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SCATTERING AND PHYSICAL AGING IN INTRINSICALLY MICROPOROUS POLYMERS

A Dissertation in

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by

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ABSTRACT

Polymers of intrinsic microporosity (PIMs) form glassy, rigid membranes featuring a large concentration of pores smaller than 1 nm, a large internal surface area, and high gas permeability and selectivity. Porosity in these materials—closely related to free volume arises from an unusual chain structure combining rigid segments with sites of contortion. Linear PIMs can be easily solution-cast into films whose interconnected networks of micropores can be exploited for applications such as gas separation and storage. Like other glasses, though, PIMs are subject to physical aging: a slow increase in density over time. This is accompanied by a decrease in permeability that reduces their performance as gas separation membranes.

Several characterization methods are routinely employed to measure the structural properties of microporous materials, but none are as widely available and as easily applied to film samples with varied sample histories as small- and wide-angle X-ray scattering (SAXS and WAXS). Although it is possible to derive useful information such as surface areas and pore sizes from the scattering patterns of many porous materials, scattering from PIMs includes some unusual features whose interpretation is not readily apparent.

In this work, a robust interpretation of PIM SAXS and WAXS features is developed with support from molecular dynamics simulations. The sensitivity of these patterns to time, temperature and film thickness is shown to be qualitatively consistent with physical aging, demonstrating that high-free-volume, porous polymeric glasses present a unique opportunity to study structural changes during physical aging using scattering methods. Models for extracting quantitative information about changes in the sizes and volume fraction of pores are also explored. Although quantitative interpretation of scattering patterns remains challenging, results of the aging study suggest that there may be two distinct mechanisms of aging in PIMs.

Several tangential investigations are also presented, including (1) a study of smallmolecule porous materials using scattering experiments; (2) a preliminary study of alcohol adsorption in PIMs using small-angle neutron scattering (SANS) and quartz crystal microbalance (QCM) techniques; and (3) a study of the low-*q* power-law scattering observed in a wide variety of amorphous, homogeneous polymers, including PIMs.

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Chapter 1

Introduction

The focus of this dissertation is the characterization of polymers of intrinsic microporosity (PIMs) using scattering methods. PIMs are glassy polymers that undergo physical aging; these concepts are introduced in this chapter. PIMs are also examples of microporous materials, to which several other experimental structural characterization techniques have been applied. These techniques as well as results previously obtained for PIMs are reviewed. The application of scattering methods to amorphous polymers is also introduced here, although discussion of specific models is deferred to Chapter 4.

In Chapter 7, an investigation of the low-*q* scattering upturn observed in a wide variety of polymers is reported. Because this study is tangential to the rest of this work—related only because scattering methods are used and the phenomenon is observed in PIM-1—background information specific to that investigation is reserved for Chapter 7.

1.1 Amorphous Polymers

Amorphous polymers are those that contain no crystalline component, which can be verified by the absence of sharp diffraction peaks in wide-angle X-ray scattering (WAXS) patterns. In calorimetric experiments they exhibit a single glass transition. In contrast, semi-crystalline polymers exhibit WAXS diffraction peaks as well as a phase transition temperature arising from the melting of crystalline regions.

1.1.1 The Glass Transition

Above the glass transition temperature T_g , bulk amorphous polymers exist in a disordered liquid state. Segments of polymer chains above T_g are capable of coordinated motion and the material exhibits liquid-like mechanical properties. As a polymer melt is

cooled through T_{g} , this segmental motion ceases and the material takes on the mechanical properties of a solid. However, there is no abrupt change in the structure of the material; like liquids, glasses lack long-range order.

Crystalline melting is an example of a first-order phase transition, including a discontinuous change in density and a latent heat of melting. However, the glass transition includes neither of these and is generally considered a second-order phase transition. Both types of phase transitions include changes in heat capacity as well as in the rate of change in density with respect to temperature (Figure 1-1).



Figure 1-1. A comparison of the glass transition (right column) with melting (left column), reproduced from ref [1]. Both involve discontinuities in properties related to the second derivative of free energy (bottom row), such as heat capacity, compressibility, and the thermal expansion coefficient. However, melting involves a discontinuity in properties derived from the first derivative of free energy (volume, enthalpy, and entropy), while the glass transition does not (top row). As a result, melting is considered a first-order phase transition and the glass transition is often considered a second-order phase transition.

1.1.2 Physical Aging in the Glassy State

The glass transition is not a true phase transition in the strict sense of a change from one thermodynamically equilibrated state to another, and there is debate over whether there is an underlying thermodynamic transition or whether it is purely a kinetic phenomenon [1, 2]. As a polymer is experimentally cooled through T_g , it changes from an equilibrium liquid state to a kinetically trapped configuration—in fact, the precise T_g measured is affected by the cooling rate [3]. If the glass is held at a constant temperature below T_g , however, its properties continue to evolve in the same direction. This phenomenon is known as *physical aging* and notably includes an asymptotic increase in density toward some presumed equilibrium value [4] (Figure 1-2).



Figure 1-2. When a polymer is cooled at a constant rate, the specific volume v (reciprocal density) decreases at different rates above and below T_g (blue lines). If the polymer is held at a constant temperature below T_g but above the temperature of the highest secondary transition T_β (i.e, that associated with the onset of local molecular motions), over time the specific volume decreases toward an equilibrium value. Figure adapted from ref [4].

1.1.3 Free Volume

The glass transition and physical aging can both be roughly understood¹ by considering the circular relationship between mobility and a quantity termed *free volume*, v_f . Molecules or chain segments in a glass former move more quickly when there is more unoccupied volume (with a weaker direct dependence on temperature). In turn, any change in density required to reach equilibrium can occur more quickly when mobility is higher (Figure 1-3) [4].

The glass transition occurs when mobility becomes very small—or equivalently, when free volume becomes very small. Below T_g , a glass always has higher free volume (lower density) than its equilibrium value. However, the amount of free volume is already so small that mobility and thus dv_f/dt (the rate of change of free volume) is also very small. As aging progresses at a constant temperature, mobility continues to decrease and the aging process continues to slow [4].



mobility facilitated by free volume

Figure 1-3. Amorphous materials contain more unoccupied volume than crystalline materials (top row). When sufficient free volume—related but not equivalent to unoccupied volume—is available, molecules or chain segments are able to move relative to one another (bottom). Figures reproduced from ref [1].

¹ A competing class of glass-transition theories arises from considering configurational entropy as a starting point, rather than free volume [2]. Free volume is significantly more relevant to this work.

The glass transition and physical aging are complex phenomena constituting an active area of research. In porous polymers, one of the most important properties affected by aging is permeability. The relationship between permeability P and free volume v_f is exponential:

$$P = DS = Ae^{-B/v_f} \tag{1-1}$$

with *A* and *B* representing empirical constants for a given gas molecule [5]. Changes in free volume have a large impact on the diffusivity *D* with minimal effect on the solubility *S* [6].

1.1.3.1 Terminology: Porosity and Free Volume

The 'porosity' in microporous polymers—in the context of gas adsorption, positron annihilation, and scattering experiments discussed throughout this dissertation—is equivalent to the difference between the specific volume occupied by the bulk polymer and the specific volume occupied by its atoms. This specific *unoccupied* volume, or pore volume fraction, is difficult to calculate accurately for polymers, but a number of group contribution methods have been explored [5].

Precise definitions of the term 'free volume' vary depending on context [7]. When the concept of free volume is invoked to explain dynamic phenomena or mechanical properties, it is sometimes taken to be the unoccupied volume *in excess* of that which would remain at equilibrium, maximum packing, or 0 K [1, 7]. Fractional free volume calculated using the Bondi group-contribution method uses the van der Waals volume multiplied by a universal factor of 1.3 [8], implying that free volume is proportionally smaller than unoccupied volume (porosity). A similar method with variable coefficients, empirically determined for specified gases and chemical groups, yields improves permeability predictions using Equation 1-1; the majority of these coefficients are larger than 1 [5].

Porosity and free volume are thus closely related but not precisely equivalent. During physical aging, fractional free volume and pore volume fraction clearly both decrease. However, the proportionality constant between the two may be specific to the polymer and, in the case of permeability, the probe gas molecule. By some definitions, in a fully aged or equilibrium sample free volume might be zero while porosity remains finite. In this work only changes in porosity are measured and discussed, but it can be inferred that free volume changes in a qualitatively similar manner.

1.1.4 Dependence of Aging Rate on Temperature and Film Thickness

For several polymers, faster aging in thinner films has been reported (Figure 1-4) [6]. This increase in aging rate is not well explained by reduced T_g in thinner films. However, diffusion of free volume elements toward the surface has been suggested as a mechanism of aging, and such diffusion would likely occur more quickly in thinner films [6, 9]. In addition, aging occurs more rapidly when films are held at higher temperatures (Figure 1-4) [10]. This can be explained by the availability of additional thermal energy for whatever dynamic process is involved in aging.



Figure 1-4. The rate of change of permeability (a measure of aging rate) versus glassy polysulfone film thickness is plotted at three temperatures, showing that aging is faster at higher temperatures (all below T_g) and in thinner films. Figure reproduced from ref [10].

1.2 Structural Characterization of Porous Materials

1.2.1 Classification of Porosity

The polymers of intrinsic *micro*porosity studied in this work are named in accord with the IUPAC nomenclature [11] defining 'microporous' materials as those featuring pores smaller than 2 nm (Table 1-1). This convention has resulted in considerable disorganization in the literature: because materials with micron-sized pores are often termed 'microporous', true 'microporous' materials are frequently described as 'nanoporous' to avoid such confusion.

