, and the beamstop stopping the direct beam from hitting the CCD detectors (E) and (G). Adapted from ref. 20 with permission. (2021) Institute of Physics. ALS, Advanced Light Source; NSLS-II, National Synchrotron Light Source-II; RSoXS, resonant soft X-ray scattering; TEM, transmission electron microscopy

at the National Synchrotron Light Source-II (NSLS-II),<sup>20</sup> which while free for use by merit-based proposal process, limit the general availability and the practical scope of potential experiments. For energies at the upper end of the soft range (>2 keV), often called tender X-ray scattering facilities are more widely available.<sup>81–83</sup>

The newer instrument at the SST-1 beamline has effectively doubled the user access to RSoXS with a wider energy range and similar polarization capabilities.<sup>20</sup> A unique quality of this newer instrument is the larger and lower noise area detectors and increased automation of the process to locate ideal sample positions. However, ALS 11.0.1.2 is more capable of reflectivity geometry measurements. The layout of each chamber is shown if Figure 4. The reflectometer-based circular design of the 11.0.1.2 chamber gives great flexibility in placement of the single detector to collect scattering in different geometries. Meanwhile the two fixed locations for the larger detectors in the SST-1 chamber allow for fixed small and

wide-angle measurements. The SST-1 chamber also as built in TEM sample holder compatibility for one of the sample manipulators. An additional chamber with TEM sample holder capability is in commissioning at 11.0.1.2.

Carbon contamination of beamline optics is always a problem for any carbon edge measurements, leading to lower and varying levels of flux at key energies along with potentially disrupting polarization states of the beam. Often a good practice is to use a clean portion of a mirror if possible, although work to reduce or eliminate this issue<sup>84,85</sup> has the potential to increase signal intensity and dependability, thus increasing throughput and time resolution. Implementation of these mitigation methods at the SST-1 beamline has proven successful in largely eliminating the carbon dip thus far.<sup>20</sup> This effort, plus next-generation soft X-ray detectors<sup>86</sup> could push typical exposure times to well below a second, enabling new in situ experiments, and greatly increasing throughput and therefore access.

An important aspect of soft X-ray beamlines, which is not often mentioned in spectroscopy, but is quite important for scattering is the presence of higher harmonics of the intended energy being present in the X-ray beam. This is because most common sources of monochromatic soft X-rays, (undulators, grating monochromators) both having quite strong responses to these higher energies, and it is difficult to remove them. In particular, the odd orders 3, 5 times the indented energy can be intense, although even orders are also present. The reason these harmonics are pernicious in scattering experiments, is because they cause extra scattering features to be present which can confuse analysis. This is often more evident when there are sharp peaks, but it is perhaps more prone to misinterpretation when the features are broader and the integer multiple of size scales present in the primary beam are not as apparent. These higher harmonic features are hopefully not resonant, and so their resonant effects should not be a problem, which is why in spectroscopy they can generally be seen as a background shift, this is not always the case. For instance, features at the oxygen edge might show up as second order of carbon, or nickel might show up as third order. When combined with the carbon dip discussed above, the effect directly at the carbon edge can be even worse, with even a majority of photons being higher harmonic contamination.<sup>19</sup> Both of the discussed beamlines have mitigation efforts to remove this contamination, but one of these efforts, using additional optics at higher angles, though effective, can increase the carbon dip as these optics become coated with carbon as well. Future beamline designs might use modified sources such as aperiodic undulators<sup>87-89</sup> and specially designed optics<sup>90</sup> to sacrifice a small amount of flux but largely remove the higher harmonics. The suggested best practice at current facilities is to be aware of this effect and wary of integer multiples of similar scattering patterns (scattering features at q also being present at q/2, q/3, etc.) during analysis, and check the energy dependance of each part of the scattering signal to try to decompose the effects.

#### 3.2.3 | Acquiring RSoXS data

Nearly universally, RSoXS is conducted in transmission geometry, with the X-rays at 90° incidence, normal to the thin film, as depicted in Figure 3C. For such an experiment, there are four main considerations: measuring a representative part of the sample, choosing the energy at which to measure, detector placement to determine the angular range of scattering that is collected, and finally choosing an appropriate exposure time. For all these considerations, knowing as much about the sample as possible from accessible benchtop methods helps to ensure the most useful data is collected.

To ensure that a representative part of the sample is measured, visible light microscopy of a sample can be used to locate film cracks or dust to be avoided. Additionally, acquiring scattering patterns at many positions across a sample at a fixed energy are good practices to find a representative position. While blatantly poor sample regions will be clear in the raw charge-coupled device (CCD) image pattern, identification of subtle differences to critical aspects (e.g., feature q-position and intensity) will require immediate data processing and plotting into scattering profiles at the beamline. Both instruments employ software to do this, although as we discuss in Section 3.4.9, improved live analysis software will be needed as experimentation time is decreased.

To decide on what scattering angles to collect, one must consider the size scale of the expected structure in a sample and which absorption edge will be used. It is a good idea to collect the largest angular range that time allows to ensure unexpected structures are not missed. A broad range of size scales usually requires at least two sample detector distances. At the 11.0.1.2, this is accomplished by translating the detector, while at SST-1 there are two detectors just for this purpose.

To ensure the optimal X-ray energies are used, measurement of the NEXAFS spectra of the raw materials (molecules) ahead of time is recommended. Even conversion of NEXAFS spectra into complex optical constants and calculation of binary contrast functions can greatly aid in selection of the best photon energies of interest. Lacking this, one can measure scattering patterns at many energies across an absorption edge, so that points near maximal and minimal contrasts are always collected. This approach requires more experimental time and sample damage can become an issue, but is generally a best practice. It is of note that NEXAFS spectroscopy itself is possible at both RSoXS beamlines and can provide basic information on energies of interest.

Normal scattering intensities from polymers generally produce adequate scattering intensity in 1 s to 1 min exposures. Too short of an exposure results in noisy data, while too long has the chance of saturating the detector pixels and damaging and changing the very structure one is trying to measure. Unfortunately, staying in one place and exposing much energy for a long time will eventually damage most soft matter samples, so balancing all of these concerns is a challenge, which merits redundant samples and careful experimental planning in collaboration with the beamline scientist of the facility in question. Spot checking scattering patterns at a few energies at different locations before and after a long set of exposures 1214 WILEY- POLYMER SCIENCE

on a sample are the best way to check for beam damage. To mitigate damage, shortening exposures or spreading out scans across similar locations or similar samples can help, although some overlap is necessary to ensure the areas are equivalent. This is where sampling many positions is useful in identifying multiple similar areas across a sample.

If a sample is expected to have anisotropic properties, either a preferential whole-film in-plane orientation or any locally oriented regions, it is also recommended that scattering patterns from two polarizations are measured (horizontally and vertically polarized in the lab frame or, although it is not yet widely used, circular and linear). First this disentangles true polarization-dependent scattering from whole-film in-plane molecular orientation effects (e.g., from a stretched film). Second, the two datasets can be subtracted to eliminate both parasitic scattering (e.g., from dust which is almost always anisotropic) and be used to significantly enhance signal to noise of the anisotropic ratio—a typical target measurement discussed in Section 3.4.8.

In addition to the scattering patterns themselves, spectroscopy best practices apply as well.<sup>91</sup> The most important secondary measurement is the incident flux for each energy.<sup>78</sup> At some beamlines, the incident flux can vary by more than an order of magnitude across the carbon absorption edge. Comparison with contrast functions (and therefore positive identification of the source of scattering features as described in Section 2.7) will require first normalizing scattering intensities to the incident flux. Additional ancillary measurements highly suggested to be collected at the time of an experiment are any calibration samples to ensure sample and detector geometry are well understood, and detector background images.

A supporting measurement that can be important depending on the level of analyses desired is transmission NEXAFS spectroscopy on all samples at the position where scattering was done. This is because background X-ray fluorescence (XRF) is not filtered out with current detector technology. Knowing absorbance at each energy, one can calculate the XRF signal and subtract it later if necessary. Another use of the NEXAFS spectra is to calculate film thickness of the actual patch of film illuminated for scattering, which can be used to calculate scattering volume and therefore normalize scattering intensities appropriately. Finally, the features in the NEXAFS spectrum itself can be used to both confirm energy calibration and confirm the materials in the sample were those expected. This is collected by a diode in the direct beam, blocking the direct beam from hitting the CCD detector. Because of the sensitivity of CCD detectors, and the relatively lower intensity of scattering from the direct beam in

soft X-rays, the direct beam not only cannot be collected, but can damage the CCD detectors if it is incident for long, so a beam stop must be carefully aligned in front of the detectors anyways.

To accurately measure three-dimensional structure within a thin film quantitatively it is suggested to measure scattering of the sample when tilted away from normal incidence (sometimes up to 70 degrees from normal can be achieved).<sup>58</sup> This allows measurement of the out-of-plane morphology and has been used effectively to allow quantitative analyses.

In addition to collecting enough data, ensuring the quality of data during the experiment is equally important. All the general rules for collecting good scattering patterns, getting adequate signal to noise in the q range of interest of course apply, while at the same time the rules for collecting good spectroscopy apply. Processing the data into scattering profiles at the beamline during the experiment is highly recommended, so there is adequate time to remeasure samples that resulted in poor data.

#### 3.3 | What can RSoXS measure

RSoXS provides a unique intersection of capabilities for characterizing soft matter morphology. We will discuss the limits and applicability of RSoXS as a guide to what kinds of samples RSoXS can help to measure. First the different levels of size scales which RSoXS can measure, which can be often confusing, the local molecular information inherent in the resonant phenomenon, the scattering size scales from spatial fluctuations, and finally the beam-scale size sensitivity. Then we discuss how the beam damage consideration generally distinguishes the measurement considerations of RSoXS for otherwise similar techniques, and how RSoXS is most powerful as part of a multimodal characterization of materials.

#### 3.3.1 | Molecular orbital information

The X-ray resonance is an advantage of RSoXS as a morphological tool, as described in comparison to visible wavelengths and nonresonant wavelengths in the Section 2. Unlike techniques sensitive to the nucleus, such as neutron scattering and Nuclear Magnetic Resonance spectroscopy, RSoXS encodes unoccupied electron orbital structure in its spectral response. In this sense, the size sensitivity of RSoXS reaches the molecular structure scale, and gives a unique orientational probe of molecular structure independent of any unit cell.

# 3.3.2 | Morphological correlation information

Because the scattered intensity is fundamentally a measure of spatial frequencies present within a material, like other small angle scattering techniques there is no unique real-space structure, which can be directly reconstructed. The size scales that are available to RSoXS through scattering depend on the angle of scattering, which can be collected. Practically this sets a small size limit at half of the wavelength of the X-ray where the scattering angle is 180 degrees (and at ~80 deg<sup>20</sup> and ~120 deg<sup>19</sup>) and an upper size limit of the minimum scattering angle collectable near the beamstop which is limited by the beamsize and sample detector distance, which at modern facilities<sup>19,20</sup> results in about 0.1 degrees. In real numbers at the carbon absorption edge, this means spatial variations between 3 nm and 3  $\mu$ m are directly measurable.

As with other scattering techniques fitting a model that is imposing some other knowledge about the sample can allow considerably smaller features to be fit to RSoXS data, although they cannot be seen directly. This can include exploiting an artificial or natural crystalline lattice and using diffraction anomalous fine structure (DAFS) to recover sub unit cell resolution.

#### 3.3.3 | Morphological real-space information

A single RSoXS measurement measures all of the sample within the illuminated footprint of the X-ray beam on the sample. This means that rastering the beam across a sample can map the sample at a resolution of the beam footprint, which is generally between 10 micrometers and 1 mm in size depending on the beamline settings. Because RSoXS in general does not exploit full coherence, RSoXS beamlines are not designed to utilize phase retrieval schemes such as coherent diffractive imaging and ptychography. Although there are some successes in certain cases,<sup>50,92,93</sup> the radiation damage due to the beam has significantly limited the application of these techniques in soft matter systems.

