

## Feature article

# Reprint of: Combining theory and experiment for X-ray absorption spectroscopy and resonant X-ray scattering characterization of polymers<sup>☆</sup>



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## ABSTRACT

An improved understanding of fundamental chemistry, electronic structure, morphology, and dynamics in polymers and soft materials requires advanced characterization techniques that are amenable to *in situ* and *operando* studies. Soft X-ray methods are especially useful in their ability to non-destructively provide information on specific materials or chemical moieties. Analysis of these experiments, which can be very dependent on X-ray energy and polarization, can quickly become complex. Complementary modeling and predictive capabilities are required to properly probe these critical features. Here, we present relevant background on this emerging suite of techniques. We focus on how the combination of theory and experiment has been applied and can be further developed to drive our understanding of how these methods probe relevant chemistry, structure, and dynamics in soft materials.

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## Contents

1. Introduction .....	343
2. X-ray absorption spectroscopy and resonant scattering probe chemistry and structure .....	343
2.1. Connections between X-ray absorption and scattering contrast .....	343
2.2. Core-level X-ray absorption spectroscopy .....	343
2.3. Resonant reflectivity and scattering .....	344
3. Looking ahead: combining chemistry, morphology, and dynamics .....	347
3.1. Going beyond the carbon K edge .....	347
3.2. Simulating resonant X-ray scattering patterns .....	347
3.3. <i>In situ</i> and time-resolved studies for dynamics and chemical kinetics .....	347
3.3.1. <i>In situ</i> X-ray absorption spectroscopy .....	348
3.3.2. Probing changes in interfacial structure and chemistry .....	348
3.3.3. Time-resolved dynamics with photon correlation spectroscopy .....	349
4. Applications and outlook .....	351

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4.1. Polymer-based membranes .....	351
4.2. Doped semiconducting polymers .....	352
5. Conclusions .....	353
Acknowledgments .....	353
References .....	353

## 1. Introduction

The intricate connections among chemical structure, local intermolecular and global morphology, and kinetics in polymeric materials determine the fundamental properties of many polymer-based applications. These include flexible electronics [1–4], gas separations [5–7], polymer electrolytes for batteries, fuel cells, and water desalination [8–10], and lithographic patterning [11–13] just to name a few. It has remained challenging to fully understand the relationships between chemistry and structure, and the growing demand to characterize polymers under *in situ* or *operando* conditions relevant to a specific application and as a function of time creates additional challenges. Probing detailed information such as this requires advanced characterization methods that need to be complemented by theory. Energy-tunable soft X-rays are the basis for a unique set of tools that are sensitive to molecular and electronic structure, spatial and orientation information, and time-resolved dynamics.

Soft X-rays span an energy range that includes the core-level 1s electronic transitions (K edges) of some of the most common elements found in polymers, for example, carbon, nitrogen, and oxygen. Soft X-ray spectroscopy has an inherent ability to not only selectively probe for the presence of these elements, but also be sensitive to various bonding environments, functional groups, and the orientation of chemical moieties. In addition to the chemistry, soft X-rays can be used for energy-dependent scattering experiments that probe spatial information and characteristic length scales that range from a few nanometers to hundreds of nanometers. The interdependence of spectroscopy and scattering allows for unique capabilities to understand the length scales associated with certain components, moieties or molecular orientations. However, understanding the relationships that connect molecular structure, spectroscopy, and scattering can be very complex, and complementary simulations are needed to build fundamental knowledge and help interpret experiments. An improved ability to leverage theoretical predictions will enable soft X-ray methods to move forward into the realm of *in situ* characterization and bridge the gaps among chemistry, morphology, and dynamics in polymers and soft materials.

## 2. X-ray absorption spectroscopy and resonant scattering probe chemistry and structure

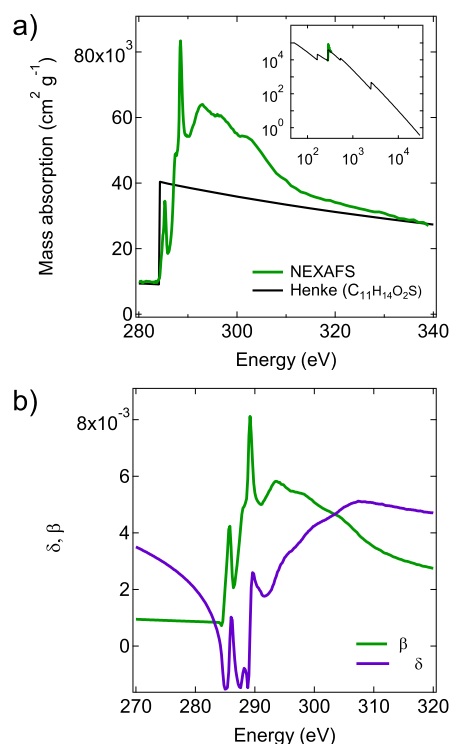
### 2.1. Connections between X-ray absorption and scattering contrast

Near edge X-ray absorption fine structure (NEXAFS) spectroscopy and resonant soft X-ray scattering (RSoXS) and reflectivity (RSoXR) are naturally complementary techniques, and information regarding a materials absorption properties is needed to understand RSoXS and RSoXR. Unlike hard X-ray scattering or electron microscopy where contrast arises due to differences in electron density, at energies near an absorption edge the complex index of refraction,  $n(E) = 1 - \delta(E) + i\beta(E)$ , and hence scattering contrast, varies significantly. NEXAFS data provides information related to  $\beta$ , and this can be extended in energy range and scaled based on a

material's composition using the Henke atomic scattering factor database [14]. The real part of the index of refraction,  $\delta$ , can be calculated from  $\beta$  through a Kramers-Kronig integral relation and the resulting contrast between different phases,  $\Delta\delta^2 + \Delta\beta^2$ , determined as a function of energy. This procedure is often done for organic systems, and an example is shown in Fig. 1. It is clear that at energies near an absorption edge, scattering contrast even between materials with similar electron densities can be greatly enhanced. This is one of the main advantages that soft X-rays have for characterizing polymers. However, the detailed connections between a materials absorption properties and resonant scattering can make it challenging to discern features such as contributions from specific chemical moieties or orientation effects. This is an area where progress in effective combination of theoretical predictions and experiments is needed to improve advanced characterization.

### 2.2. Core-level X-ray absorption spectroscopy

Fundamental knowledge of NEXAFS is a prerequisite to also understanding RSoXS and RSoXR. The subtleties in scattering contrast between polymers stems from the unique absorption



**Fig. 1.** Measured NEXAFS data can be scaled and extended with the Henke database, as shown in (a). The inset shows a log-log plot to demonstrate how the Henke database is used to approximate values at energies outside of where NEXAFS data was collected. The real part of the complex index of refraction,  $\delta$ , determined through a Kramers-Kronig relation, is plotted with the imaginary part,  $\beta$ , in (b). The example here is for a polythiophene, poly[3-(ethyl-5-pentanoate)thiophene-2,5-diyl].

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