Table 1-1. IUPAC classification of porous materials [11] and characteristics typical of each size range [12]. ^(*) Isotherm shapes are illustrated in Figure 1.5.

Classification	Pore width	Isotherm characteristics
micropore	< 2 nm	adsorbate interacts with multiple walls; type I (*)
mesopore	2 to 50 nm	capillary condensation; type IV (*)
macropore	> 50 nm	difficult to characterize via isotherm

While the naming scheme may be unfortunate, this division of size scales corresponds to significant differences in properties that impact both performance in potential applications and the suitability of various characterization techniques [12]. In microporous materials, the size of pores is comparable to the size of small molecules that might flow through the bulk material or adsorb onto its interior surface. Such small molecules then interact with multiple pore walls simultaneously. As a result, microporous materials are particularly effective as adsorbents, and adsorption isotherms used to characterize their porous structures have a characteristic shape. These same effects make microporous materials ideal for gas separation: pore sizes can be tuned to discriminate based on molecule size, and the effect of interactions arising from the chemistry of the material is amplified by multi-wall interactions.

1.2.2 Gas Adsorption Isotherms

In an isothermal adsorption experiment, the porous material is exposed to the probe vapor at a controlled relative pressure; the system is allowed to equilibrate and either the mass or volume of gas adsorbed into the porous material is measured. This produces one data point on the plot. The process is then repeated at additional relative pressures. Because hysteresis frequently appears (such as in Types IV and V isotherms, shown in Figure 1-5), usually attributed to swelling [12, 13], both adsorption and desorption isotherms are commonly measured.



Figure 1-5. Gas adsorption isotherm types. Microporous materials exhibit the fast adsorption at low relative pressures seen in Types I, II, IV and VI due to adsorbate interactions with multiple pore walls. Figure reproduced from ref [12].

From an adsorption isotherm, a measure of the specific surface area of the porous material can be calculated. First, it is necessary to estimate a value a_m for the cross-sectional area of the adsorbate molecule, which can then be related to the specific surface area A by

$$A = n_m a_m N_a \tag{1-2}$$

using the Avogadro constant N_a and the monolayer capacity n_m in moles of adsorbate per gram of adsorbent [12, 14]. If only monolayer adsorption is assumed to occur, n_m can be extracted from fitting the adsorbed quantity n versus pressure p to the Langmuir equation [12]:

$$\frac{n}{n_m} = \frac{Bp}{1+Bp} \tag{1-3}$$

where *B* is fundamentally related to the heat of adsorption and adsorption/desorption rate constants, but in practice is empirically fit. However, use of the Langmuir monolayer model yields unreasonably high surface areas for microporous materials, so a multilayer adsorption model is required [12]. The Brunauer-Emmett-Teller (BET) model extends the Langmuir model to multiple adsorbed layers by treating all layers after the first as identical, becoming a bulk liquid at $p = p^\circ$, where p° is the saturation vapor pressure):

$$\frac{p}{n(p^{\circ}-p)} = \frac{1}{n_m C} + \frac{C-1}{n_m C} \frac{p}{p^{\circ}}$$
(1-4)

with larger values of the fitted parameter *C* corresponding to sharper knees in the adsorption isotherm as well as stronger adsorbate-adsorbent interactions (relative to adsorbent-adsorbent interactions) [12]. Despite criticism of the BET model, such as the neglect of any dependence on fractional surface coverage and of any heterogeneity in adsorption sites [12], it has become the standard surface area reported for microporous polymers [13].

A pore size distribution (PSD) is also commonly calculated from adsorption isotherm data using the Horvath-Kawazoe (HK) method [13]. This approach is based on the fundamental assumption that the smallest pores fill at the lowest relative pressures. Because it is difficult to access low enough pressures to characterize pores smaller than about 6 Å, an artificially sharp peak often appears near the low end of the PSD [13].

1.2.3 Positron Annihilation Lifetime Spectroscopy

In positron annihilation lifetime spectroscopy (PALS), positrons are injected into a porous material. Once a positron slows down to thermal energies, it captures an electron to form positronium. The lifetimes and gamma-ray decay products of the different spin states of positronium are known; furthermore, positronium lifetimes are perturbed in known ways by interactions with atomic electrons in the porous material. By measuring the intensity of gamma rays over time, the mean free path of positronium can be deduced. Depth profiling is also possible by controlling the initial energy of implanted positrons [15].

The mean free path measured by PALS is interpreted as a measure of the size of 'holes' [16], 'free volume elements' [16, 17], 'elementary free volumes' [18], or 'electron free volumes' [19]. When applied to microporous polymers, it sometimes taken as a measure of pore size [15, 19]. Taken together, this suggests that porosity and free volume are equivalent [20], but this usage of terminology seems imprecise (Section 1.1.3.1). Because in PALS—like X-ray scattering (Section 1.4)—the probe particles interact with electrons, 'unoccupied volume' is a better description of the quantity measured.

1.3 'Intrinsically' Microporous Polymers

1.3.1 Definition and Example

Most polymers fill space too efficiently to exhibit a microporous structure in the glassy state without some sort of templating or crosslinking. However, polymers of intrinsic microporosity (PIMs) employ a novel strategy, combining rigid segments with sites of contortion (Figure 1-6). The resulting structure is too irregular to crystallize and lacks the conformational freedom to fill space as completely as most amorphous polymers. PIMs feature high gas permeability [13] and are described as 'high free volume' polymers [21], although as noted in Section 1.1.3.1 the quantitative relationship between porosity and free volume is poorly defined. Rather than consisting of a bulk phase with discrete pores, they are glassy materials with well-connected unoccupied volume (porosity). PIMs' porosity is

termed 'intrinsic' because they exhibit unusually high free volume and permeability regardless of processing conditions, although precise values of measured quantities are sensitive to sample history.



Figure 1-6. Chemical structure and single-chain conformation of PIM-1. Figure reproduced from ref [22].

1.3.2 Properties of PIM-1

PIM-1 is easily cast into a film from solution in chloroform, and it exhibits no glass transition below its decomposition temperature of 370 °C [23]. BET analysis of powder adsorption isotherms using N₂ at 77 K has yielded surface areas ranging from 760 to 850 m^2/g [13, 23].

1.3.2.1 Pore Size Distribution

When PIM-1 is subjected to various characterization techniques, pore sizes are invariably found to be smaller than ~ 1 nm (Figure 1-7). Pore size distributions can be measured by techniques such as gas sorption isotherms and PALS, but the results are sensitive to assumptions in the models used to interpret this data [14, 24]. An artificially sharp peak near the small size end of the nitrogen PSD derived from the HK model is evident, and PALS data are interpreted with a bimodal distribution, although a broad unimodal distribution is another possible interpretation [13].



Figure 1-7. Differential pore size distributions in PIM-1 as measured by molecular dynamics simulations (blue) [25], nitrogen adsorption (red) [26], and PALS (green) [27]. Figure reproduced from ref [25].

1.3.2.2 Permeability

In the design of microporous materials for separation applications there is an inherent trade-off between permeability and selectivity [28]: if pores are made smaller, selectivity related to molecule size is enhanced. At the same time, the mobility of molecules that are still small enough to flow through the membrane is also reduced (Figure 1-8). PIM-1 performs well by both measures and was one of several materials that prompted a revised empirical upper bound in 2008 [13, 29].

Notably, the precise values of permeability and selectivity for a PIM-1 film depend on its history. A film recently swollen in methanol and then dried exhibits higher permeability but lower selectivity (Figure 1-8). Comparing these performance metrics with direct structural measurements is of interest, but gas adsorption studies are performed only on powders due to slow adsorption kinetics. In principal, PALS could be applied to films aged for different times, but such studies have not been reported.



Figure 1-8. O_2/N_2 selectivity plotted versus O_2 permeability for a variety of polymers, illustrating the tradeoff between permeability and selectivity. Lines represent empirical upper bounds given by Robeson, reported first in 1991 [28] (solid line) and revised in 2008 [29] (dashed line). A PIM-1 film recently swollen in methanol and then dried (filled circle) exhibits higher permeability but lower selectivity than other PIM-1 film samples (open circles). Figure adapted from ref [13].

1.3.2.3 Film Aging and Rejuvenation

Like other glasses, PIM films physically age over time: density increases, which means that porosity and free volume also decrease. A decrease in permeability over time, attributable to aging, has been measured in PIM-1 (Figure 1-8) [24] and in other glassy polymers [6].

In typical studies of physical aging in polymers, the aging 'clock' is reset by heating a film above its T_g [6]. The absence of an observed glass transition in PIM-1 prevents use of this strategy. Alcohol treatment, which causes PIM-1 to visibly swell and increases its

permeability to that of an un-aged film [24], is thus considered a 'rejuvenation' technique analogous to annealing above T_{g} .



Figure 1-9. Change in permeability coefficients over time for PIM-1 films after soaking in methanol. Films were 107 μ m thick, and gas chromatography measurements on a similar film showed that no residual methanol was present after 1 day of exposure to ambient conditions. During the 45-day observation period, P(O₂) decreased by 23%, P(N₂) decreased by 40%, and the permselectivity P(O₂)/P(N₂) increased from 3.3 to 4.2. Figure and other information reproduced from ref [24].