#### 3.3.4 | Beam damage to soft materials

One of the defining features of many soft matter systems which make it fundamentally inappropriate for hardcondensed matter resonant scattering techniques and has proven difficult for modern diffractive imaging techniques using coherence is the fact that any probe which creates free high-energy electrons in soft materials will generally damage the material when exposed for long enough a time in a small enough area. The struggle with the design of soft matter X-ray measurements is obtaining enough information about a molecular system before significantly altering it. Although the measured scattering is elastic, and imparts no energy to the system, this is only a small component of interactions. Other interactions result in free electrons, which have many times the energy needed to break bonds. A defining difference between nanoscale imaging techniques like TEM or STXM and a scattering technique like RSoXS is that beam damage can be mitigated in scattering by simply increasing the footprint of the beam, spreading the radiation out across a larger area. Whereas when imaging near a molecular scale, generally spatial resolution can only be gained by probing each molecule until a satisfactory signal to noise in that spot is achieved, by being an ensemble measure of a material, scattering can spread the same flux over a larger region, and spatial resolution is gained by collecting the scattering at high angles. Thus, many molecules can contribute to the signal, and each individual molecule can receive a signifyingly smaller radiation dose. Other mitigation techniques, which are proving highly successful recently in TEM are cooling the soft matter system cryogenically and controlling the dose and mapping a system with the bare minimum of electrons to retrieve the structure from the measurement. While this approach can also work with RSoXS, it limits truly in situ measurements, so using the natural benefit of having a larger beam is in many cases preferable.

#### 3.3.5 | Multimodality

Because RSoXS is a scattering technique and limited to spatial correlations within a sample, the lack of the scattered phase in the measured signal means there is no way to recover the real space image of the sample directly, adding information from other techniques is often necessary. This extra information about a sample can both guide a choice of parameter space to measure and allow accurate fitting of RSoXS scattering patterns. Any real space microscopy which can guide the choice of a model are wise to measure ahead of beamtime.

NEXAFS spectra of the individual materials can also be critical to a successful RSoXS experiment. Ahead of an experiment, determining strategic measurements including points of non-resonance, isosbestic points, and binary contrast maxima and minima can all be used to ensure a successful RSoXS measurement. When analyzing RSoXS data, matching scattering intensity to a particular contrast, distinguishing vacuum contrast from different materials, or doing quantitative contrast variation will enable you to get the most out of your RSoXS data. For all these activities, NEXAFS spectroscopy of pure materials must be measured.

#### 3.4 | Analysis of RSoXS

Having collected scattering patterns across an absorption edge, the question of how to analyze the data is the next concern. Depending on the level of information known about the sample, this can proceed quite differently.

#### 3.4.1 | RSoXS processing

RSoXS data consists 2D scattering patterns acquired using several photon energies across an elemental absorption edge. Thus adding a dimension of spectroscopy to the scattering patterns, RSoXS can be thought of as a three-dimensional dataset. This fundamental RSoXS dataset is called hyperspectral scattering. Because a hyperspectral dataset has both scattering data and spectroscopy, the processing of these datasets must follow the best practices of both scattering and spectroscopy.

There are numerous sources of instrument fixed pattern noise which need to be identified and generally avoided, but if they cannot be, must be masked out of data before further processing. These sources can include any dark signals (why we have measured dark frames for each detector modality) parasitic scattering from upstream in the beamline (hopefully mitigated by slits, but often unavoidable), imperfections or dust on a samples (ideally avoided by taking images in a clean spot). Often it might be necessary to create a unique mask for each sample when doing final analysis. There is hope that machine-learning techniques might make this process considerably faster in the future, but now must be done by hand. At each location of the sample and detector, geometric corrections should be made correcting for the solid angle of scattering which that pixel collects, and the two dimensional  $q_x$ ,  $q_y$  position of each detector pixel, which changes with both in X-ray energy and CCDsample distance and geometry is calculated. At any given energy, these corrections are the same as done in a nonresonant scattering beamline and using traditional 2D scattering analysis tools. These levels of processing should be setup at the beamline, although exactly which corrections have been automatically applied to collected data should be understood and discussed with the beamline staff.

#### 3.4.2 | RSoXS data reduction

Once a processed dataset is produced, the first task is generally reduction of the hyper spectral dataset into 1D slices or averages. With current software, this is done generally one scattering pattern at a time, and once the parameters are selected, it is then applied to all of the scattering patterns in a hyperspectral set. These visualizations of individual scattering patterns, corrections, and processing can be done with the same software as is used in nonresonant scattering techniques using scattering reduction packages,<sup>94–99</sup> which are often ready for use at the beamline. If the pattern is symmetric about the transmitted beam, the pattern is typically integrated azimuthally into 1D intensity profiles as a function of q-magnitude I(q).

If the scattering pattern is not symmetric about the transmitted beam, the azimuthally integrated I(q) profile loses information and other visualizations and processing is necessary. For instance, polarization-dependent scattering anisotropy can result in sinusoidal intensity dependence with azimuth. In this case, the anisotropy can be visualized by extracting scattering profiles at varying azimuth to identify where the scattering is most anisotropic. For a quantitative measure of the anisotropy, the anisotropic ratio (*A*) can be calculated as both a function of q and energy. To do this, the scattering profile in the direction parallel to the photon polarization ( $I_p$ ) is compared with the scattering profile perpendicular to the photon polarization ( $I_s$ ) in the following "difference over sum" formula:

$$A = \frac{I_p - I_s}{I_p + I_s}.\tag{14}$$

With this formula, values of A range from +1 to -1 with A = 0 when the signal is isotropic.

#### 3.4.3 | Data visualization

The scattering intensities vary by many orders of magnitude generally falling off with a  $q^{-\alpha}$  power law where  $\alpha$ typically varies from 2 to 4.<sup>2</sup> A typical measurement qrange can span two or three orders of magnitude.<sup>19,20</sup> Thus, a hyperspectral dataset often contains a considerable dynamic range of intensities. The first obstacle is viewing the data in a single useful form. Each single scattering pattern can be viewed as an image with false color usually log-scaled intensities, and a spectrum can be viewed either as a movie, or as a grid of 2D datasets.

Generally, it is more informative to visualize and compare different datasets by examining the 1D profiles in a waterfall of profiles at different energies showing the spectral dependence of the scattering. This is the quickest way to visualize a complete hyperspectral dataset at once. With scattering patterns reduced to 1D, the spectral dimension can also be incorporated into 2D image plots

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with chemical information represented on the energy axis and spatial information on the q-axis.

Anisotropy can be visualized directly as by plotting A(q) for each energy, or the individual  $I_p(q)$  and  $I_s(q)$  profiles (generally adding shading between each pair helps to visualize anisotropy) in a 1D profiles and waterfalls. This can also be visualized for a full hyperspectral dataset as a pair of 2D plots of A and I both plotted in a 2D image, with one axis q, and one axis energy.

It is usually the case that multiple samples or multiple conditions of one sample need to be compared. In this common case, visualizing multiple complete hyperspectral datasets eventually becomes infeasible, so slices at particular q or energy values, or summations across different axes become necessary. In these cases plotting TSI versus energy or an integrated A versus energy are helpful simplifications, although equating these integrated values to structure directly should be done carefully.

Although the visualizations described in this section are often the first step in analysis and are typical of those exhibited in the literature, they are by no means the only ones. They are, however, most closely related to the familiar visualizations of nonresonant SAXS and SANS data, enabling one to use analyses and intuitions developed for those techniques to be applied to RSoXS. Further processing visualization strategies are applicable in more advanced levels of analysis.

#### 3.4.4 | Model-free analysis

What can a scattering profile tell us about a sample, without applying any other knowledge about a system? Because a scattering pattern is a Fourier transform of structure within a film, it can be thought of as a spatial frequency representation of the system. This is similar to a power spectral density analysis of microscopy, which provides a statistical size distribution of the spatial fluctuations (from phases, crystallites, etc.) in the sample, although scattering covers a much more statistically significant region (typically at least a  $10^5$  increase).

The rules of traditional scattering theory all apply in RSoXS and the clearest examples of a model free analysis, which can be quite powerful, is the determination of a classical structure factor or form factor. These are characteristic scattering patterns which indicate well-defined crystalline structure and monodisperse local structure respectively, and their appearance should be recognized as it can make analysis considerably easier if they exist. There is extensive coverage of structure factors and form factors in the traditional scattering literature,<sup>2,51</sup> we will only briefly cover ways to recognize them in a scattering pattern here, and readers are

directed to this literature for further steps. Structure factors are characterized by well-defined peaks in a I(q) profile, or a ring or even diffraction spot in a scattering pattern. Because of the nature of Fourier transforms, this can only arise from a periodic structure with a coherence length  $\xi_c$  related to the width of the peak  $\Delta q$  of  $\xi_c = 2\pi/\Delta q$ . Form factors on the other hand often have a characteristic fringe like pattern at higher q. If a structure factor or form factor are recognized, there are well known models which can be applied to the data to extract information about the structure of the system.

More commonly in disordered systems, if there is a shoulder or peak in the scattering profile, this can be assigned to an increased variation of those spatial wavelengths in the system commonly known as a characteristic length  $L_C$  often calculated from  $L_C = 2\pi/q^*$  where  $q^*$ is position of the scattering feature. Care must be taken here to not jump to a conclusion that  $L_C$  is the size of any particular structure without some other information, which would support this claim. By itself, it is just an indication that there are material variations at this size scale. This can best be seen in the example of scattering from dilute spheres or other well-defined form factors. While the diameter might be the most important feature size we are interested in, the scattering pattern will contain many "peaks" at q-values corresponding to much smaller sizes than the diameter. If we were to assign particular domain sizes or sphere diameters based on one of these peaks we would be misled about the structure of the system. Further discussions about the potentials for model free analysis can be found in the literature.<sup>51</sup> One particularly useful conversion of I(q) into real space is an inverse Fourier transform into the autocorrelation function g(r), but to do so, extrapolations of q from 0 to infinity are required.<sup>51</sup> Such an analysis, can provide model-free information on size of scatterers (domain, crystal, etc.) in a system, although identification of those features is not possible without outside information.

The most complete model-free analysis of a hyper spectral scattering set is an agnostic contrast variation decomposition, as outlined in Section 2. While possible (given the assumptions about the symmetry of materials discussed in that section—i.e., we know the materials are isotropic), to date a completely agnostic decomposition has yet to be demonstrated on an RSoXS dataset.

#### 3.4.5 | Model-based analysis

A model of some sort is necessary to go beyond this level of analysis and should always be stated. The most common models used will be those familiar from nonresonant scattering, including small angle X-ray and neutron scattering world.<sup>2,51</sup> Although we will not cover these in depth, they are always useful to try when fitting a single energy. As with each of the models we will present, these will take some bit of information about the sample and allow for much more precise and typically relevant information to be concluded. It is always important to understand and present clearly in the analysis exactly what assumptions the chosen model is making and how those choices are justified. In classical scattering analysis, these can be as simple as the number of materials and material phases and their volume fractions to assuming a specific structure (e.g., spherical core-shell morphology) within the sample. In RSoXS the simplest spectroscopic model might be adding in some knowledge about the chemistry of a component (e.g., an aromatic ring). All of this should be guided by outside knowledge such as sample preparation methodology, or other measurements such as spectroscopy and microscopy measurements of the samples. For example, a sample can be modeled as a two-phase system with roughly balanced volume fractions based on microscopy data or knowledge of thermodynamic interactions between the components. With such a model,  $L_C$  is often characterized as proportional to the domain spacing in phase-separated blends.<sup>100,101</sup> However, specifying  $L_C$  as a specific structural parameter (e.g., domain size or spacing) without firm justification to support the model can lead to misinterpretation.

The unique power of RSoXS is in the variation of scattering across an edge, often this information in itself can be extra information, which allows more determinative conclusions about structure from the scattering patterns. One can identify nonresonant structure, such as film roughness, at energies where vacuum contrast dominates (far from absorption edges) and compare that to scattering near an edge. If the scattering shape changes dramatically at resonance (e.g., a particular scattering feature is enhanced), then we assign that change to materialmaterial structure within the system. For example, in Figure 3D, the enhanced scattering peak can be assigned to material domain structure at 10s of nm compared to the suppressed feature at sizes near 1 um which can be assigned to roughness or voids in the sample. Unfortunately, once again, we cannot determine too much with simply the spectral data without some other knowledge about the symmetry or spectroscopy of the individual components. It is important to recall, as discussed in Section 2, that without information of what the materials are and their contrast functions, assigning materials to scattering features is not possible. For instance, the increased scattering might be a single material with different orientations (orientational self-contrast), or multiple materials, or some combination. With additional information, we

can eliminate some possibilities. For example, we might know a material is isotropic due to molecular symmetries, or that there are only two materials in the system, or that some unique spectral signature such as an aromatic resonance is only possible in a certain material. Any of this outside information might be used to justify conclusions about the origins of scattering features.