1.4 Scattering Methods Applied to Amorphous Structures

In a scattering experiment, a beam of probe particles such as X-rays or neutrons is passed through the sample and onto a detector. The scattered intensity is measured as a function of the angle 2θ between incident and scattered beams. Particles that are deflected from adjacent crystal planes (for example) travel slightly different distances, depending on the scattering angle, the wavelength λ of the particle, and the distance *d* between these planes. If this path-length difference $2d \sin \theta$ is an integral multiple of λ , constructive interference occurs and a maximum in scattered intensity is observed. This relationship between real space and 'reciprocal space' is expressed as Bragg's law:

$$q = \frac{4\pi \sin \theta}{\lambda} = \frac{2\pi}{d} \tag{1-5}$$

where use of the wavevector q eliminates the dependence on λ , which may vary from one experiment to the next. (For a fuller discussion, see for example ref [30].)

Soft materials often feature microphase separation arising from the chemical dissimilarity of various components that constitute covalently bound components of large molecules. These chemically dissimilar regions generally differ in electron density (as well as neutron scattering length density), and this scattering contrast gives rise to scattering features at a larger size scale—in the small-angle scattering (SAS) domain, approximately 1 to 100 nm.

In general, scattered intensity I(q) from discrete particles—whether atoms, micelles, or pores—can be represented as the product of a structure factor S(q) and a form factor P(q):

$$I(q) = P(q)S(q) \tag{1-6}$$

The form factor is related to the shape of scattering bodies, while peaks in the structure factor arise from correlations among distance between pairs of scattering bodies—these are the interference maxima mentioned above. Because only I(q) is observed directly, developing a model that accounts for both contributions can be challenging, especially in the SAS domain.

The structure factor is related by a Fourier transform to a quantity known as the radial distribution function g(r): the probability of finding an atom at a distance r from a reference atom at the origin. In a crystalline material, g(r) is a perfectly periodic function, and S(q) correspondingly contains a sharp peak. In an amorphous material, however, g(r) is a damped oscillating function with only a few clear peaks, and the corresponding structure factor contains a much broader peak. The scattered intensity from amorphous polymers includes such broad 'amorphous halos' at large angles, associated with characteristic distances between adjacent polymer segments [31].

1.4.1 Complementary Molecular Simulations

This relationship between g(r) and S(q) also makes scattering experiments and molecular simulations naturally complementary. Scattering experiments provide ensembleaveraged structural information of good statistical quality, sampled from a large volume (easily 1 mm³) over a period of minutes to hours. However, features in scattering patterns are not always straightforward to interpret; scattered intensity is the sum of all structure factors, each multiplied by the corresponding form factor. In atomic-scale simulations, g(r) is straightforward to calculate, and the local arrangement of atoms or other domains giving rise to a peak can be examined directly. The challenge is simulating a structure representative of the ensemble average with a limited sample size and limited simulation duration. It is therefore advantageous to validate simulated structures by calculating scattering patterns and to then use those simulated structures to understand scattering features.

1.5 Motivation for PIM Structural Characterization Using Scattering Methods

For gas separation applications, porous polymers in film form rather than powders are of interest. It is also clear that the structure is sensitive to sample history, including aging over time, swelling in nonsolvent organic liquids, and plasticization by soluble gases. Other structural characterization methods provide basic information about PIM pore sizes but are unable to characterize the porous structure in PIM *films*, as a *function of sample history*:

- Gas sorption measurements make use of a probe gas molecule that cannot infiltrate the smallest free volume elements and causes the material to swell, as evidenced by hysteresis in isotherms. In addition, studies are carried out exclusively on powders due to the slow adsorption kinetics in relatively thick films.
- Simulations provide a valuable pre-synthesis screening process but are not targeted toward reproducing specific sample histories. The equilibrium molecular dynamics simulations already performed on PIMs [25, 32] may be used to examine the structure at specific densities, and other techniques such as non-equilibrium molecular dynamics may provide a means of investigating changes in structure over time [33, 34].
- Positron annihilation lifetime spectroscopy (PALS) may have the greatest potential to interrogate film samples in a manner similar to scattering. In fact, depth-resolved

PALS could be especially helpful in studying the thickness dependence of aging rate [15]. However, PALS instrumentation is much less widely available than SAXS/WAXS, and the technique can only be applied to voids, not pores filled with adsorbed gases or swollen in liquids. The apparent bimodal pore size distributions yielded by this technique are also at odds with all other measurements of PIM pore sizes, which yield unimodal distributions [13].

Scattering methods are ideally suited to study PIM films of well-defined sample history. Because PIM porosity is closely related to free volume, and scattering patterns evolve during physical aging, these materials also provide a unique opportunity to study changes in the structure of unoccupied volume (porosity) that occur during physical aging. The challenge of applying scattering methods to PIMs lies in accurately fitting models to the data in order to quantitatively derive physical parameters of interest, such as pore volume fraction, pore size distributions (PSDs), and specific surface areas.

1.6 Dissertation Organization

Following from this introduction, Chapter 2 will describe sample preparation techniques as well as a variety of scattering methods and other techniques used throughout this work. Figure 1-10 illustrates the organization of data chapters.

The main thread of this work runs through Chapters 3, 4 and 5. In Chapter 3 an unambiguous interpretation of the features in PIM scattering patterns is established, based on both molecular dynamics simulations and PIMs of a variety of chemistries and sample histories. Chapter 4 builds on this interpretation to evaluate different models for extracting semi-quantitative structural information from PIM scattering patterns. In Chapter 5, these models are applied to study changes in PIM porosity during physical aging using time-resolved X-ray scattering; data is summarized within Chapter 5 and presented in detail in Appendix B. Appendix C describes a preliminary study of the relationship between PIM swelling and organic vapor adsorption using quartz crystal microbalance (QCM) experiments as well as small-angle neutron scattering (SANS). Chapter 7 summarizes the methods developed (Chapters 3 and 4) and information gained (Chapter 5 and Appendix C)

through these scattering studies of PIMs.



Figure 1-10. Diagram of dissertation organization.

This work also includes two investigations that are largely independent but have some connection to Chapter 3. Chapter 8 describes an extensive investigation of the low-*q* power-law scattering exhibited by virtually all amorphous polymers. Because this group includes PIMs, this provides some additional justification for the treatment of this scattering feature in the analysis and modeling of PIM scattering data, which is essentially to ignore it. Appendix A describes wide-angle scattering studies of organic molecules of intrinsic microporosity (OMIMs), which are similar to PIMs. This data is discussed in relation to a previous investigation making use of a method developed in Chapter 3, examining partial structure factors from simulations to validate the interpretation of scattering features.

Chapter 2

Methods and Materials

The materials (PIMs) described below are studied in Chapters 3–5 and in Appendix C. The X-ray scattering methods detailed here are used throughout Chapters 3–5, Chapter 7, and Appendices A and B. Appendix C employs distinct experimental methods and sample preparation procedures, which are described internally.

2.1 Materials

PIM-1 and thioamide-PIM-1 (TA-PIM-1) samples in film and powder form were provided by Prof. Peter Budd's research group, including Louise Maynard-Atem, Christopher Mason, Nhamo Chaukura, and Carin Tattershall. Powder samples of other linear PIMs were provided by Prof. Neil McKeown's research group, including Kadhum Msayib and Mariolino Carta. The synthesis of PIM-1[35], TA-PIM-1[36], and some variant linear PIMs[37] has been described elsewhere. PIM chemical structures are illustrated in Figure 2-1.

2.2 Sample Preparation

2.2.1 Powders

Most materials were received in powder form after precipitation from solution in tetrahydrofuran (a good solvent for PIMs) by the addition of methanol (a nonsolvent). Immediately prior to scattering measurements, powder samples were degassed in a vacuum oven at 120-130 °C for at least 24 h. For scattering measurements, powder samples were contained in cells between two Kapton films windows with a thickness of 0.2 mm.


Figure 2-1. Chemical structures of polymers of intrinsic microporosity (PIMs) discussed in Chapters 3 through 7. Modifications to the nitrile group of PIM-1 are denoted with a prefix, while altered spirocenter substituents are named with a prefix.

2.2.2 Solution-Cast Films

PIM-1 films were cast from solution in chloroform using leveled borosilicate glass petri dishes as a substrate. During casting, solutions were placed in a dessicator containing fresh dessicant to minimize the presence of water vapor. The valve of the dessicator was left open inside a fume hood to allow a slow rate of evaporation at ambient temperature. Samples received already in film form had been cast to a thickness of approximately 100 μ m with evaporation occurring over 3 to 4 days. This is the standard film thickness used in permeability studies; initial solution concentrations in other studies vary but are approximately 20 mg/ml.

A large quantity of PIM-1, batch LMA-25, was received in powder form and cast into films as needed for experiments in Chapters 5 and 6. One variable investigated in scattering experiments was film thickness, and thinner films evaporated over a shorter period of time. In some experiments, as noted, a different substrate was used (mica or <111> silicon wafer) to achieve a more uniform thickness when stacks of films as thin as 20 μ m were required.

'Degassed' films were stored in a vacuum oven at 120-130 °C for at least 24 h immediately prior to scattering measurements. Films described as 'methanol-treated' were soaked in methanol for at least 24 h before degassing.

2.3 Wide-angle X-ray Scattering (WAXS)

WAXS patterns were collected in transmission geometry using a Rigaku DMAX-RAPID instrument with pinhole-collimated Cu-K α radiation (λ = 1.54 Å), a beam collimated to 0.3 mm, and an image-plate detector. Isotropic two-dimensional patterns were azimuthally averaged into one-dimensional profiles of intensity I(q) vs. scattering wavevector $q = 4\pi(\sin \theta)/\lambda$, using AreaMax software. Corrections for polarization, integration line length, and an estimated dark count were automatically applied. Corrections for absorption and incoherent scattering were not included, but transmission values were high enough that these corrections would have little effect on intensity values in the range of interest, primarily q < 2 Å⁻¹ (2 θ < 30°). Backgrounds were subtracted from all patterns according to

$$I_{corrected} = I_{measured} - \frac{T_{sample}}{T_{background}} \frac{t_{sample}}{t_{background}} I_{background}$$
(2-1)

where *T* is transmission and *t* is the data collection time.

Because the DMAX instrument does not allow a direct measurement of sample transmission values, these were estimated in one of two ways. For film samples, T_{sample} was

measured with the SAXS instrument on the same film sample. Powder samples were contained in cells with Kapton windows, and $T_{sample}/T_{background}$ was adjusted to eliminate the characteristic Kapton scattering peak at 0.4 Å⁻¹.

2.4 Small-angle X-ray Scattering (SAXS) Instrumentation and Data Reduction

Data in Chapters 3, 4 and 5 were obtained using laboratory SAXS and WAXS instruments at Penn State (Sections 2.3, 2.4.1). Ultra-small-angle X-ray scattering (USAXS) patterns are presented primarily in Chapter 7, with several included in Chapter 3.

2.4.1 Laboratory SAXS

Small-angle X-ray scattering (SAXS) patterns were collected under vacuum using a Molecular Metrology instrument with pinhole-collimated Cu-K α radiation (λ = 1.54 Å), a multiwire area detector, and a sample-to-detector distance of either 1.5 m (chamber 1) or 0.5 m (chamber 2). A silver behenate standard was used for wavevector calibration. Using SAXSGUI software, isotropic two-dimensional patterns were azimuthally averaged and backgrounds were subtracted according to Equation 2-1. Additional corrections were also applied during this reduction procedure:

- A flat-field correction was used to compensate for variation in detector sensitivity, calibrated using isotropic radiation from a radioactive Fe-55 sample. This was a pixel-by-pixel correction applied to the 2D data before azimuthal averaging.
- A mask was created to exclude the beamstop and damaged areas of the detector from azimuthal integration.
- A glassy carbon standard was used to determine a vertical scaling factor to place data on an absolute scale [38]. The standard was also used to verify the *q* range in which data was quantitatively accurate.

2.4.1.1 Combined SAXS/WAXS Patterns

WAXS measurements were not inherently calibrated on an absolute-intensity scale. However, there was sufficient overlap in wavevector range between WAXS patterns and SAXS patterns to vertically scale the WAXS data, producing the continuous patterns spanning 0.02 < q < 3 Å⁻¹ shown in Chapters 3 and 4. (Higher and lower limits are possible but did not include features of interest for these materials.)

Using a smaller collimator during WAXS pattern collection—0.3 mm instead of the usual 0.8 mm—allowed the use of a beamstop producing a smaller shadow on the detector. This reduced the minimum wavevector accessible by WAXS, increasing overlap with SAXS data. The smaller collimator also reduced resolution effects, which can alter the scattered intensity at low wavevectors. The disadvantage was lower incident beam flux and longer data collection time.

2.4.2 Ultra-Small-Angle (USAXS) Instrumentation and Data Reduction

USAXS patterns were collected at beamline 32-ID [39, 40] of the Advanced Photon Source using a Bonse-Hart camera with slit collimation and an incident energy of 12 keV (λ = 1 Å). Backgrounds were subtracted and patterns were desmeared using Irena tools [41] for the application Igor.

2.5 Molecular Dynamics (MD) Simulations

Simulations of PIM-1 and characterization of simulated structures were performed using a method developed by Larsen, *et al.* [25, 32]. To model PIM-1, chains were grown at a low density (0.07 g/cm³) and then compressed using a 21-step scheme to a realistic density (~1 g/cm³) using LAMMPS [42] with bonded parameters from GAFF [43], non-bonded parameters from TraPPE [44], and charges from *ab initio* calculations with Gaussian 03 [45] and RESP [46], as given in ref [32].

An initial study of contributions to PIM scattering patterns using simulated partial structure factors (Section 3.3.1) was performed using boxes 45 Å in size (at 1 bar) packed

with chains up to 10 repeat units long, the same simulated structures created by Gregory Larsen and described in ref [25]. Because the wavevector range of simulated scattering patterns is limited by the box size $L-q_{min} = 2\pi/(L/2)$ —larger boxes were required to investigate the broad SAXS feature in PIM-1. Section 3.2.1 describes original, significantly larger boxes simulated using the same method. These cubic boxes were ~80 Å in length at 1 bar.

In addition to scattering patterns, other quantities can be calculated from simulated structures: pore volume fraction, pore size distribution, and specific surface area. All of these quantities were averaged over 10 independent boxes with standard deviations reported as error bars.

2.5.1 Calculation of Scattering Patterns from Simulations

The X-ray scattering structure factor S(q) was computed using ISAACS software[47].² The total structure factor for an isotropic system can be computed from a Fourier transform of the sum of partial radial distribution functions $g_{AB}(r)$ weighted by atomic X-ray scattering lengths b_i and mole fractions c_i [30, 47]:

$$S(q) = 1 + 4\pi\rho \int_0^\infty \left[\frac{1}{\langle b^2 \rangle} \left(\sum_{A,B} c_A b_A c_B b_B g_{AB}(r) \right) - 1 \right] \frac{\sin qr}{qr} r^2 dr$$
(2-2)

where $g_{AB}(r)$ represents the probability of finding an atom of species B at a distance r from an atom of species A, normalized to 1 at large distances, and

$$\langle b^2 \rangle = \left(\sum_i c_i b_i\right)^2 \tag{2-3}$$

² In general, the experimentally measured scattering intensity I(q) can be expressed as the product of a structure factor S(q), arising from correlations among distances between pairs of scattering bodies, and a form factor P(q), arising from the shape of scatterers. Because these calculations treat X-ray atomic form factors (corresponding to the spatial distribution of electrons) as q-independent, it is appropriate to denote simulated scattering patterns as S(q) rather than I(q). This approximation has greatest impact at high q where there are few features of interest in PIMs.

with the index *i* spanning the atom types present in the simulated structure. This is equivalent to the Debye equation[47]

$$S(q) = \frac{1}{N} \sum_{j,k} b_j b_k \frac{\sin(q|\mathbf{r}_j - \mathbf{r}_k|)}{q|\mathbf{r}_j - \mathbf{r}_k|}$$
(2-4)

where *j* and *k* are atomic indices and *N* is the number of atoms in the simulated system.

2.5.1.1 Partial Simulated Structure Factors

Expressing S(q) directly in terms of $g_{AB}(r)$ enables efficient calculation via Fourier transformation. It also facilitates a simple definition of partial structure factors $S_{AB}(q)$, similar to the Faber-Ziman definition but scaled by mole fractions and scattering lengths[22]:

$$S_{AB}(q) = \frac{c_A b_A c_B b_B}{\langle b^2 \rangle} \left(1 + 4\pi \rho \int_0^\infty [g_{AB}(r) - 1] \frac{\sin qr}{qr} r^2 dr \right)$$
(2-5)

so that the total structure factor is a simple sum of partial structure factors:

$$S(q) = \sum_{A,B} S_{AB}(q) \tag{2-6}$$

2.5.2 Other Simulated Characterization

A geometrical measure of surface area was calculated using a Monte Carlo integration procedure developed by Düren, *et al.*[48]: a spherical probe with the diameter of a nitrogen molecule (3.681 Å) was randomly inserted at many points and tested for overlap with atoms in the simulated structure. Accessible surface area was then derived from the fraction of test points that did not overlap (Figure 2-2). Incorporating a probe

molecule with a finite radius provides a measure of surface area that is more directly comparable to gas adsorption experiments (for metal-organic frameworks [48]) than the Connolly surface area (Figure 2-2).



Figure 2-2. Calculation of the accessible surface area from a simulated structure. Figure reproduced from ref [48].

Pore volume fraction (called 'fractional free volume' in related works [25, 32, 49]) and pore size distribution (PSD) were calculated using a different Monte Carlo integration method described by Gelb and Gubbins [50]. In this method, the simulated structure is overlaid with a three-dimensional grid of points. As above, each point is tested for overlap with atoms in the simulated structure—but here the test is performed as a function of probe size *r*. The pore volume fraction is defined as the fraction of accessible grid points with a probe size of zero. Taking the volume fraction of pores of size *r* to be the difference between the pore volumes V_{pore} accessible to probe of size *r* and r + dr, the PSD is then defined as the negative derivative of pore volume fraction.

Chapter 3

Interpretation of Scattering Features from Linear PIMs with Insight from Molecular Dynamics Simulations

The data and general discussion in parts of this chapter, including Sections 3.1 and 3.3.1, have been published in ref [22]. However, the text is not reproduced word for word.

3.1 General Features of PIM X-ray Scattering Patterns

Scattering patterns from PIM-1 films include three principal features: power-law (I $\propto q^{-3}$) scattering at low q, a broad SAXS/WAXS feature with a maximum near 0.27 Å⁻¹, and several weak peaks at 0.9 Å⁻¹ and larger wavevectors. Figure 3-1 illustrates these in comparison with a pattern from atactic polystyrene (aPS), a typical nonporous amorphous polymer.