#### 3.4.6 | Phase purity and composition

Many RSoXS studies investigate domain purity in phaseseparated blends based on total (or "integrated") scattering intensity (TSI or ISI). This is based on the Porod Invariant formalism with the mechanism being that as domains become purer (irrespective of their size and shape) their scattering signal will become stronger due to increased contrast between increasingly different domain optical properties. Such a formalism was developed for a two-phase system by integrating Equation (8) over the three-dimensional q-space:

$$TSI = \int I(q)q^2 dq \propto \Delta n_{12}^2 \phi_1 \phi_2, \qquad (15)$$

where 1, 2 represents the phase (not material) and  $\phi$  are the phase volume fractions constrained by  $\phi_1 + \phi_2 = 1$ . The (q-integrated) structure factor in Equation (8) becomes the product of volume fractions. The difference of domain composition or purity ( $\Delta x$ ) resides in the contrast function where for a two-phase system of two materials *A* and *B* can be represented as

$$\Delta n_{12} = \Delta n_{AB} \Delta x_{12}. \tag{16}$$

Here  $\Delta n_{AB}$  is the material contrast function described earlier. On the other hand  $\Delta x_{12}$  is the root mean squared (RMS) composition fluctuation throughout the sample. Without a measure of absolute scattering intensity, a quantitative measure of  $\Delta x_{\rm RMS}$  is not possible, however, a thickness-normalized sample series can be compared for relative domain purity and is done frequently in organic electronics blends.<sup>29,102-105</sup> Such a measurement depends on several key assumptions, however, which cannot be made lightly. First there is an assumption that there are no other scattering signals (or other signals are insignificant). If RSoXS is acquired at a photon energy just below the first resonance, other signals such as scattering from roughness or voids are suppressed, XRF signals are usually insignificant, while material scattering is still enhanced (see arrow in Figure 3A). Orientational scattering, however, may still be present. Therefore, comparison of binary contrast functions, including

orientational self-contrast as described above, is important to confirm these assumptions are appropriate. Another important assumption in the integral is isotropic scattering. In particular, scattering in the out-of-plane direction can be significantly different due to thin film effects. Thus it is important to confirm that the bulk of the scattering signal comes from an  $L_C$  that is significantly smaller than the film thickness. RSoXS measurements with the film tilted as described above can be analyzed correct for this issue.<sup>58</sup> A third assumption that is there are only two phases in the system. However, through contrast variation decomposition described in Section 2.7.3, the TSI of a single phase can be extracted to measure domain composition.<sup>58</sup> A final assumption is that the phase volume fractions ( $\phi$ ) do not change significantly throughout the sample series. Although not definitive, evidence to support this assumption is can be obtained via microscopy of each sample to estimate  $\phi$ . It is important to address these four assumptions when attempting to calculate relative domain purity, and it should be noted that without other measurements or considerations, the TSI analysis only reveals the difference in domain purity between domains ( $\Delta x_{12}$ ), not the absolute purity for each domain  $(x_1 \text{ or } x_2)$ .

## 3.4.7 | Explicit model fitting of nanostructure

Having information about the system can also allow development of a model to fit the data. This can be a complete I(q) profile or the individual structure factors S(q) found through contrast variation decomposition. The use of models and fits, including Porod analysis, Guinier plots, Teubner Strey and more complicated polymer models are all covered well elsewhere<sup>1,2,51</sup> and should proceed the same as in traditional scattering. Common small angle scattering form factor (e.g., spheres, ellipsoids, rods, etc.) and structure factor (hard sphere, etc.) models are widely available,<sup>96</sup> with software for fitting discussed in Section 3.4.10 below.

While not described in detail here theoretically, resonant X-ray reflectivity (RXR) is a form or resonant scattering that is analyzed with model-based fitting. In this case, the depth profile of SLD is traditionally extracted using nonresonant X-rays or neutrons. RXR can be used to convert SLD into chemical identity and concentrations, which will be explored in Section 4 below. To analyze such data, the same concepts of separating spectrally resolved chemical information from spatially resolved structural information (this time exclusively in the direction normal to the sample film plane) can be achieved. Fitting software is widely available although currently limited to isotropic materials.<sup>106,107</sup>

#### 3.4.8 | Scaling scattering profiles

A common but controversial practice in RSoXS, which is perhaps more prevalent than other scattering fields, is to emphasize features in a scattering profile by scaling the intensity by a power of q as in the Lorentz correction. There are several cases where different scaling factors can be justified, including representing a 3D morphology from a 1D scattering pattern, or when correcting for a background. However, care should be taken doing any fit of a scattering pattern that has been scaled, which is known to cause shifts of form factor scattering (scattering from the shape of particles).<sup>108</sup> As a rough guide, size scales larger than the thickness of the film being measured should not be Lorentz corrected unless there is some outside reason to suggest that the scattering is coming from intra-domain correlations and not inter-domain correlations. If uncertain, rotating the sample out of plane to collect some of the out-of-plane scattering information is the best practice.<sup>109</sup> In general, decomposing at minimum the nonresonant and resonant scattering components to remove a background and developing a scattering model and fitting the data is the safest and most correct quantitative practice.

That being said, for qualitative comparisons scaling is an effective way to emphasize small changes and locate shoulders that might be hard to see without scaling in many high-volume fraction systems. Being clear about justifying the purpose of scaling data, checking that features in the scaled data appear at the same q value in the original I(q) profile, and refraining from peak fitting scaled data in any way is our suggested best practice, instead using a model based fit to measure quantitative size scales.

#### 3.4.9 | Analyzing molecular orientation

There are generally two X-ray polarization effects in RSoXS used to assess molecular alignment and orientation within a sample containing polymers or small molecules. One is the extra scattering that originates from orientational self-contrast (Section 2.7.4) which typically creates an isotropic pattern. The other comes from molecular alignment correlated to other features such as domain boundaries and is manifest as an anisotropic scattering pattern that is rotates with the X-ray polarization. The first can be used in liquid crystal samples to determine orientational correlation length (OCL) and has even been used to measure correlated crystal orientations of neighboring grains in polycrystalline films such as pentacene.<sup>63</sup> Determination of OCL comes from identifying the scattering features from an  $L_C$  in the scattering profiles and confirming through comparing with material, vacuum, and orientational contrast functions, the feature follows the orientational self-contrast. As peaks in scattering represent a period, the  $OCL = L_C/2$ .

The second effect (polarization induced scattering anisotropy or PISA) is more complicated and has mostly been treated qualitatively as arising from preferential molecular alignment within a domain or at domain interfaces. Unfortunately, to date, no quantitative analysis has been developed to determine definitively where the molecular alignment is occurring, although the preferential direction can be determined (parallel or perpendicular to domain boundaries) based on analysis of orientational contrast functions described above. Thus far, the most promising analysis arises from qualitative comparison of the anisotropic ratio as a function of both energy and q: A(E,q) to forward simulated scattering patterns generated via computational voxel models30 (described in more detail in Section 4.5). Fitting such patterns to parameterized morphologies that include molecular orientation are on the horizon and appear to be the most feasible way to measure spatial distribution and statistical participation in molecular alignment within a sample. Notably, although crystalline materials will often produce scattering anisotropy, the alignment need not originate from crystals. Thus, polarized RSoXS is sensitive to noncrystalline molecular alignment. The only other means of measuring noncrystalline alignment is via visible and infrared techniques. However, the much smaller wavelength of X-rays enables one to resolve molecular orientation into the nanoscale. Thus, further development of analytical methods for polarized RSoXS is of high priority. (Section 2.7.5).

#### 3.4.10 | Analysis software

As a young technique, mature RSoXS analysis packages have yet to be produced. Usual small angle scattering solutions<sup>94–99</sup> are the most common method of analyzing RSoXS data. These work very well for scattering data reduction and model fitting, but are generally not well equipped and optimized to deal with spectroscopy, and the process of processing each energy independently can be logistically difficult for large hyperspectral datasets. Similarly, while spectroscopy solutions<sup>44,110,111</sup> are excellent for analyzing and visualizing the spectroscopic axis of hyperspectral data, they are not well equipped and optimized to deal with scattering datasets and are usually

designed to deal with only a handful of channels of data, not a 2D scattering image or 1D scattering profiles at each energy. This has meant that generally each RSoXS experiment is analyzed with custom software. Generally, these solutions are specialized, and there is a need in the community to develop well supported, user friendly, high-performance packages for handling spectral scattering data. Spectroscopic imaging by comparison has some more developed tools,<sup>112</sup> although they too are not applicable to scattering data. Until there are well supported, universally available, and trusted solutions, new RSoXS users likely must rely on beamline analysis resources and aid from beamline scientists for data analysis. Each of the growth directions of RSoXS, in situ and environmental measurements, quantitative contrast variation and forward simulation-based quantitative fitting of anisotropic material systems will produce considerably more data and new parameter spaces to visualize and analyze. As such it will be essential for analysis programs to match or exceed acquisition and provide live analysis during experiments. There are promising modern acquisition and analysis frameworks<sup>113-115</sup> under development, which might allow for such a solution.

#### 4 | RSoXS EXAMPLES

#### 4.1 | Organic electronics

Many early contributions of RSoXS were to the field of organic electronics. I particular, bulk heterojunction organic photovoltaic (OPV) devices were under extensive development at the same time that RSoXS was emerging. These solution printable thin film devices are composed of semiconducting polymer and or small molecule blends, which when phase separated, create an electron donor-acceptor interface that separates the charges under solar illumination. RSoXS has proven to be useful in answering questions related to the phase-separated nanostructure relevant to device performance. Other devices such as organic field effect transistors (OFETs) and organic electrochemical transistors (OECTs) also continue to benefit.<sup>63,116,117</sup>Previous reviews have discussed RSoXS of organic electronics quite well, so we point the reader to those sources for further depth.<sup>9-11</sup> Here we will review a few highlights of the decade of work as well as some of the more recent advances.

Generally, studies take advantage of the dramatically increased contrast between components of similar density in the active layers over nonresonant SAXS, better revealing the nanoscale morphology that is critical to organic electronic function. Most typically, this means determining the size scale of phase separation between materials in a phase separated mixture. Different processing techniques are seen to produce differing performance, which can be explained by variation of the nanodomain size scale. If the contrast between components is measured, the volume fraction of the components is known, and the thickness of the film is measured, the precise level of phase size scale and phase purity can also be measured. These measurements have been particularly important for OPV devices where resonant X-ray studies confirmed that component miscibility in the blends often results in impure phases quenched into morphologies potentially far away from thermodynamic equilibrium.<sup>29,102,103,105,118</sup> Additionally there were early attempts to measure the domain size distribution.<sup>100</sup> The most definitive studies leverage microscopy to provide an appropriate interpretation of scattering. By combining the two techniques, quantitative parameters can be assigned to a local model of the nanostructure. Often, STXM is particularly powerful when paired with RSoXS due because of its similar contrast mechanism, and the ability of RSoXS to effectively extend beyond STXM's resolution limit toward the critical exciton diffusion length of  $\approx 10$  nm. A recent example of using RSoXS to quantify domain size is shown in Figure 5A where the RSoXS revealed that early quenching of the morphology evolution during phase separation correlated well with higher device performance in polymer-polymer solar cells.<sup>119</sup>

Domain purity within nanoscale domains has been a major focus recently for OPV devices to better understand

the role of mixed phases in charge generation and recombination. This is accomplished by virtue of the TSI analysis described above in Equations (15) and (16). Although there are many assumptions in the analysis that must be addressed, relating TSI as proportional to domain purity can be quite useful when comparing a series of samples composed of the same materials but possibly varying processing steps.<sup>29</sup> An example of this analysis is shown in Figure 5B where several noncrystalline OPV systems that eliminates a possible third crystal phase were investigated.<sup>105</sup> The work demonstrated that increasing domain purity increases OPV performance metrics across a variety of systems.<sup>121</sup> A study of domain purity in all small molecule blends found the opposite trend, pointing to the role of polymer tie chains in electron transport that is lacking in small molecule cells.<sup>122</sup>

This analysis can be taken further by measuring domain purity of a single sample in the series through other means such as STXM composition analysis.<sup>122</sup> Such a measurement calibrates absolute scaling of domain purity in RSoXS for all other samples in the series even if they are not resolved with microscopy. Recently it has been demonstrated (see Figure 5C) that by combining RSoXS TSI analysis with relative degree of crystallinity measurements, the third polymer crystal phase could be quantified along with the two noncrystalline phases, including the composition of the mixed phase. Combining this phase analysis with simultaneous measurements of device physics and performance on the exact same



**FIGURE 5** Examples of RSoXS applications in organic electronics. (A) Locations of peaks in RSoXS profiles reveal the domain size in a series of organic photovoltaic active layer blends which (bottom) correlate to device performance (short circuit current and fill factor). Adapted from ref. 119 with permission. (2019) Elsevier. (B) A unified use of domain purity to explain performance in bulk heterojunction solar cells formed from low crystallinity polymers. Adapted from ref. 105 with permission. (2018) springer nature. (C) RSoXS TSI (top left) fit to a 3-phase model incorporating volumes of pure polymer crystal  $\phi_p$ , fullerene aggregate  $\phi_f$ , and volume  $\phi_m$  and composition  $x_m$  of a third mixed phase (bottom left) as a function of fullerene loading in a polymer-fullerene OPV. CT-state separation efficiency (top right,  $\eta_{sep}$ ) and charge extraction efficiency (bottom right,  $\eta_{ext}$ , SC = short circuit, MPP = max power point) anticorrelates with  $\phi_m$ . Pearson  $n_{sep} \leftrightarrow \phi_m$  correlation is >99%. Adapted from ref. 120 with permission. (2019) American Chemical Society. OPV, organic photovoltaic; RSoXS, resonant soft X-ray scattering

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samples, a better than 99% Pearson correlation between the mixed phase volume fraction and charge separation efficiency was revealed.<sup>120</sup> The strategy of combining RSoXS and XRD phase analysis with characterization of device physics has led to an increasing body of work with near quantitative structure–property correlations, which is an important step in establishing causal relationships in these complex systems.<sup>101</sup> With new OPV performance records nearing 20% efficiency based on ternary and quaternary blends,<sup>121,123,124</sup> RSoXS multiphase analysis through contrast decomposition may continue to contribute to the field. Additionally, devices involving mixed ion-electron transport such as OECTs are beginning to take advantage of RSoXS.<sup>125</sup>

Analysis of molecular orientation is a third means by which RSoXS has contributed to the field of organic electronics. Through polarization effects, RSoXS has revealed molecular orientation with respect to donor-acceptor interfaces in OPVs as well as how OCL dominates charge mobility and conductivity in polymer OFETs. The details of these contributions are discussed in Section 4.5 below.

Recently, there has been expansion beyond the carbon edge to sulfur, where at  $\approx 9 \times$  the energy, the wavelength is small enough that crystalline peaks can be seen. Because organic semiconductor electronic materials often contain sulfurs, such as in thiophene units, the location and orientation of those sulfur atoms within crystalline lattices can be directly solved for by collecting the resonant intensity across the sulfur absorption edge. This higher energy is often called tender rather than Soft, but many of the sample requirements are still quite important, and all measurements take place in a vacuum environment with thin samples supported on a substrate in transmission geometry.<sup>64,77,126</sup> The use of sulfur edge for RSoXS measurements allow for analysis more akin to REXS, where utilizing the extra information of a unit cell can allow for much more concrete information content to be available. In cases of polymers containing these higher Z atoms, it is highly advantageous to collect measurements at each of those edges to determine the structure completely, although spanning many energies would likely require multiple beamlines and measurements.

#### 4.2 | BCP physics

Although RSoXS has gained major use in organic electronics, its beginnings were in characterizing thin film BCP nanostructure and thermodynamics. These materials that self-assemble into a diverse array of nanostructures have a potential in many applications.<sup>127</sup> The pioneering work by Virgili<sup>5</sup> demonstrated that lateral structure in a 50 nm thin film could be characterized in

transmission due to the orders of magnitude enhanced contrast at unique bond resonances at the carbon edge. Scattering signal fidelity and structural analyses compared well between these thin films and the >1 mm thick films measured in standard hard X-ray scattering. A recent study has used this capability to investigate how the length of periodicity in bottlebrush BCP thin films increases via chain extension due to confinement in everthinner films.<sup>128</sup> Another unique capability of RSoXS was highlighted in another early study where chemical organization within an ABC triblock copolymer nanostructure was solved without the need for staining.<sup>55</sup> Instead, the chemical organization was determined by setting the X-ray photon energy to values where the refractive index for pairs of the blocks was matched. This contrast matching (done with considerable difficulty and potential disruption via selective deuteration in SANS discussed previously in the theory section) resulted in the extinction of certain Bragg peaks. Reasoning out the chemical structure factor was therefore possible, and this basic structure was confirmed with electron tomography staining. Using contrast enhancement and tuning to identify BCP ordering has been subsequently used in several studies. 52,66,129-131

An example of a third unique capability for RSoXS is presented in Figure 6A, which revealed evidence of ordered polypeptoid BCP backbones above the lamellar order-disorder transition (ODT) temperature.<sup>132</sup> As pictured in the schematic, the diblock polypeptoid was composed of hydrophobic decyl and hydrophilic poly(ethylene oxide) side chains. The random phase approximation (RPA) of a linear-chain BCP models a collapsed coil conformation above the ODT. Traditional SAXS measurements suggested a similar behavior of this molecule.<sup>134</sup> The oxygen atoms in the molecule exist in two unique chemical states. These states were targeted to probe the molecular conformation near and above ODT at the oxygen K-edge.<sup>132</sup> As shown in Figure 6A, the carbonyl oxygen resonance is spectrally separated from that of the ether oxygen. Scattering (green) from the ether shows a more defined peak representing the periodic lamellar structure due to its localization within one of the blocks, while scattering from the carbonyl oxygen (red) shows a weak peak mostly due to superposition on the tail of ether-originating Bragg peak. Above the ODT, oxygen atom scattering form factors of an extended chain conformation matched experiment at both resonant energies better than scattering simulations of a collapsed conformation. This result provides evidence that RPA models do not capture all of the side-chain thermodynamic effects for these brush-like molecules.

Initial demonstrations of the advantage of RSoXS over existing characterization techniques have been



**FIGURE 6** Investigations of block copolymers. (A) Scattering intensity as a function of q and photon energy across the oxygen K-edge of a polypeptoid with blocked decyl and poly(ethylene oxide) side chains (molecular structure inset). Scattering from the ether oxygen transitions are indicated at 536 and 538 eV, respectively, and the carbonyl backbone oxygen scattering is highlighted in red at 532 eV. Adapted from ref. 132 with permission. (2017) American Chemical Society. (B) Total scattering intensity measurements (TSI, red crosses) across the carbon K-edge from PS-b-PMMA. The black line is a fit to a spectral model that includes vacuum contrast (yellow trace, from roughness), material contrast (blue trace), and X-ray fluorescence (green trace). Right top is an AFM image of the sample, while right bottom is a reciprocal space map measured at 285.1 eV by tilting the sample with respect to the beam to correct the TSI. Adapted from ref. 58 with permission. (2017) American Physical Society. (C) RSoXR measurements and model fits for an ABC bottlebrush triblock terpolymer at three photon energies near the carbon K-edge. (D) Single unit cell profiles of the SLD (top) and composition (bottom) for the terpolymer extracted from the RSoXR fits. Bottom colors represent the three chemical blocks of the terpolymer (E) simulated depth profile from SCFT calculations. Colors coincide with colors in (D). Traces are simulated SLDs at the three RSoXR energies. (F) Chain conformation schematic based on the combined results (C–F) adapted from ref. 133 with permission. (2018) American Chemical Society. RSoXR, resonant soft X-ray reflectivity; RSoXS, resonant soft X-ray scattering; SCFT, self-consistent field theory; SLD, scattering length density

impressive. However, to thoroughly impact and contribute to the understanding of nanostructure formation and potential applications, a more quantitative analysis is necessary. Recently, Ferron<sup>58</sup> developed a spectral model of RSoXS to separate and quantify contributions to the TSI across the carbon absorption edge that includes multiple chemical species, roughness or porosity, and absorption and fluorescence effects. These contributions were able to rigorously fit RSoXS data spanning two orders in magnitude as shown in Figure 6B. Importantly, this analysis only requires NEXAFS spectroscopy measurements of the BCP sample itself (transmission during the scattering experiment) as well as of films of the individual polymer blocks, making such an analysis easily accessible to any BCP material.

An additional advance of this work was in putting the signal on an absolute scale—thus measuring total absorption cross section—using the dominant XRF signal at high angles. This is typically done with calibration samples of known cross section, but all available standards are too thick for soft X-rays. Verification of this relatively simple calibration procedure was demonstrated recently on BCPs above their ODT.<sup>109</sup> The procedure only requires a thin polymer film with a known atomic structure that is fairly robust to radiation damage (e.g., polystyrene–PS). Calibrating the absolute scattering allowed quantification of the intrinsic width of mixing

between the blocks at the nanostructure interfaces for base-centered cubic spheres, hexagonal cylinders and standing lamellae in polystyrene-b-poly(methyl methacrylate) (PS-b-PMMA).<sup>58</sup> Interfacial mixing lowers total scattering compared to sharp interfaces. Thus quantifying this difference via the absolute scattering enabled the measurement of interfacial width. Such an intrinsic measurement of lateral interfaces is particularly difficult and agreed with more traditional reflectivity measurements on planar structures. It was also revealed that correcting the measured TSI with the out-of-plane scattering was critical to an accurate analysis. This was measured by tilting the sample to express the component of scattering in the z-direction-typically done in grazing incidence experiments (GISAXS) but in transmission the analysis retains the simplicity of the Born Approximation. These measurements (an example shown in Figure 6B to the right) revealed that TSI corrections are required for most thin film samples and must be measured directly. Since TSI is a typical measurement for domain purity in blend films such as OPVs, the result here demonstrates that the accuracy of domain purity analyses can be compromised without such considerations.

The measurement of interfacial width between blocks of a BCP structure reveals the basic thermodynamics of self-assembly and is especially important in applications such as DSA for sub-10 nm photolithography.<sup>135–139</sup> For this application, the interfacial width  $w_i$  limits the smallest possible features, for example the BCP long period or pitch  $L_0$ . To achieve smaller  $L_0$ , the degree of polymerization N is lowered and monomers with a high Flory-Huggins interaction parameter  $\chi$  are used to maintain the high-segregation strength  $\gamma N$  necessary for selfassembly. Feature sizes as small as 3 nm have been shown possible,<sup>140</sup> but  $w_i$  may limit viability for photolithography. Self-consistent field theory (SCFT) predicts the ODT in an AB diblock copolymer to occur at  $\chi N \cong 10.5$ ,<sup>141,142</sup> indicating another lower physical limit to  $L_0$ . The scaling of  $L_0$  and  $w_i$  near the ODT, with very high  $\chi$ , and any deviations of behavior from SCFT predictions is a critical area of polymer physics exploration for the success this application.