3.1.1 Comparison with Amorphous Polymers

Nonporous amorphous polymers typically exhibit amorphous halos observable in wide-angle scattering experiments, negligible small-angle scattering, and a power-law upturn at low q with onset near 0.1 Å⁻¹ (see Chapter 7 for a detailed discussion of the low-q upturn). Such scattering patterns reveal some short-range order: the average distance between nearest-neighbor chain segments can be derived from amorphous halos using the Bragg equation. On the other hand, the absence of SAXS features indicates that there is no order or phase separation at a scale larger than a few nanometers.

In PIMs the principal source of scattering contrast is between polymer and empty space (free volume). Because pore sizes are defined by distances between neighboring chain segments, one might expect to observe amorphous halos shifted to slightly lower q compared with nonporous polymers, indicating larger intersegmental distances. However,

the patterns observed are more complex. PIM-1 films exhibit strong scattering throughout the SAXS range. This broad feature is centered at 0.27 Å⁻¹, and the corresponding Bragg spacing of 23 Å is much larger than any pore size measured in PIM-1 (Section 1.3.2.1). Superimposed on this broad SAXS/WAXS feature are a number of peaks, and although their wavevectors are comparable to those of typical amorphous halos, their intensities are much weaker.



Figure 3-1. Broad *q* range X-ray scattering data for a PIM-1 film (red), shown in comparison with atactic polystyrene (grey). Data includes combined USAXS, SAXS and WAXS patterns, with SAXS and WAXS data scaled to overlap with USAXS data. The top axis shows the equivalent Bragg spacing. Inset: the same data plotted on a linear-linear scale.

3.1.3 Hypotheses

It is reasonable to hypothesize that the strong small-angle scattering observed in PIMs is related to their large free volume, but the relationship between porosity, pore sizes

and scattering features is less than clear. In this chapter, these relationships will be explored using complementary simulations as well as PIMs of varying chemistries and sample histories. Scattering arising from porosity is expected to decrease in intensity when porosity is lower, due either to sample history or polymer chemistry. If peaks correspond directly to pore sizes, they are expected to shift to higher or lower wavevectors as pores decrease or increase in size.

3.2 Broad SAXS/WAXS Peak

The broad scattering feature observed in PIM-1 films with a maximum near 0.27 Å⁻¹ appears to be related to porosity. Interpreting it simply as an amorphous halo indicating a large intersegmental distance, however, does not seem reasonable: all experimental techniques suggest that most pores in PIM-1 are no larger than 10 Å (Section 1.), much smaller than the equivalent Bragg spacing of 23 Å. The asymmetry of the peak on a linear scale (Figure 3-1, inset) also contrasts strongly with typical amorphous halos.

3.2.1 Effect of High Density on Simulated Scattering Patterns

As described in Section 2.5, it is possible to characterize a simulated structure by calculating surface area, pore size distribution, density, and simulated scattering structure factors. The structure generation process for PIMs includes compression under high pressures, up to 50,000 bar. This provides an opportunity to examine the effect of a large change in porosity on PIM scattering. Because the wavevector range of simulated scattering patterns is limited by the box size, larger boxes than typically studied—80 Å in length, compared to 45 Å—were necessary to study scattering in the range of the broad SAXS peak.

As expected, density increased as pressure increased, virtually eliminating porosity (Table 3-1 and Figure 3-2). Simulated scattering patterns (Figure 3-2) exhibited a high intensity below 1 Å⁻¹, although the maximum near 0.27 Å⁻¹ was not reproduced clearly. The patterns shown are the average of 10 independently generated boxes; scattering patterns from each included a number of extra low-*q* peaks that appeared at different wavevectors in each box, producing large error bars at low *q*. Despite the imperfect agreement with

experimental data, several things are clear: the strong scattering below 1 Å⁻¹ was reproduced by simulations with no pores larger than 10-12 Å in diameter, and this scattering diminished as the porosity of the simulated structures decreased.



Figure 3-2. Effect of increased density on simulated scattering patterns and pore size distributions from PIM-1. Error bars represent the standard deviation over 10 boxes (≈ 81 Å in length at 1 bar).

Table	3-1.	Surface	area	(N ₂	probe	size)	and	density	of	large	PIM-1	boxes	during
compression and decompression.													

Pressure (bar)	Surface area (m ² /g)	Density (g/cm ³)
1000	385 ± 22	1.00
30000	0.37 ± 0.26	1.46
50000	0.02 ± 0.02	1.57
25000	$0.47 \pm .27$	1.44
5000	64 ± 9	1.17
500	386 ± 45	0.99
1	573 ± 36	0.94

3.2.2 Sensitivity to Sample History and PIM Chemistry

Aged PIM films have larger densities and therefore lower fractional free volume. But because experimental pore size distributions are derived from gas sorption measurements on powders—film kinetics are too slow for practical measurements—the effect of aging on pore *size distributions* has not been experimentally measured. The simulated pore size distributions at high densities in Figure 3-2 suggest that both narrowing and a shift in the PSD maximum are possible.



Figure 3-3. Effect of sample history on absolute-intensity SAXS/WAXS patterns from PIM-1 (left) and TA-PIM-1 (right) films. Green patterns are from solution-cast films aged for 2 years (PIM-1) or 6 months (TA-PIM-1) before scattering experiments. Larger scattering intensities are observed from films soaked in methanol (red) or ethanol (blue) for 24 hours prior to scattering measurements. (SAXS measurements were performed under vacuum, removing residual alcohol molecules.)

Soaking aged PIM films in alcohols has been shown to reverse the effect of aging, as quantified by permeability measurements [24]. Figure 3-3 illustrates the effect of this 'rejuvenation' procedure on scattering patterns from PIM-1 and thioamide-PIM-1 films: recently swollen films have larger scattering intensity, which strongly supports the association of this scattering feature with porosity. In addition, scattering intensity is larger in PIM-1 than in TA-PIM-1, which is a post-synthesis modification with lower porosity and permeability than its parent PIM-1 polymer [36].

Notably, in both PIM-1 and TA-PIM-1 the scattered intensity is higher for methanoltreated than for ethanol-treated films, suggesting that methanol may be more effective at reversing physical aging. Chapter 4 discusses semi-quantitative methods of extracting information about porosity from this feature, and Chapter 5 investigates aging as a dynamic process as well as the apparent dependence on swelling liquid.

3.3 Weak High-q Peaks

The weak high-*q* features have little dependence on sample history in experiments or on density in simulations. This suggests that they do not provide a direct measurement of either fractional free volume or pore sizes.

3.3.1 Partial Simulated Structure Factors

Figure 3-4a compares a simulated wide-angle scattering pattern from a 45-Å box to WAXS patterns from PIM-1 samples with different histories: a powder precipitated from solution, a solution-cast film, and an identical film recently swollen in methanol. There is a small extra peak near the low-q limit of S(q), which is likely a box-size effect. However, it is clear that the relative intensities of the high-q peaks are very similar to both film samples while somewhat different from the powder sample, which is presumably further from equilibrium. Scattering from treated and untreated films differs below 1 Å⁻¹, and the simulated scattering pattern aligns better with the treated film.

Using partial radial distribution functions and partial structure factors, S(q) can be separated into contributions from different groups of atoms. Grouping atoms based on whether they are located in spirocenters or rigid segments (Figure 3-4b) yields an interesting result: correlations among atoms in rigid segments predominantly give rise to the high-q edge of the broad SAXS/WAXS feature, while correlations among atoms in spirocenters contribute mainly to the weak high-q features. This suggests that high-qfeatures represent characteristic distances between spirocenters on different chains, a subtle distinction from the usual interpretation of amorphous halos as arising from intersegmental distances.



Figure 3-4. Simulated X-ray scattering structure factor S(q) from a 45-Å box. In (a), S(q) is compared to experimental WAXS intensity of PIM-1 films with varying sample histories: a precipitated powder, a solution-cast film, and an identical film treated with methanol prior to the WAXS measurement. In (b), S(q) is separated into contributions from sites of contortion (S_{S-S}) and rigid segments (S_{R-R}). Figures reproduced from ref [22].

3.3.2 Experimental Data from PIMs of Varied Chemistries

WAXS patterns from powder samples of several variants of PIM-1 were collected (Figure 3-5). In most cases only small quantities were available (~2 to 15 mg) and the polymers were insoluble (unlike PIM-1), so films could not be cast.

While wide-angle scattering from PIM films and powders is similar, in powders the broad SAXS feature is overwhelmed by very intense power-law scattering with onset near 0.2 Å⁻¹. This is typical of particulate materials and is indicative of the fractal nature of powder particle packing. Presumably the faster kinetics during precipitation compared to solvent-casting radically alter the polymer's organization beyond the local scale. As a consequence, the broad SAXS feature can only be meaningfully studied in films.

Small differences in the relative intensities of the weaker high-q features between films and powders were also noted in section 3.3.1. In spite of these limitations, there are some interesting trends in high-q features resulting from alterations of PIM-1's spirocenter

substituents as well as substitutions of nitrile groups.

Changing spirocenter methyl groups to the larger Ph or 2Ph (Figure 3-5, top) gives rise to an additional peak (Table 3-2) similar to the 15-Å segment length, which could be related to increased scattering contrast from larger groups separated by this characteristic distance. This structural change also influences the relative intensities—but not wavevectors—of other high-*q* features that do appear in PIM-1. This supports the idea, suggested by examination of partial simulated structure factors in 3.3.1, that high-*q* features are related to the organization of the spirocenters, which function as sites of contortion along chains.

In contrast, changing nitrile groups to fluorines or pyridines, or creating crosslinks at nitrile sites, shifts the Bragg spacing of the \sim 7-Å feature by up to 1 Å (Figure 3-5, bottom, and Table 3-2), causing the distinct high-*q* features to merge together. These functional groups are more polar than any of the spirocenter substituent variants, so it is likely that they influence electrostatic interactions between chains. This would affect either intersegmental distances or characteristic distances between spirocenters, so this observation is less useful in discriminating between different interpretations of high-*q* features.