RSoXR studies have contributed considerably toward probing the polymer physics of BCP interfacial width. Reflectivity is a technique that can non-destructively extract depth profiles of thin films based on SLD. Neutron reflectivity is often used on BCP films with lamellae laying down on the substrate and one block deuterated to create SLD contrast. However, deuteration has been shown to change  $\chi$ ,<sup>59,60</sup> which is undesirable for these studies, and deuteration for these new polymers can be both synthetically challenging and expensive. Instead, RSoXR uses the intrinsic bond contrast without labeling with early studies demonstrating excellent sensitivity, contrast variability, and high precision.143-145 RSoXR studies on BCP  $w_i$  have demonstrated the efficacy of additives in increasing effective  $\chi$  and therefore reducing  $w_i$ .<sup>146,147</sup> These studies also showed that the additives integrate evenly throughout the compatible block rather than segregated to the interface. It was further determined that the effect can be stronger than a simple linear combination of the materials' two  $\gamma$  values with the opposing block but results from specific interactions between the compatible block and the additive, such as hydrogen bonding.146 Another study used RSoXR to investigate the scaling of  $L_0$  and  $w_i$  of high- $\chi$  BCPs near ODT.<sup>148</sup> The study revealed that  $L_0 N^{3/4}$  for three separate BCP systems, which is a stronger power than SCFT predicts in either the weak or strong segregation limits. These results were also used to develop scaling relationships between  $w_i$ ,  $L_0$  and  $\chi N$  in the intermediate segregation regime. Obtaining vertical lamellae from high-y polymers often requires approaches such as topcoats to modify the surface energy at the top of the films. This can be quantified through reflectivity measurements of polymer/topcoat bilayers, an approach which has been used to identify the ideal copolymer compositions where the polymer/topcoat surface energies are identical for both blocks.<sup>149</sup>

One particularly novel use of RSoXR is highlighted in Figure 6C-F. In this study, a concentration-dependent depth profile of each component of a bottlebrush ABC triblock terpolymer was measured using RSoXR.<sup>133</sup> This was accomplished using three reflectivity profiles at energies strategically chosen to vary the contrast between the three components. Fits to these profiles (Figure 6C) resulted in three effective SLD profiles (Figure 6D bottom), which could be compared with the SLD of the individual blocks (known via NEXAFS spectroscopy) to extract the composition depth profiles (Figure 6D top). These depth profiles revealed a bilayer morphology that included a partially mixed lamella, with the shorter block of the mixture trending toward the interface to lower the effective  $\gamma$ . SCFT calculations support this conclusion (Figure 6E) and together with the RSoXR results, revealed significant looping conformations of the central block inside its pure lamellae (Figure 6F). Additionally, the presence of the central block at the top surface (further confirmed by electron-yield NEXAFS spectroscopy) requires the surface to be dominated by looped conformations. This was surprising in two ways: first for the capability and even preference of loop conformations in a bottlebrush polymer (typically stiff due to the high-graft density) and second for the preference of the mixing block to locate at a buried interface. Thus, in this study RSoXR demonstrated its powerful capability to reveal connections between molecular architecture and mesoscale domain structure. It further did this by quantifying three unique chemical species simultaneously in one sample without the need for labeling—something impossible with any other technique.

#### 4.3 | Membranes

Research in chemical seperation membrane structureproperty relationships is a beneficiary of resonant X-ray scattering. These materials are used and developed for a variety of applications such as fuel cells, gas separation, battery separators, and reverse osmosis (RO) water purification.<sup>150–155</sup> For success, these materials require complex nanostructures that can include a pore network, hydrophilic pore coatings to encourage water uptake and reduce fouling, and a structural network for mechanical strength (often composed of hydrophobic and/or crystalline materials). Such a complex, interwoven multispecies nanostructure that evolves (swells) with operation is particularly difficult to characterize in a meaningful way that will move the technology forward. Traditional SAXS studies are particularly hindered due to reliance on density contrast, whose signal is swamped by the pores. Electron microscopy can be used to image nanoscale inhomogeneities,<sup>156,157</sup> but often rely on staining and only show localized regions. Resonant X-rays are, therefore, particularly well suited to target the critical chemical moieties that makeup the rest of the network and how they relate to the pores or overall heterogeneity.<sup>158</sup>

An early RSoXS study by Wong and coworkers, brought attention to this unique capability in mesoporous membranes composed of a PS-PE-PS triblock copolymer (PE = polyethylene) blended with sacrificial PS to later form templated pores.<sup>52</sup> Contrast function analysis  $(C_{xy} = |n_x - n_y|^2 |\Delta n_{xy}|^2$  where x and y could be the species PS, PE, or vacuum) showed index matching  $(C_{xy} = 0)$  was possible between different pairs of species by careful



**FIGURE 7** Resonant X-ray investigations of porous membranes. (A) Schematic of internal structure of polyamide-based RO membranes with key chemical groups highlighted. INSET: Permselectivity (*a*) versus the concentration ratio (hydroxyl to carbonyl groups as determined through oxygen edge RSoXR) for three RO membranes synthesized via different chemistries. BOTTOM: Concentration depth profiles of carbonyl and hydroxyl groups within a bilayer, demonstrating highly accurate and quantitative functional group density  $\rho_s$  profiles. Adapted from ref. 159 with permission. (2018) American Physical Society. (B) and (C) RSoXS at 282.2 eV (non-resonant) and 285.1 eV (C=C  $\pi^*$ , resonant), respectively, of four RO films with varying acid-to-amine ratios "PA." Black lines are DAB fits with extracted correlation lengths  $L_C$  displayed as a function of PA ratio in (D). Adapted from ref. 160 with permission. (2018) American Oher extra protogenic groups added to the side chains. (F) Schematic of the complex internal structure of a sulfonic acid terminated PFSA (top) and variants with extra protogenic groups on the side chains (bottom). Adapted from ref. 161 with permission. (2019) American Chemical Society. DAB, Debye-Anderson-Brumberger; RO, reverse osmosis; RSoXS, resonant soft X-ray scattering; RSoXR, resonant soft X-ray reflectivity

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selection of photon energy, similar to the previous nonporous ABC triblock copolymer analysis.55 This resulted in the capability to selectively focus on the pore structure versus the pore coating/mechanical (PS/PE) network and showed that RSoXS can distinguish between templated and nontemplated mesoporous films. A subsequent study demonstrated this capability of RSoXS and its superiority to the more difficult scanning TEM tomography when the PS coated membrane pores were further sulfonated to increase water uptake.<sup>130</sup> One limitation in both techniques, however, centered on the limited resolution, since some of the membranes exhibited proton conductivity despite no evidence of pores using either technique. In particular, the longer X-ray wavelengths at the carbon absorption edge limits the bulk resolution without using pattern enhancement techniques as discussed in Section 3.4.2.

Spatiochemical organization into domains within RO membranes have also been characterized in several resonant X-ray studies highlighted in Figure 7. The critical salt rejection layer is typically less than 1 µm thick, which is ideal for soft X-ray techniques but too thin for hard X-rays. The thin polyamide-based active layers are composed of a complex mixture of carboxylic acid units and amide crosslinkers as pictured in Figure 7A<sup>159</sup> with desalination performance linked to these chemical groups.<sup>162</sup> Sunday and coworkers studied model smooth polyamide membranes fabricated via a layer-by-layer process with RSoXR. RSoXR quantified the index of refraction of control samples with known OH and C=O density  $\rho_s$ , enabling them to calibrate oscillator strengths at the oxygen edge for each functional group.<sup>159</sup> They then used these calibrations to quantify  $\rho_s$  of each chemical group within polyamide RO films synthesized via different chemistries. They found that permselectivity ( $\alpha$ ) in these layers is highly anticorrelated to the functional group ratio (OH)/(C=O) (Figure 7Ainset). This can be understood from the standpoint that the hydroxyl group only exists in non-crosslinking monomers while carbonyl groups are in all monomers (Figure 7A). Thus as this ratio increases so does water permeability. The group then measured  $\rho_s$  of both chemical groups as a function of depth in a sample (Figure 7A bottom). Although RSoXR measurement of layer thickness of pure synthetic polymers is typical as discussed above, this was the first time it was used to quantify the concentration profile of a specific chemical bond within a complex material of many bonds. Moving forward, such capabilities could be used to quantify the chemical depth dependence of other complex materials such as biological membranes.

Culp et al. took a different approach in their study of similar polyamide RO membranes removed from the underlying support layer using transmission RSoXS at the carbon edge.<sup>160</sup> Shown in Figure 7B–D, the structure of films of varying "PA" ratio of acid to amide groups (determined by FTIR) were investigated using RSoXS at a non-resonant (Figure 7B) and C=C  $\pi^*$  resonant (Figure 7C) energy. Correlation lengths  $L_C$  (Figure 7D) within the film were extracted via fits to the Debye-Anderson-Brumberger (DAB) model of a randomly distributed two phase system. Nonresonant  $L_C$  were interpreted as the length scale of the surface roughness ("ridge-and-valley" structure), while the  $L_C$  measured at resonance was interpreted as distance between regions of higher phenol density due to amide crosslinking. Binary contrast function analysis supported the interpretation that  $L_C$  at resonance was from crosslinked regions. The correlation of  $L_C$  with PA ratio also supported this interpretation.

With the emerging synchrotron capabilities at the tender X-rays (1-8 keV), sulfur edge research has recently turned back to ion exchange membranes for several reasons. First, these membranes are typically on the order of 10s of µm thick-too thick for transmission using soft X-rays and too thin for hard, but just right for tender energies. Second, sulfur-containing moieties represent the proton donating functionality of these structures, enabling water uptake and ion transport. Third, the wavelength is  $\sim 10x$  shorter at the S-edge than the Cedge, enabling easy measurement of the appropriate 2-5 nm size scale associated with the nanophase separated morphology.

A recent study by Su and coworkers demonstrates the power of resonant X-ray scattering at the S-edge to reveal this critical but complex structure.<sup>161</sup> In this work, perfluorinated ionomers with varying side-chain lengths and chemistry were investigated. The perfluorosulfonic acid ionomer studied has a reduced side chain length compared to the prototypical Nafion, and this was compared to multi acid side-chain variants with one or two extra protogenic groups based on bis(sulfonyl)-imide. Water uptake and water conductivity were both higher in the polymers with extra protogenic groups across all relative humidities (RH). These variants performed especially better at low RH, important for the difficult "hot-dry" conditions. RXS profiles of all four types (including Nafion) are displayed both dry and in situ hydrated in Figure 7E. Broad features at low-q reveal spacings between crystallites of the Teflon backbones that provide the mechanical structure. Sharper peaks at high-q reveal the ionomer peak that represents spacing between the hydrophilic sulfonated domains. Analysis of the dry ionomer peak position reveals a near perfect correlation between ionomer domain spacing and side chain length among the four membranes, implying that designed side-chain length

could be used to tune phase separation length scales. Ionomer peaks shift to lower q values upon hydration indicating swelling of the ion channels during water uptake. Polymers with extra protogenic groups exhibited the largest RXS-measured increase in pore size, consistent with higher water uptake. Additionally, ionomer peak FWHM narrowed significantly for the polymers with extra protogenic groups, indicating more evenly spaced pores within the nanostructure as depicted schematically in Figure 7F. A follow-up study used S K-edge RXS to show changes in the intercrystalline peak in Nafion membranes cast from dispersions of varying water/n-propanol ratios.<sup>163</sup> A related study on Nafion with side-chains modified to contain photoacid dyes for light-driven ion pumps showed similar results. The addition of the large dye molecule to the side chains controlled the ionomer domain size and drove the polymer to increased backbone packing.<sup>164</sup> These results, plus an indication that NEXAFS spectroscopy is sensitive to hydration of the sulfur groups in these membranes bodes well for S-edge X-rays to continue to contribute to this application space.

#### 4.4 | Directed self-assembly

One area that has been particularly synergistic between RSoXS development and an industrially relevant application space is in metrology for DSA. As mentioned above,

FIGURE 8 Resonant CDSAXS analyzed via a TICG physical model. (A) Experimental setup where X-rays transmit through the BCP sample (left) and scatter into a line of many Bragg peaks on the detector (right). Peak intensities vary as a function of sample rotation angle  $\phi$ . (B) Experimental intensities (circles) for each Bragg peak are plotted as a function of  $q_{\tau}$  which is calculated from the experimental geometry. Blue lines are scattering from the best-fit TICG model. (C) Renderings of the TICG model for five PS-b-PMMA BCP films on substrates with varying width of the PS-guiding stripe. Sample name on the right indicates the ratio of the stripe width to the BCP long period (times 100). Adapted from ref. 168 with permission. (2017) American Chemical Society. BCP, block copolymer; CDSAXS, critical dimension SAXS; PS, polystyrene; TICG, theoretically informed coarse-grained



BCPs are being investigated for bottom-up assembly with the target of sub-10 nm nanolithography based on standing lamellae. Chemoepitaxy is used to guide the assembly of the BCP, amplifying the chemical pattern and accessing pitch lengths that are either technically challenging or very expensive with traditional lithographic techniques.<sup>135-139</sup> However, the success of such a technology relies on both the ability to measure the buried structure as well as an accurate predictive physical model to guide processing to produce defect-free morphologies over large areas. Electron-based microscopies either only study the top surface or require demanding sample preparation that eliminates in-line or large area characterization. Critical dimension SAXS (CDSAXS) has become increasingly important in non-destructive characterization of the buried structure, significantly aiding in the development of DSA techniques.<sup>165</sup> In 2010, Stein and coworkers demonstrated how CDSAXS could be accomplished at the carbon absorption edge (i.e., res-CDSAXS).<sup>166</sup> Subsequent work showed that the information content of res-CDSAXS is dramatically enhanced over hard X-rays.<sup>167</sup> Amplifying the contrast at the carbon edge enabled the reconstruction of the buried shape, in particular the wetting of the template, the details of this structure would be inaccessible with the limited scattering from hard X-rays. It importantly could identify

minimized in order to ensure the desired performance of the integrated circuit.

The res-CDSAXS experiment is demonstrated in Figure 8A, where the BCP thin film on a soft X-ray transparent substrate is rotated ( $\phi$ ) while diffraction peak intensities are recorded on a CCD. The intensity evolution for each peak is extracted and plotted as shown in Figure 8B for one sample. The intensities are then fit to a real space model. The model involves a stack of computationally convenient trapezoids to represent the lamellae that captures the shifts in the interface position as a function of depth, as well as possible wetting defects at the interface of the polymer and chemical template. The original res-CDSAXS study even showed that this analysis is sensitive to the parameters of the buried chemical template itself.<sup>167</sup> Importantly, the regular structures of these samples enable quantitative analysis below the so-called diffraction limit (geometrical precision  $\tilde{\lambda}/2$ ) because the information is encoded in intensity rather than angle, enabling precise measurements down to  $\sim 1$ Å. This analysis has since been further developed to increase the geometrical sensitivity (through splining), to determine the ideal number of model trapezoids, and applied to more complex chemical templates.<sup>169</sup> Recently, the technique has been expanded to grazing geometry, enabling simple Si substrates and applied to patterns developed within a homopolymer photoresist.<sup>170</sup> Rather than two different polymers, the scattering contrast comes in this case from chemical changes occurring in the regions of the homopolymer exposed to the photolithographic light pattern. Such intrinsic information on the state of the pattern prior to chemical liftoff would provide insight that might enable much more exquisite control over lithographic processes. This is especially important in the current extreme UV (EUV) resists to help understand how exposure leads to the etched resist profiles.

Beyond measuring buried structure, efforts have focused on combining res-CDSAXS information with physical theories of self-assembly to refine predictive models that can inform DSA processing parameters. Theoretically informed coarse-grained (TICG) modeling is used extensively to simulate the BCP self-assembly process.<sup>171–173</sup> Figure 8C displays the results of these models fit to res-CDSAXS data where the chemical template geometry and material thermodynamic properties are used as fit parameters.<sup>168</sup> Five different PS-b-PMMA BCP films with varying width of a crosslinked PS-guide stripe (chemical template) were measured and fit to the TICG physical model. One example model fit is shown in Figure 8B with the results only marginally worse than the trapezoid method. Importantly, this analysis revealed that the PS-guide-stripe sidewalls were PMMApreferential due to the oxidation from the plasma etch

that was used to form the trenches. Additionally, the random copolymer used to back fill the trenches was found to be slightly PS-preferential rather than fully neutral. Another finding was that when the PS-guide stripe width grew beyond the BCP long period  $L_0$  (sample W114), the structure switched from the PS block centered on the stripe to the PMMA block centered on the stripe. Finally, the TICG models could be analyzed for LER at each of three unique lamellae interfaces and even as a function of depth, informing on the effects of local thermodynamic interactions with the chemical template as well as at the surface. This combination of modeling and scattering thus produced a design metric for DSA: A relationship between  $\chi N$  and LER. A similar analysis was applied to the same res-CDSAXS data but using the computationally simpler SCFT theory with similar success.<sup>174</sup> Here LER analysis was not possible due to the lack of thermal fluctuation physics involved in the theory, but the simplicity of the theory may enable real-time structure analysis during an experiment. Future improvements of this analysis are expected to include diffuse scattering information and a full 3D analysis of the scattering data (adding  $I(q_v)$  which will have information of the length scales of LER). Finally, adding complementary techniques such as hard X-ray GIWAXS for the smaller length scale details will improve this powerful analysis further.

Another experimental modality which has promise to reveal internal polymer interfaces structure is measurement the off-specular reflected intensity, which has been used to characterize thin film<sup>175,176</sup> morphology, and utilizing refractive index matching has been shown to reveal interface diffuse structure in special circumstances utilizing both contrast variation and grazing incidence reflective and refractive properties to further isolate an interface.<sup>56</sup>

#### 4.5 | Polarized RSoXS

Although the capability of RSoXS to spectrally probe chemical nanostructures is now contributing robustly to several fields of polymer science, the even more unique capability of polarized RSoXS to elucidate molecular orientation is still in its infancy. Sensitivity of X-rays at an absorption edge to molecular orientation has been well established over decades in spectroscopy<sup>25</sup> and even microscopy.<sup>27,42</sup> This is due to these techniques' straightforward reliance on dichroism (absorption depending on light polarization). Scattering signals' additional dependence on birefringence (phase shifts in the light wave depending on polarization), complicates data interpretation. This is discussed at length in Section 2. However,



**FIGURE 9** Two types of resonant polarization effect in RSoXS. (A) Schematic diagram of the first type: Scattering from orientational correlation length (OCL). Aligned crystalline grains appear as one domain at resonance due to their common orientation, causing a new scattering peak at a smaller angle (low-q). Adapted from ref. 178 with permission. (2012) springer nature. (B) the second type is anisotropic scattering as shown in the raw CCD detector image (left) with the scattering feature at  $q = 0.03 \text{ nm}^{-1}$ . White dashed lines indicate scattering profiles shown as green lines in the plot (right). The anisotropy appears as a variation of feature intensity with angle from the electric field polarization of the photon (yellow vector left). The anisotropy disappears away from resonance as demonstrated in the black profiles. (C) Interpretation of initial scattering anisotropy from a polymer–polymer blend film where the orientation of the yellow TDM of the 1 s- $\pi^*$  transition rotates with the polymer around a phase separated domain. Adapted from ref. 63. RSoXS, resonant soft X-ray scattering

spatial resolution in a scattering experiment can be much higher than that of microscopy. Scattering can resolve structures beyond the diffraction limit ( $\lambda/2$ , e.g., dynamic light scattering and ellipsometry) without the focusing optics or subwavelength stability which often limit imaging techniques. Thus, developing and employing this powerful capability is of high interest.

Initial X-ray reflectivity and transmission scattering experiments demonstrated several powerful capabilities of polarized RSoXS (p-RSoXS). Using polarized reflectivity (p-RSoXR), Mezger and coworkers<sup>177</sup> demonstrated the capability to determine molecular orientation in a side-chain LC polymer film that was too thin to exhibit birefringence in the visible spectrum. This indicated that reflectivity could be used to determine molecular orientation as a function of depth with nanometer resolution, something impossible to measure with any other technique. P-RSoXS in transmission geometry through organic electronic thin films were demonstrated by Collins and coworkers,<sup>63</sup> revealing two separate types of polarization effects in this experiment. Figure 9 presents the two types of scattering, OCL scattering and polarization-induced scattering anisotropy and their origin. The first effect was demonstrated on all-polymer transistors where the OCL between the LC-like polymers

in the channel resulted in a new polarization independent scattering feature at resonance with the q-position of the feature indicating the OCL. The OCL in polymer transistor films exponentially correlated with field effect hole mobility. The lack of correlations between X-ray diffraction and mobility indicated that OCL is fundamentally a different measurement of molecular orientation that does not require crystallinity.

The other effect of p-RSoXS discovered in the study was the appearance of an anisotropic scattering pattern in polymer blend films (see Figure 9B,C).<sup>63</sup> Rather than a new feature, a scattering feature representing phase separated nanodomains became anisotropic at resonance, scattering more in the direction perpendicular to the Xray polarization (S-polarization) than parallel (P-polarization). The (barbell-like) pattern followed the polarization direction rather than sample rotation, indicating it came from molecular orientation relative to local nanodomain interfaces, rather than any global polymer orientation. A subsequent study of polymer-fullerene OPV blends revealed a strong correlation between the scattering anisotropy ratio A (Equation (14)) and photocurrent from the cell under solar simulated conditions.<sup>179</sup> With A interpreted as measuring a preferential molecular orientation at the donor-acceptor interface, this result suggested that



**FIGURE 10** Applications and development of polarized RSoXS. (A) Seebeck coefficient of the polymer pBTTT (molecular structure inset) for two different p-type dopants (blue and orange symbols) as a function of orientational correlation length (OCL). (B) Power factor (PF) for the same films as a function of OCL. Adapted from ref. 117 the authors, some rights reserved; exclusive licensee AAAS. Distributed under a CC BY-NC 4.0 license. (C) Left: Pure polymer film modeled as a type two polymer fibril (white lines represent polymer backbones). To reproduce experiment, fibrils needed to be modeled with a disordered shell at higher density than the amorphous polymer matrix. Right: Forward simulated scattering profiles I(q) at three indicated energies. P and S polarization are indicated as "Para" and "perp," respectively with the color fill between the two traces indicating the sign of the anisotropic ratio *A*. (D) Left: Experimental A(q,E) and right: Simulated A(q,E). Color represents the values of A = [-1,1]. Dashsed black lines indicate the energies in C left. Adapted from ref. 180 with permission. (2021) Wiley. (E) Molecular model of posaconasole with  $\pi^*$  TDMs indicated with red arrows and  $\gamma$  indicating the molecular tilt. (F) Fits (lines) to p-RSoXR data (circles) at 284.7 eV. P/S polarization is red/blue. Inset bottom is zoom of low-q data, while inset top is schematic of the molecular orientation model. Adapted from ref. 48 with permission. (2020) American Chemical Society. RSoXS, resonant soft X-ray scattering

molecular orientation at the distributed device junctions control charge generation and recombination. This capability to determine noncrystalline molecular orientation within nanostructures is quite powerful as all other techniques rely either on crystallization to reveal orientation or—in the example of polarized microscopy—involve wavelengths that cannot resolve the nanoscale.

Subsequent to the initial work, both types of polarization effects have been employed in a number of polymer systems with the OCL-type providing the most definite results so far. One study used p-RSoXS to measure a 3 nm OCL for both the phenyl groups and the backbone within atactic polystyrene.<sup>65</sup> While phenyl orientation correlations were expected, the surprising backbone orientations were revealed in a spectroscopically separated signal. This noncrystalline molecular alignment is impossible to measure any other way. More recently, OCL was measured in a semiconducting polymer film as a function of amount and type of p-type doping, confirming the large effect of OCL on charge conductivity  $\sigma$ .<sup>117</sup> Dopants premixed in the casting solution were found to disrupt the OCL, while subsequent vapor doping of neat polymer films did not. Contrary to its correlation with  $\sigma$ , the OCL had no influence on the Seebeck coefficient  $\alpha$  as shown in Figure 10A. A figure of merit in thermoelectric devices is the power factor ( $PF = \alpha^2 \sigma$ ), but typically if  $\sigma$  increases in a material,  $\alpha$  decreases. The favorable behavior of both parameters with OCL was shown to result in dramatic increase in the PF as shown in Figure 10B.

Scattering anisotropy from p-RSoXS is more complex to interpret than OCL because instead of a modulation of molecular refractive index, it involves a modulation of scattering contrast between two components. Thus, interpretation of the sign, energy dependence, and q-dependence of *A* simultaneously requires an optical and spatial model—all of which are still being developed. Thus far most studies interpreting anisotropic scattering (almost exclusively in organic electronics) only employ qualitative claims regarding molecular orientation across domain interfaces that are difficult to verify.<sup>181</sup> More recently, a spatiooptical model was developed to interpret molecular orientation of a semicrystalline polymer within a BCP lamellar structure.<sup>66,182</sup> Off-axis scattering anisotropy (maximum scattering not aligned with the polarization OR perpendicular to it) was interpreted as a tilt angle of the polymer chains with respect to the interfaces between block interfaces.<sup>66</sup> However, as discussed in Section 2.7.5, scattering anisotropy arises from a tensor optical interaction and this optical model ignored depolarized scattering. Still, this work represented some of the first efforts to apply models to polymer physics.