Series	Polymer	q (Å-1)	<i>d</i> (Å)
	PIM-1	0.91	6.9
Modified nitrile	Network PIM-1	1.00	6.3
groups	Py-PIM-1	0.97	6.5
(Figure 3-5, top)	F-PIM-1	0.91	6.9
	Py,F-PIM-1	1.05	6.0
Modified spirocenter	PIM-1	-	-
substituents	PIM-1-Ph	0.49	12.8
(Figure 3-5, bottom)	PIM-1-2Ph	0.56	11.2

Table 3-2. Wavevectors and equivalent Bragg spacings of scattering features from powder samples of PIM-1 variants, indicated with dashed lines in Figure 3-5.



Figure 3-5. WAXS patterns from (top) PIM-1 with modified spirocenter substituents and (bottom) PIM-1 with modified nitrile groups. Larger versions of the chemical structures on the right are shown in Figure 2-1.

3.4 Low-q Power-Law Scattering

The origin of low-*q* power-law scattering in polymers, of the general form

$$I(q) \propto q^{-\alpha} \tag{3-1}$$

is an unresolved question that is discussed extensively in Chapter 7. Here it suffices to note that the upturn is present in a wide variety of *non*porous polymers and that in PIM-1, the intensity and exponent of this low-q scattering are within the range observed for nonporous amorphous polymers (Figure 3-6a). In addition, this scattering feature is not sensitive to sample history, which certainly affects porosity (Figure 3-6b).



Figure 3-6. (a) USAXS patterns from PIM-1 (red) compared to assorted amorphous polymers. (b) USAXS patterns from PIM-1 films with different sample histories. The scattered intensity and q^{-3} power law are not sensitive to sample history.

Power-law scattering is frequently interpreted as a fractal dimension, with mass fractals giving rise to exponents α between 1 (sparse) and 3 (dense), and surface fractals giving rise to exponents between 3 (rough) and 4 (smooth)[30]. For smooth surfaces, the Porod equation relates specific surface area *S/V* to scattered intensity:

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$$\lim_{q \to \infty} \frac{I(q)}{Q} = \frac{2\pi}{\varphi_1 \varphi_2} \frac{S}{V} \frac{1}{q^4}$$
(3-2)

where φ_1 and φ_2 are the volume fractions of the two phases, and Q is the scattering invariant

$$Q = \frac{1}{2\pi^2} \int_{0}^{\infty} q^2 I(q) dq$$
 (3-3)

Although there are modified versions of Equation 3-2 suitable for diffuse surfaces, it is crucial to recognize that the Porod equation represents the *high-q limit* of scattering from objects whose form factors (shapes and sizes) contribute to scattering at still lower *q*. Thus, a specific surface area calculated from PIM-1's low-*q* power-law scattering would describe the surface area of objects larger than several microns, not of pores smaller than 1-2 nm.

A specific surface area for PIMs could in principle be derived from data in the approximate range of 1 to 5 Å⁻¹, but there are two complications. First, it is unclear that the surface in question is 'smooth'—micropores are only a few times larger than the atoms that define the interior surface area and whose orbiting electrons determine their interaction radii. Second, a number of weak peaks are superimposed on this *hypothetical* high-*q* power-law scattering. In combination, these factors make fitting high-*q* PIM scattering data to a Porod law impractical.

3.5 Recommendations for Qualitative Interpretation of PIM Scattering Data

It has become common in the literature to interpret wide-angle scattering peaks from PIM powders as a measurement of pore sizes [51, 52]. However, results reported here caution against such a naïve analysis. Simulated partial structure factors and the sensitivity of these weak high-q features to PIM chemistry both strongly suggest that they represent the local organization of sites of contortion on adjacent chains, which undoubtedly is related to pore sizes. However, despite the known influence of sample history on porosity, it has little influence on the wavevectors of these high-q scattering features. There is also no evidence of multimodal pore size distributions from any characterization technique, including simulations that reproduce these scattering features.

Full information about the porosity in PIMs must be obtained from films, with careful attention to sample history. Overlapping SAXS and WAXS patterns should be combined and ideally placed on an absolute-intensity scale. Films of the same polymer with different sample histories (aging, swelling) can be compared, as can films of two different PIMs with the same sample history. In both cases, higher overall scattering intensity corresponds with larger porosity.

Chapter 4 will attempt a more quantitative analysis of the broad SAXS/WAXS peak in PIM films, with the aim of extracting pore volume fraction and pore sizes. Based on the results presented in this chapter, it is appropriate to include both the low-*q* power-law scattering and weak high-*q* peaks as additive terms in the models discussed.

Chapter 4

Modeling Scattering Data from PIMs

4.1 Failure of Simple Models for Porous and Two-Phase Materials

Typical scattering patterns from porous materials include power-law scattering at high q leveling off to flat scattering at low q [53]. The wavevector corresponding to the transition between these two scattering regimes depends on the size of the pores (Figure 4-1, left). In the case of q^{-4} power-law scattering at high q, the Porod equation can be applied to extract a specific surface area, as discussed in Section 3.4.



Figure 4-1. Typical scattering patterns from porous materials (left) compared with scattering from PIM-1 (black line, right) along with model components suggested by the analysis in Chapter 3. The model (purple) is the sum of a q^{-3} term (grey, thin), three Gaussian peaks related to the local organization of spirocenters (red, dashed), and another term (blue, dashed) arising from the porosity whose functional form is addressed in this chapter. The figure on the left is adapted from ref [53].

If pores are modeled as particles, a radius of gyration R_g can be determined by applying the Guinier equation [30] to low-q scattering data:

$$I(q) = \rho_0^2 v^2 e^{-\frac{1}{3}q^2 R_g^2} \tag{4-1}$$

where *v* is the particle volume and ρ_0 is the scattering contrast.

If porosity is considered to be a continuous (nonparticulate) phase, a correlation length ξ can be determined using the Debye-Bueche equation [54, 55]:

$$I(q) = \frac{8\pi \langle \eta^2 \rangle \xi^3}{(1+q^2\xi^2)^2}$$
(4-2)

where $\langle \eta^2 \rangle$ is the average fluctuation in electron density between the two phases. This functional form can ideally be applied to the entire q range, encompassing flat scattering at low *q* and reducing to the Porod equation ($I \propto q^{-4}$) at high *q*.

Several difficulties arise when attempting to apply these models to scattering from PIM films. In Chapter 3 it was argued that including the low- $q q^{-3}$ scattering and the weak high-q peaks as additive terms (Figure 4-1, right) is reasonable. However, neither Equation 4-1 nor Equation 4-2 can account for the broad SAXS maximum near q = 0.27 Å⁻¹, which was established in Chapter 3 as closely related to porosity but not directly indicative of pore sizes.

In this chapter, both particulate and nonparticulate models of greater complexity will be examined in an attempt to model the broad SAXS peak, treating PIM-1 as a twophase system consisting of porosity (unoccupied volume) and polymer chains. In addition, the scattering invariant (Equation 3-3) will be examined as a model-independent measure of porosity.

4.2 Particulate Hard-Sphere Model

The equivalence of scattered intensity from a particulate system to the product of a form factor P(q) and structure factor S(q) was introduced in Section 1.3. The Guinier equation (Equation 4-1) is essentially a form factor for a system of polydisperse objects of arbitrary shapes [30]. Approximating the structure factor as 1 is valid for low concentrations of scatterers, as is easily understood from the most general form of the structure factor [30]:

$$S(q) = 1 + \langle n \rangle \int_{0}^{\infty} 4\pi r^{2} \{g(r) - 1\} \frac{\sin qr}{qr} dr$$

$$(4-3)$$

where $\langle n \rangle$ is the number density of particles. At higher concentrations I(q) depends on the pair distribution function g(r) describing the spatial distribution of particles. However, as long as there are no long-range interactions and particles cannot completely overlap, S(q) < 1 at small q and $S(q) \approx 1$ at high q. Thus if the maximum of P(q) is at q = 0 (the case for the Guinier law as well as simple hard spheres), the effect of dense packing is to move this maximum to a finite q [30] (Figure 4-2).

Since particles are pores in this case, any 'interactions' between them arise indirectly through chain statistics and packing; it is difficult to predict what functional form this might take. Hard-sphere interactions are assumed as a default starting point: particles are not allowed to overlap but experience neither repulsive nor attractive forces. The form factor due to monodisperse hard spheres is given by [30]

$$P(q) = \rho_0^2 v^2 \frac{9(\sin qR - qR \cos qR)^2}{(qR)^6}$$
(4-4)

where *R* is the sphere radius, *v* is the particle volume and ρ_0 is the scattering contrast between particle and matrix.