Recently there has been significant development of models to interpret scattering anisotropy from p-RSoXS. In 2016, we and others constructed a full tensor, forward simulation platform for transmission p-RSoXS that employs user-constructed, voxel-based nanostructures defining a coarse-grained volume of chromophores.<sup>30</sup> Statistical participation in molecular alignment in each voxel is defined by an isotropic component weighted against an aligned portion with a 3D vector representing the transition dipole moment (TDM). Each oriented molecule is simulated as a uniaxial 3x3 tensor (diagonal along the principle axes of the TDM with two independent components  $n_{\parallel}$  and  $n_{\perp}$ ). This simulation was shown to reproduce  $I_S(q,E)$  and A(q,E) for a polymer fullerene blend very well with the model of polymer nanofibrils surrounded by a fullerene matrix. The two independent optical tensor components were derived from angle dependent NEXAFS spectroscopy of a pure polymer film. Recent work by Mukherjee and coworkers<sup>180</sup> has used this platform to distinguish between type 1 and type 2 polymer fibrils.<sup>183,184</sup> The simulation process is demonstrated in Figure 10C,D where first the fibril nanostructure is created with molecular orientation assigned within the nanostructure, next scattering profiles are simulated for each scattering at polarization parallel and perpendicular to the electric field vector at each energy, then A(q,E) is assembled into the full 2D dataset, and finally it is compared with experimental data. In this study, it was additionally found that to have any q-dependence in A for a pure semicrystalline polymer film, correlated changes in density at the fibril edges was also required. This result demonstrated that characterizing molecular orientational and density substructure is possible with this technique-including at domain interfaces. Further development and use of the simulation platform will enable increasingly complex polymer nanostructures to be characterized.

Development of p-RSoXR has progressed significantly alongside transmission p-RSoXS. First the ability to quantify the tilt angle of 1,4-benzenedimethanethiol selfassembled monolayer (SAM) on Au was demonstrated by using DFT to simulate the polymer's optical tensor.<sup>185</sup> Instead of fitting Keissig fringe patterns, the lineshape of the S and P polarized reflectance as a function of energy  $[R_S(E) \text{ and } R_P(E)]$  was fit across the carbon absorption edge with only two parameters: film thickness and molecular tilt angle. Both fit parameters ( $\theta_{\text{tilt}} = 28^{\circ}$  and t = 1.5 nm) were well constrained and agreed with previous characterization of the SAM. Importantly, only an optical model of parallel aromatic groups reproduced experiment, while a herringbone orientation model failed. A second similar analysis on approximately 5 monolayers of a conjugated small molecule on an Au<sup>111</sup> substrate confirmed the flat-lying molecules and compared DFT-derived versus NEXAFS-spectroscopy-derived optical models.<sup>186</sup> In the future, it may be helpful to combine both ab-initio (DFT) information with experimental measurements to generate the most accurate optical models.

Most recently, full orientational depth profiling has been demonstrated on glassy posaconasole small molecule films where nothing but molecular orientation changes as a function of depth into the film.<sup>48</sup> Success of this analysis again required construction (this time from NEXAFS spectroscopy measurements) of a molecular optical tensor model for the film as exhibited in Figure 10E. Here the optical model focused on the lowest-energy transition involving the phenyl carbons with TDMs pointing in any direction perpendicular to the molecular backbone as shown in the figure. Because spatial distribution of orientation was important,  $R_{SP}(q)$ were fit at only two key energies: A nonresonant energy (250 eV) to establish the total film thickness and roughness, and an energy just below the first (phenyl) resonance to probe orientation with depth. The resulting fits at resonance, shown in Figure 10F, have excellent agreement with data and reveal a monolayer vertical surface orientation compared to a random bulk molecular orientation (see Figure 10inset). This result was consistent with bulk-sensitive ellipsometry and surface-sensitive NEXAFS spectroscopy measurements. The spatial sensitivity of the depth profile to even a single molecular layer bodes well for this technique to be applied to a diverse range of molecular thin film studies.

#### 4.6 | Chiral LC materials

One research field that has found pRSoXS to be critical is in the development and characterization of chiral LC structures composed of organic achiral molecules. Chiral structures lack mirror symmetry and are important in biology and medicine as well as in LC materials for optoelectronic applications.<sup>187–190</sup> Much work has been accomplished in this field using resonant X-rays with full details reviewed elsewhere.<sup>191</sup> Here we provide a brief overview. Resonant scattering was originally used to 1232 WILEY – JOURNAL OF

distinguish various models of chirality in smectic chiral LC structures through the emergence of forbidden diffraction peaks at resonance that have polarization dependence.<sup>192,193</sup> This occurred due to symmetry breaking based on the tensor form factor required to describe scattering at a resonance versus the simpler scalar interaction off-resonance. Such studies were more definitive and easier to accomplish than alternatives such as freeze-fraction electron microscopy.<sup>194,195</sup> However, without access to soft X-rays, these early studies relied on inserting hetero atoms into the LC mesogens (rigid molecular segments responsible for orientation effects) such as sulfur or selenium, potentially altering the LC structure itself.

In 2015, Zhu et al.<sup>196</sup> demonstrated the first pRSoXS measurement of LC helical nanofilaments at the carbon edge without the need for heteroatom labeling, thus ensuring measurement of the intrinsic LC structure. As expected, a polarization-dependent forbidden reflection

appeared at resonance, revealing the helical pitch. In situ temperature-dependent studies revealed the equilibrium pitch measured after cooling from the melt was not the same as the pitch when originally drop cast due to guest molecules within the initial structure.

The same group further published the first in situ study regarding the helical pitch of the recently discovered twist-bend nematic (N<sub>TB</sub>) phase.<sup>197</sup> It demonstrated large-scale coherence of the heliconical pitch (>100 periods) that fractured into smaller domains with different pitches due to the strain from heating. Such a result was particularly impressive as the sample's nematic ordering lacks electron density modulation required for traditional diffraction techniques. At this point, it was clear that pRSoXS would be superior to existing alternative techniques, which also often could not involve in situ stimuli and were less precise.<sup>194,195</sup> Several subsequent studies have characterized other molecules and



**FIGURE 11** RSoXS investigations of liquid crystal phases. (A) In situ temperature evolution of RSoXS intensity (bottom, see color scale just above) of asymmetric achiral molecule (structure top). Scattering wave vector magnitudes (q) is on the left while periodicity (p) is on the right. Temperatures are posted relative to the smectic to twist-bend nematic phase transition. Multiple scattering features indicate different levels of orientational alignment that evolve with temperature. (B) A comparison of on X-ray scattering on resonance (black, 283.7 eV) on off-resonance (red, 263.7 eV)) of a pure small molecule film demonstrating the dramatic and unique sensitivity of polarized RSoXS to orientational ordering in LC materials. Adapted from ref. 204 with permission. (2019) springer nature. (C) Three compounds (structures top) that assemble into the double gyroid LC phase with their reconstructed electron density maps (middle) based on scattering (SAXS) measurements. The color bar shows high-electron density assigned to aromatic and hydrophilic groups in purple with low-electron density assigned to alkyl groups in red. Proposed molecular packing for compound 1 (left, rod like) and compound 2 (right, taper shape) at 3-way junctions in the nanostructure. Adapted from ref. 205 with permission. (2020) American Physical Society. LC, liquid crystalline; RSoXS, resonant soft X-ray scattering

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established the double helix structure of the  $N_{TB}$  phase in many systems<sup>198–200</sup> and revealed how dimer versus trimer molecules can exhibit very different thermal ordering behaviors. In the latter study, the helical pitch of the dimer changed by more than a factor of two with temperature, while the analogous trimer exhibited temperature-independent pitch.<sup>201</sup> Further studies have revealed photo-induced structural changes in  $N_{TB}$  phases and their dynamics, demonstrating the new possibilities that resonant scattering provides for operando experiments.<sup>202</sup>

Since the first studies, combining pRSoXS and theory has enabled the discovery of new LC phases and the characterization of novel 3D LC structures. For example, a new twist bend smectic C phase was characterized by Abberley et al in 2018,<sup>203</sup> and a multilevel chirality was discovered in asymmetric molecules, which increases the complexity of the structural phases.<sup>204</sup> Figure 11A presents the complexity of the latter study where structure from four levels of chirality are present and whose phase transitions and structures were mapped by pRSoXS. Figure 11B shows the power of resonance where all of the scattering information used to reveal this structure is completely absent away from resonance. These complex phases extend to the so called 3D Blue phases<sup>198</sup> and recently, evidence of martensitic transformations.<sup>206</sup> Finally, Cao et al.,<sup>205</sup> have recently resolved both chemical and orientational structure within double gyroid LC phases. Figure 11C shows how this phase, produced by three separate compounds, was mapped for the location of aliphatic versus aromatic moieties through electron density from nonresonant energies as well as chirality at resonance of these units near three-way junctions in the morphology. Putting together both chemical and orientational information in these studies represents the true power of pRSoXS to reveal general nanoscale ordering of molecules inaccessible any other way.

#### 4.7 | Biological systems

Recently RSoXS chemical sensitivity has been employed to probe its capability in characterizing natural and biological materials and structures. Such an endeavor has significant promise to uniquely probe chemical substructure involved with living systems to elucidate key functional mechanisms in ways not currently possible. This avenue is in some ways returning to the roots of the technique as many of the spectral concepts of RSoXS were first developed for resonant diffraction at heavy elemental edges. To date, primary methods that utilize X-ray resonance to probe biological systems involve chemical tagging of key moieties within a molecule in an ordered structure with heavy elements.74,207-209 Techniques such as multiwavelength and single wavelength anomalous diffraction (MAD and SAD) are now common measurements at synchrotrons where crystals or nanostructrues of tagged molecules use the unique optical parameters at the tag's absorption edge to solve the phase problem for the crystal and locate the tags (and therefore the tagged moieties) within the structure or even resolve electron density maps to high resolution.<sup>75,210</sup> For example, the toroidal structure of pores in lipid membranes was revealed with bromine tags on lipid tail groups.<sup>208</sup> In another example, statistics of DNA sequence lengths were measured to 0.1 nm precision via gold nanoparticle attachments acting as molecular rulers.<sup>209</sup> An excellent review on the spectrum of recent results using all resonant techniques is available.<sup>211</sup>

Despite these impressive successes using X-rays resonant with heavy element tags developed over several decades, the effect of the tag itself on the structure must always be estimated and is never assured to leave the investigated structure in its intrinsic state. Resonant scattering at soft and tender X-ray energies such as the C, N, O, and P edges open the possibility of measuring the structure of natural and biological materials with no laborious and disruptive tagging at all. The main difficulty has been with the short penetration depth of tender and especially soft X-rays where the ideal sample thickness approximately at a beam attenuation of 1/e is often well below 5 um. An initial early success involved elucidating the hierarchical structure of casein micelles within milk.<sup>212</sup> A combined hard X-ray SAXS and Ca Ledge RSoXS study identified the scattering feature associated with colloidal calcium phosphate (CaP) nanoclusters. Figure 12A shows how RSoXS was used to essentially highlight these structures at resonance where conventional SAXS could only report on the density fluctuations associated with the larger micelles and smaller protein inhomogeneities. Subsequent RSoXS studies have distinguished the correct structure among multiple proposed models<sup>215</sup> and more recently demonstrated how the CaP nanoclusters are invariant among different animal species while the larger micelle structure changes.<sup>216</sup> Other work has also employed RSoXS at the Ca L-edge to resolve the 20 nm spacing of cellulose microfibrils within a Ca-rich matrix in onion epidermal cell walls even distinguishing it from the nearby waxy cuticle layer.217

In these initial studies, RSoXS was used to enhanced contrast of a heteroatom in a carbon matrix that was intrinsically present rather than added synthetically. Subsequent work has begun to take advantage of the specificity of RSoXS to bond moieties of the carbon structure itself. Figure 12B highlights one such study where the 1234 WILEY – POLYMER SCIENCE



**FIGURE 12** RSoXS investigating biological structures. (A) Nanostructure of casein micelles in milk. Top: The proposed structure involving a porous micelle network with embedded calcium phosphate (CaP) nanoclusters. Adapted from ref. 213 with permission. (2010) Elsevier. Bottom: SAXS is sensitive to large voids at low-q and protein inhomogeneities at q = 0.08/Å, but misses CaP revealed by Ca L-edge RSoXS at q = 0.03/Å. Adapted from ref. 212 with permission. (2015) Royal Society of Chemistry. (B) Experimental (circles) and predicted (lines) scattering of bovine serum albumin (BSA) demonstrating chemical selectivity of the technique to highlight different chemical substructures. Left: RSoXS at 285.3 eV which is at the C=C bond resonance. Only these bonds were simulated for the predicted curve. Right: RSoXS at 288.3 eV, involving backbone bond resonances. The simulated scattering is shown in the orange trace. (C) Left: NEXAFS spectroscopy of BSA revealing the two main resonance features. Middle: BSA visualization with all carbon atoms (gray mesh), backbone CONH (blue), and aromatic rings (pink). Right: Red envelope functions generated from RSoXS data at 285.3 eV highlighting the location of aromatic groups with respect to the blue BSA backbone structure. Adapted from ref. 214 with permission. (2018) Elsevier. RSoXS, resonant soft X-ray scattering

structure of the protein bovine serum albumin (BSA) suspended in solution was characterized with RSoXS.<sup>214</sup> BSA is a well-characterized model carrier protein that regulates fluid distribution local to blood vessels.<sup>218</sup> Resonant scattering at the  $C1s \rightarrow \pi^*_{C=C}$  (285.3 eV) and  $C1s \rightarrow$  $\pi^*_{CONH}$  (288.3 eV) transitions compared favorably with simulated patterns that only included the appropriate moieties (Figure 12B). This indicates that bond arrangement within protein structures could be characterized with spectrally resolved RSoXS at the C-edge. The work further used the scattering data to model the protein envelope function (Figure 12C) which agrees well with the crystallography-resolved model of the protein. In this case, however, the envelope function could be specific to the aromatic side chains of the individual protein residues. These results suggest that RSoXS could contribute to characterizing the chemically resolved structure of noncrystallizable proteins in the future.