Because g(r) depends on the particle volume fraction η , S(q) is also a function of η and its derivation requires an assumption about the nature of many-body interactions known as a closure relationship. For hard spheres with liquid-like order, the Percus-Yevick closure has been broadly successful. (See for example ref [56] for a full discussion.) The resulting structure factor has a complex functional form, given in many sources but notably in ref [57] with no typographical errors:

$$S(q, R_{HS}, \eta_{HS}) = \frac{1}{1 + 24\eta_{HS}G(2R_{HS}q)/(2R_{HS}q)}$$
(4-5)

where

$$G(A) = \frac{\alpha}{A^2} (\sin A - A \cos A) + \frac{\beta}{A^3} [2A \sin A - (2 - A^2) \cos A] + \frac{\gamma}{A^5} [-A^4 \cos A + 4([3A^2 - 6] \cos A + [A^3 - 6A] \sin A + 6)]$$
(4-6)

and

$$\alpha = \frac{(1+2\eta_{HS})^2}{(1-\eta_{HS})^4} \tag{4-7a}$$

$$\beta = -6\eta_{HS} \frac{\left(1 + \frac{\eta_{HS}}{2}\right)^2}{(1 - \eta_{HS})^4}$$
(4-7b)

$$\gamma = \frac{\eta_{HS}}{2}\alpha \tag{4-7c}$$

Here η_{HS} and R_{HS} are taken to be equal to the η and R that appear in the form factor, but various core-shell models exist in spheres of size R interact with a larger or smaller effective radius R_{HS} .



Figure 4-2. Effect of pore volume fraction on scattered intensity from monodisperse, Percus-Yevick hard spheres with a constant radius.

Figure 4-2 illustrates the effect of increasing pore volume fraction on the shape of the scattered intensity from hard spheres: a peak appears at finite q. In Figure 4-3, the pore (particle) size is varied with the pore volume fraction fixed at a value of 0.25, a reasonable value for PIM-1. The peak moves to lower q when the pore radius is increased, like any

scattering feature. However, because the peak position also depends on the pore volume fraction, it does not give a direct indication of pore size (e.g. $d = 2\pi/q$).



Figure 4-3. Effect of pore size on scattered intensity from monodisperse hard spheres at a constant pore volume fraction. Other curves from Figure 4-2 are shown in grey.



Figure 4-4. Comparison of experimental PIM-1 scattering with scattering from monodisperse hard spheres with a radius of 10 Å at a volume fraction of 0.25. Other curves from Figures 4-2 and 4-3 are shown in grey.

Comparing the hard-sphere model with experimental scattering data from PIM-1, the broad SAXS maximum can be reproduced with a volume fraction of 0.25 and pore radius of 10 Å (Figure 4-4). Although this pore size is two to three times that expected from other characterization data (Section 1.3.2.1), these parameters are overall physically reasonable.

The monodisperse hard-sphere model discussed up to this point fails to reproduce the breadth of the observed peak. Real pores are not monodisperse, and incorporating polydispersity increases the breadth of the peak while smearing out secondary maxima in the monodisperse form factor (Figure 4-5). A 'locally monodisperse' model of polydispersity [58] previously applied to a system with larger pores [59] is used here. The form factor and structure factor are weighted by a pore size distribution n(r) and integrated to yield the total intensity:

$$I(q) = \int_{0}^{\infty} n(R)P(q,R)S(q,R,\eta_{\text{total}})dR$$
(4-8)

Although the high-*q* agreement is improved in the polydisperse model, the agreement with experimental data below the peak maximum is reduced (Figure 4-5).



Figure 4-5. Effect of polydispersity on scattered intensity from hard spheres using Equation 4-8. Log-normal pore size distributions with a constant peak radius of 10 Å and constant total pore volume fraction of 0.25 of increasing polydispersity are shown at left with corresponding color-coded modeled scattering patterns at right. Experimental scattering from a PIM-1 film is shown in black.

The primary problem with this hard-sphere model, however, is larger apparent size of pores: scattering from pores of a 10-Å radius matches experimental data fairly well, but other structural measurements suggest that PIM-1 contains pores primarily smaller than 10 Å in diameter (Section 1.3.21). Since pores have sizes only because their borders are defined by polymer segments, it could be postulated that pores interact with $R_{HS} > R$, with $(R_{HS} - R)$ related to the width of a polymer segment. However, it is also clear that the porosity in PIMs must be well-connected: permeability is high, but gas molecule transport cannot be facilitated by polymer mobility when segments do not move on the time scale of gas molecule motion. This means that many pore 'particles' are in direct contact, with $R_{HS} = R$. In addition, the decrease in pore volume fraction during aging could be described by interpenetrating pores with $R_{HS} < R$.

An accurate hard-sphere model would seem to require significant anisotropy, with pores interacting with an effective radius depending on their relative orientation: pores separated by a polymer segment would interact with $R_{HS} > R$, while pores able to contact one another would interact with $R_{HS} = R$. A model could account for changes in PIM scattering during aging by multiple mechanisms, including both shrinking pores and pores in direct contact ($R_{HS} = R$) gaining the ability to overlap ($R_{HS} < R$). Such a model would require several unmeasurable, arbitrary parameters. Considering hard-sphere models for porosity provides some basic insight and further support for the association of the broad SAXS maximum with porosity. However, such a model is not ideal for quantifying changes in PIM structure during aging.

4.3 Nonparticulate, Bicontinuous Teubner-Strey Model

In a nonparticulate system, there is no distinction between form factor and structure factor. Instead of the radial distribution function g(r) that describes particulate systems, the real-space analog of scattered intensity from a nonparticulate two-phase system is the correlation function $\gamma(r)$, a Fourier transform of I(q) normalized to 1 at r = 0 [30]:

$$I(q) = 4\pi V \langle \eta^2 \rangle \int_0^\infty \gamma(r) r^2 \frac{\sin qr}{qr} dr$$
(4-9)

where $\langle \eta^2 \rangle$ is the mean square fluctuation in scattering length density. If the two phases are randomly distributed with a well-defined interface, then the correlation function takes an exponential form [54]:

$$\gamma(r) = e^{-r/\xi} \tag{4-10}$$

where ξ is the correlation length appearing in the Debye-Bueche equation (Equation 4-2). It is the assumption of this exponential form in Equation 4-10 that leads to the absence of an intensity maximum in Equation 4-2. Despite the validity of the Debye-Bueche equation for a number of non-polymeric porous materials even at a high volume fraction of pores [54], it can be inferred that the distribution of porosity (unoccupied volume) in PIMs is *not* random. This may be due to the fact that pores are simply the space not occupied by polymer chains; there are relatively few degrees of freedom in the configuration of a PIM chain, so there may be correlations in the locations of nearby pores.

The Debye-Bueche equation has been applied successfully to a wide variety of systems, and there are few examples of alternate functional forms of the correlation function. One example was derived by Teubner and Strey [60] for microemulsions, one example of which are bicontinuous mixtures of water and oil with a surfactant stabilizing the interface:

$$\gamma(r) = \frac{d}{2\pi r} e^{-r/\xi} \sin \frac{2\pi r}{d}$$
(4-11)

corresponding to scattered intensity of the form

$$I(q) \propto \frac{1}{a_2 + c_1 q^2 + c_2 q^4} \tag{4-12}$$

In addition to the correlation length ξ , a parameter d arises corresponding to a domain size or periodicity. In terms of the fit parameters, these are given by

$$\xi = \left[\frac{1}{2} \left(\frac{a_2}{c_2}\right)^{1/2} + \frac{1}{4} \frac{c_1}{c_2}\right]^{-1/2}$$
(4-13a)

and

$$d = 2\pi \left[\frac{1}{2} \left(\frac{a_2}{c_2} \right)^{1/2} - \frac{1}{4} \frac{c_1}{c_2} \right]^{-1/2}$$
(4-13b)

In the derivation of these equations, a_2 , c_1 , and c_2 are coefficients appearing in an order-parameter expansion of the free energy density. A maximum in scattered intensity as given by Equation 4-12 requires $a_2 > 0$, $c_1 < 0$, $c_2 > 0$, and $4a_2c_2 - c_1^2 > 0$, corresponding to the thermodynamic characteristics of microemulsions.



Figure 4-6. Two least-squares Teubner-Strey model (Equation 4-12) fits to a PIM-1 scattering pattern. Fitting the entire range of experimental data shown (black) with only the constraints listed above produces the red curve, which captures the breadth of the scattering pattern but not does reproduce the maximum ($\xi = 1.1$ Å, d = 7.3 Å). Using only data below 0.36 Å⁻¹, and constraining *I*(0) to be no larger than the vertical axis intercept shown, produces the blue curve, which captures the peak location but is far too narrow ($\xi = 7.6$ Å, d = 20.2 Å).

Equation 4-12 does not fit PIM-1 scattering patterns well (Figure 4-6), primarily due to the fact that the peak breadth is coupled to the intensity at q = 0 [60]. This is similar to a problem encountered with the hard-sphere model above: when polydispersity was introduced (Figure 4-5), the model more accurately captured the peak breadth at high q, but the intensity of the model below the peak maximum increased, in poor agreement with experimental data.

In the two extreme versions of the Teubner-Strey model illustrated in Figure 4-6, ξ ranges from 1.1 to 7.6 Å and *d* from 7.3 to 20.2 Å. These appear to be reasonable size scales

for describing PIM porosity, but their meaning is unclear in this context. Space occupied by atoms and space not occupied by atoms (porosity) certainly constitute two 'phases' in the sense that there is scattering length density contrast between them. However, it is questionable whether they can be treated as two phases in the usual thermodynamic sense. The observation of physical aging itself indicates that the system is not in equilibrium. In addition, the distribution of unoccupied volume is significantly influenced by atomic close-packing and connectivity constraints imposed by covalent bonds along polymer chains spanning large length scales compared to the size of pores.

Without further work to understand the meaning of the thermodynamic and structural parameters in this model, it is not ideal as a primary means of evaluating changes in PIM scattering patterns during aging. The fit of the model as developed for microemulsions is poor, but it could provide a starting point for further work.