Despite these early successes, there are still hurdles to mount before RSoXS is used regularly in studies of biological systems. First is the fundamental wavelength limit in the soft X-ray regime. The diffraction limit  $(\lambda/2\tilde{2} \text{ nm})$ 

at the carbon edge will preclude these measurements from achieving high resolution through scattering alone (recall Section 3.3). This can be seen in the low resolution of the envelope function produced in Figure 12C. However, instrument hardware (primarily single flat detectors) currently limits scattering range to less than half of its potential. Thus there are further significant improvements possible to resolution with detectors at higher angles. It is important to note that the objects involved with resonance in RSoXS of polymers are often extended or delocalized molecular orbitals, extending well beyond the atom itself, so atomic resolution is not a primary target anyway. One strength of RSoXS revealed in these initial studies is that very little sample is necessary for the measurements. In the study of the BSA protein, it was pointed out that only picoliters of solution were required to perform the measurements. This is many orders of magnitude less than required for hard X-ray or neutron scattering. Thus, the strengths and potential improvement for RSoXS applied in the area of biological materials remain a formidable opportunity for increased impact.



**FIGURE 13** Recent innovations in resonant scattering. (A) Liquid flow cell based on a TEM microfluidic insert enables soft X-ray penetration through a thin water channel between SiN membranes. Inset: Molecular structure for Pluronics F127 micelle used in the first demonstration of the instrument at the ALS. (B) RSoXS profiles of F127 micelles at five energies across the carbon absorption edge simultaneously fit to a statistical core-shell model. Structural and chemical fit parameters inset. Adapted from ref. 78. (C) Spectral analysis of the optical parameters extracted in the five-energy fit in (B). Contrast functions for two scenarios. Dashed lines are for a 100% polymer corona. Shaded areas are for 5–10% polymer corona with the balance being water. Best-fit values return 9% polymer in the corona by mass. (D) Polarization-dependent<sup>100</sup> diffraction intensity of P(NDI2OD-T2) across the sulfur K-edge. An optical tensor model based on multi-axis angle-dependent NEXAFS of aligned films fits well to the data. (E) Similar data and fits for the (001) diffraction peak. Adapted from ref. 219 with permission. (2021) American Chemical Society. ALS, Advanced Light Source; NEXAFS, near edge X-ray absorption fine structure; RSoXS, resonant soft X-ray scattering; TEM, transmission electron microscopy

#### 5 | EMERGING OPPORTUNITIES AND OUTLOOK FOR RSoXS

RSoXS is now contributing significantly to diverse investigations of polymers and molecular systems, and in some areas described above, it is a technique that has already led to new discoveries due to its unique capabilities. Yet RSoXS is still generally in its infancy with significant instrumental and analytical development still underway that will pave the way for significantly more powerful scientific contributions to polymer science in the future.

One particularly promising new development is the implementation of instrumentation for liquid samples. Due to the soft X-ray requirement of high vacuum, liquid pocket cells (sandwiched and sealed  $Si_3N_4$  membranes around a droplet) have been used previously to investigate a few biological systems.<sup>212,216,217</sup> However, these methods are extremely difficult to reproduce with a high-

failure rate due to bursting, overfilling (too thick), or leaking (usually into the sealant). Even when successful, relative signal normalization between samples is impossible, in situ stimuli are precluded, and beam damage can build up on the limited (picoliter) sample. As pictured in Figure 13A a liquid flow and mixing capability has recently been developed that will make these experiments significantly more reliable and precise. The new capability comes from a modified microfluidic flow cell insert originally designed for a TEM. The new instrumentation enables dependable and reproducible measurements and limits beam damage through sample flow. It includes two independent inlets for mixing to occur within the cell, enabling real-time measurements of chemical reactions or concentration variation. Three electrical contacts enable operando electrochemical measurements as well. At the ALS, a new chamber and low-noise detector will accept an unmodified TEM flow cell insert,

enabling swift sample changes and better signal. The NSLS-II instrument already accepts a commercially available TEM environmental cell enabling such experiments as well.<sup>20</sup> Along with instrumentation development, microfludic cell development has also progressed. For example, significant development has occurred for STXM both at the ALS,<sup>220</sup> and at SOLIEL in France.<sup>221</sup> Furthermore, new vacuum barrier materials beyond SiN have been explored such as AlOx, which have been shown to be more mechanically robust and more transparent at the nitrogen edge.<sup>222</sup>

Beyond instrumentation, more quantitative analyses are needed before RSoXS truly becomes a staple technique of choice in polymer science. One significant step toward that is demonstrated in Figure 13B,C where quantitative chemical ordering of BCP nanocarrier micelles were characterized in water using the new flow-cell RSoXS instrumentation.<sup>78</sup> As described in the Section 2.7.3 above, multicomponent contrast was used to simultaneously fit five scattering profiles in Figure 13B. This contrast variation on a single sample revealed internal spatiochemical ordering of the nanocarrier in situ. Impressively, no elemental differences but only a single methyl group provided adequate chemical contrast between the blocks as presented in the BCP structure (Figure 13Ainset). Such sensitivity to a single unique moiety bodes well for high-sensitivity measurement of multicomponent polymeric systems. In addition to the structural analysis, chemical composition within the corona of the micelle was quantified using a linear combination of optical constants to represent the corona. As shown in Figure 13C, contrast parameters extracted from the five scattering profiles were best fit by an optical model with the corona composed of only 9% polyethylene oxide (PE) by mass. Alternate contrast functions assuming 100% PE (dashed lines) were different by orders of magnitude, demonstrating further the sensitivity of the technique. Dynamics on the order of 10 s were also demonstrated, something not possible with SANS even with deuteration. Even placing the micelles in deuterated water has been shown to change micelle aqueous structure.<sup>223</sup> Thus as it is further developed, liquid RSoXS is expected to be quite uniquely powerful in investigating spatiochemical dynamics label-free. Using the partial scattering function framework, RSoXS generally has the potential to be used to analyze "massively multicomponent" mixtures in a way that would be prohibitively expensive or impractical with SANS chemical contrast variation techniques.

With advances in instrumentation and analysis for aqueous samples, novel in situ or operando RSoXS experiments are likely to expand the impact of the technique. For example, studies of aqueous nanocarriers such as those above could track internal structural integrity and quantify encapsulated species through different environments to test their behavior inside the body. Smart medicine platforms depend on the ability for local conditions to trigger release of drugs within the nanocarrier.<sup>224,225</sup> Thus, the technique could significantly speed nextgeneration drug development. More generally, the formulation and temperature control of the instruments will enable phase diagrams of micelles and other aqueous polymer structures to be characterized with ease to refine existing models of self-assembly.

Although not yet fully utilized, the electrochemical capabilities of the instrument could be very powerful. For example, the instrumentation could enable monitoring the chemical evolution of nanostructures within polymer battery electrodes, helping to better connect ion charging and transport with capacity and lifetime.<sup>226,227</sup> Operando ion transport experiments in OECT devices could also enable better connections between nanomorphology and transconductance that is so critical to their use in bioelectronics and sensing.<sup>228,229</sup> Spatiochemical investigations during evolution in polymer solution chemistry and other catalytic processes where the chemical state, location, and time are all critical dimensions is now possible with the new instrumentation.

Using the sensitivity to molecular orientation, polarized RSoXS could be used to investigate orientation evolution during solution self-assembly of molecular nanostructures that includes molecular nanocrystals as well as more exotic structures.<sup>230,231</sup> Even more advanced, would be incorporating orientation sensitivity of individual residues into current solution SAXS characterization of peptides and proteins.<sup>232,233</sup> Such work could significantly improve characterization of critical biological structures such as membrane proteins that govern permeation of cell walls but evade protein crystallography investigations.

Even with these advances in RSoXS spectral analyses, there is still a significant limit on the achievable resolution, especially at the carbon edge resulting in a diffraction limit to approximately 2 nm. Such a limit is less resolved than modern protein crystallography, for example, which reaches resolutions  $\approx 10 \times$  smaller.<sup>75,210</sup> However, with patterned structures incorporated into the sample, this limit can be bypassed. For example, recent CD-SAXS and X-ray reflectivity at the carbon edge have resolved structures with near-angstrom precision.<sup>146,147,169</sup> This is because, with such diffractive structures, spatial information is encoded in diffraction intensities rather than just scattering angle. New measurement techniques beyond the diffraction limit could aid RSoXS in achieving ultrahigh resolving power for polymer structures. Still, scattering patterns must always be modeled to extract the most information. Real space chemical maps would be quite powerful in areas that traditional scattering information lacks such as revealing local structures and connectivity. With new and upgraded synchrotron sources targeting high or even fully coherent X-ray beams, coherent diffractive imaging techniques such as ptychography are being developed. These techniques solve directly for the missing phase of the scattered wave to invert the scattering pattern from its Fourier transformed state back into an image of the sample itself. In an initial study, ptychography was performed on polymer blends that demonstrated 30-50 nm resolution with no discernable beam damage.<sup>50</sup> Although this is similar to the best achievable STXM resolution for similar samples, such an initial demonstration bodes well for eventual <10 nm chemically resolved images.

The dimension of RSoXS that needs the most development yet holds great potential is polarization dependence. The ability to determine nanoscale molecular orientation of noncrystalline origin or even macromolecular conformation in a noncrystalline sample would be a property unmeasurable any other way. To date, however, analysis has been limited to qualitative assessments with the most rigorous quantitative treatments occurring in the field of chiral LC materials. The challenge is first the inability to use the traditional contrast function approach to modeling the scattering and the second is the lack of an established, robust method to generate a molecule's optical tensor. Currently, the most robust modeling available is through the voxel-based forward simulation method described above.<sup>30,180,234</sup> Current efforts involve highperformance computing integration to enable fitting of a models' parameter space.<sup>234</sup> Development of optical models, however, are ongoing with several potential methods emerging. While the first used angle dependent NEXAFS spectroscopy to generate a basic uniaxial model,<sup>179</sup> another recently used a film with aligned polymers through bladecoating and multi-axis NEXAFS spectroscopy to reveal the full six-component optical tensor for the electron acceptor polymer P(NDI2OD-T2).<sup>219</sup> Figure 13D,E demonstrate how this optical tensor was able to reproduce polarizationdependent diffraction measurements at the Sulfur edge. Other efforts have based an optical tensor on DFT calculations, which reproduced polarized RSoXR measurements well.<sup>185,186</sup> Future methods that could incorporate both experimental and computational techniques will enable ever higher precision on determining molecular orientation within polymer systems.

All things considered, RSoXS has made important contributions to polymer science and holds a bright future in the field. It is a staple in organic electronics morphology studies, increasingly important to BCP physics, impactful in membrane structure characterization, – POLYMER SCIENCE – WILEY 1237

and is leading new discoveries in chiral LC materials. With further computational and analytical development and new experiments enabled by improving instruments, its impact will only grow. So much has been achieved as of 15 years after the first published RSoXS experiments. Expectations are just as high for new RSoXS-enabled insights into polymers for the next 15 years.

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Original data that support the findings of this study are openly available from the authors upon reasonable request while reproduced data from previous studies were derived from the cited references in each figure.

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#### ENDNOTE

<sup>1</sup> Higher shell electrons will also be excited, which is why a resonant signal must be measured as a spectrum across an absorption edge, where these nonresonant interactions are a near-flat background.

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