4.4 Model-Independent Analysis with the Scattering Invariant

The scattering invariant Q, first mentioned in Section 3.4, quantifies the net scattering power of a sample. It is determined only by the mean square fluctuation in scattering length density and is not sensitive ("invariant") to the spatial distribution of phases within it [59]. Integration of I(q) including a q^2 factor is appropriate for scattering patterns from isotropic materials which have been azimuthally integrated:

$$Q = \frac{1}{2\pi^2} \int_{0}^{\infty} q^2 I(q) dq$$
 (3-3)

In practice, I(q) is never measured over an infinite q range. For PIMs, it might be preferable to choose the integration limits q_{min} and q_{max} within an even narrower range than most of the patterns shown in order to reduce contributions that are not related to porosity, such as the low-q upturn.

If a system is assumed to consist purely of two phases (porosity and polymer) with volume fractions φ_1 and φ_2 with scattering length densities ρ_1 and ρ_2 , the invariant can be related to the difference $\Delta \rho$ by

$$Q = V(\Delta \rho)^2 \varphi_1 \varphi_2 \tag{4-14}$$

The other quantity appearing here is *V*, the sample volume illuminated during the scattering experiment. Equation 4-14 is appropriate for examining changes over time in a given sample collected with the same instrument using absolute-intensity calibration.

4.5 Recommendations for Semi-Quantitative Analysis of PIM Scattering Data

Examining the effects of pore volume fraction, pore size, and polydispersity in hardsphere models provide the clearest intuitive understanding of how the broad SAXS peak is affected by these quantities. The peak maximum can be reproduced with parameters that are physically reasonable, although pore sizes are somewhat larger than expected based on other measurements of PIM pore size distributions. A hard-sphere model modified to better fit experimental patterns with more reasonable pore size distributions would likely require anisotropy with some parameters whose physical meaning is unclear.

Particulate models are ultimately a poor structural description of the wellconnected porosity in PIMs. An existing model developed for bicontinuous, nonparticulate microemulsions does not fit PIM scattering patterns well in its current form, but the range of fit parameters is also physically reasonable. A bicontinuous structure is a more faithful model of well-connected porosity, but the thermodynamic basis of the Teubner-Strey model may not be appropriate for glasses, which are not at equilibrium.

The ultimate purpose of applying a model to PIM scattering patterns is to extract some quantitative information about changes in porosity (unoccupied volume) and/or pore sizes during physical aging, demonstrated in Section 3.2.2 and discussed throughout Chapter 5. Of the analysis options examined, the scattering invariant is most guaranteed to provide a meaningful measure of changes in—though not absolute values of—the pore volume fraction. The peak maximum provides some indication of changes in pore sizes, although it may also be sensitive to large changes in pore volume fraction.

Chapter 5

Scattering and Physical Aging in High-Free-Volume Polymeric Glasses

5.1 Background, Motivation and Hypotheses

Physical aging, introduced in Section 1.1.2, is a slow evolution of the structure of a glass held at a constant temperature below T_g . This structural change includes an increase in density and a corresponding decrease in free volume. Because porosity in PIMs is correlated with free volume, and the broad SAXS feature has been shown in Chapters 3 and 4 to be closely related to porosity, changes in scattering patterns are predicted to accompany physical aging in PIMs.

Semi-quantitative modeling of PIM scattering patterns was explored in Chapter 4. Although no ideal model for extracting a direct measurement of pore size distributions was found, the scattering invariant (Equation 3-3; discussed more fully in Section 4.4) is suitable for calculating a measure of the pore volume fraction φ . The invariant, proportional to $\varphi(1-\varphi)$, is a more sensitive measurement of changes in pore volume fraction near $\varphi = 0.25$ (a reasonable value for PIM-1) than film thickness *t*, related to φ by

$$\frac{t}{t_{\varphi=0}} = (1-\varphi)^{-1/3} \tag{5-1}$$

For example, if φ increases from 0.2 to 0.3, the invariant increases by 31% while film thickness increases by only 4.6% (Figure 5-1).

In most physical aging studies, the 'clock' is set to zero by heating the film above T_g . PIMs exhibit no glass transition temperature below their decomposition temperature; instead, immersing films in an alcohol such as methanol or ethanol is a widely used 'rejuvenation' technique. Films swell visibly while immersed in alcohols (Figure 5-2), and after removal and evaporation of residual alcohol, they exhibit higher gas permeability characteristic of freshly cast films (see Section 1.3 for a more detailed discussion).



Figure 5-1. Relative film thickness (red, dashed) and the scattering invariant (blue, solid) plotted as a function of pore volume fraction φ .



Figure 5-2. A 50- μ m-thick dry PIM-1 film (left) swells by approximately 18% (linear dimension) when immersed in ethanol (right). After removal from the swelling liquid, the film begins to shrink before the liquid has fully evaporated.

Figure 3-3, reproduced below as Figure 5-3, provided the first test of the effect of aging on PIM scattering patterns: rejuvenated films exhibit larger scattering intensity than films aged for a long period of time. Note that residual methanol or ethanol was removed: SAXS patterns were collected under vacuum, and liquid-filled pores would produce lower-intensity scattering patterns due to reduced electron-density contrast.



Figure 5-3. Effect of sample history on absolute-intensity SAXS/WAXS patterns from PIM-1 (left) and TA-PIM-1 (right) films. Green patterns are from solution-cast films aged for 2 years (PIM-1) or 6 months (TA-PIM-1) before scattering experiments. Larger scattering intensities are observed from films soaked in methanol (red) or ethanol (blue) for 24 hours prior to scattering measurements.

In addition to time, two additional variables are known to influence aging behavior: film thickness and aging temperature (Section 1.1.4). If a film is held at a higher temperature—provided it is still below T_g —more thermal energy is available for the dynamic process involved in aging (although this process is not well understood). Thinner films have been observed to age at a faster rate, as quantified by permeability measurements; the mechanism invoked to explain this is diffusion of free volume elements toward the film surface, which would occur more quickly in thinner films [6, 10].

In the experiments reported here, lower scattering intensity—as quantified by the invariant—is expected in thinner films or in films aged at a higher temperature for the same period of time following removal from ethanol.

5.2 Methods and Materials

PIM-1 films were cast from solution to thicknesses of approximately 60, 100, and 240 μ m, as detailed in Section 2.2.2. Each film was immersed in ethanol for 30 hours and then placed in a vacuum oven at one of three temperatures: 30 °C, 75 °C, or 125 °C. Films

were aged at these temperatures for 25 hours, although the two higher-temperature ovens required several hours to reach the target temperatures. The first series of SAXS patterns, labeled "1 day", was then collected. WAXS patterns labeled "1 day" were collected for a subset of samples the following day.

Samples were then returned to storage under one of three conditions: a vacuum oven at 75 °C, a vacuum oven at 125 °C, or an evacuated Desi-Vac container (VWR) containing indicating desiccant. The third condition is labeled "RT" (room temperature) in data reported below; samples initially treated at all three temperatures were included in this set. After aging for 13 days, a second series of SAXS patterns was collected. A second series of WAXS patterns was collected the following day.

For SAXS experiments, sample-to-detector distance of 0.5 m was used; other details are given in Section 2.4.1. All SAXS patterns were collected at room temperature and were calibrated to absolute intensity; it is important to note that this included normalization by sample thickness. WAXS patterns were not independently calibrated to absolute intensity but were scaled to overlap SAXS patterns with good agreement over a significant wavevector range (Appendix B).

5.3 Results and Discussion

Scattering patterns are shown to illustrate the effect of aging temperature (5.3.1) and film thickness (5.3.2). A summary discussion (5.3.3) follows, using the scattering invariant and peak positions to compare the large number of patterns more efficiently and quantitatively. All SAXS patterns are given in Appendix B.

5.3.1 Accelerated Aging at Higher Temperatures

Scattering patterns from films of the same thickness aged for 1 day exhibited lower intensity at higher aging temperatures (Figure 5-4). The strong association of this scattering feature with porosity implies that films stored at higher temperatures aged more quickly. Similar changes were observed in films of other thicknesses, but large differences were not observed between 1 and 14 days of aging.



Figure 5-4. Combined SAXS/WAXS patterns from three PIM-1 films ~100 μ m in thickness aged for one day at 30 °C (red), 75 °C (blue), or 125 °C (green). A pattern from atactic polystyrene³ (brown) is included for comparison: although PIM SAXS intensity decreases during aging at higher temperatures, it is still relatively large.

All films stored for two weeks at 125 °C exhibited a change in color from translucent bright yellow to a slightly more opaque yellow-orange, suggesting that some chemical reaction occurred. Although the color change was not apparent after only one day at 125 °C, patterns from all films exposed to 125 °C for two weeks should be interpreted with some caution. Samples treated at 125 °C for several months were still fully soluble in chloroform, suggesting that extensive cross-linking did not occur.

³ At the time the SAXS pattern was collected, the atactic polystyrene sample had been aged for several years at room temperature following sample preparation described in Section 7.3.4; it is the high-molecular-weight, slowly cooled sample.
5.3.2 Accelerated Aging in Thinner Films

Figure 5-5 compares SAXS patterns from PIM-1 films \sim 60, \sim 100 and \sim 240 µm in thickness, aged for one day at 30 °C (left) or 75 °C (right). At both temperatures, 100-µm films exhibited slightly lower scattering intensity than 240-µm films, and 60-µm films exhibited significantly lower intensity.



Figure 5-5. Combined SAXS/WAXS patterns from PIM-1 films aged for one day at 30 °C (left), 75 °C (middle), or 125 °C (right) with thicknesses of ~240 μ m (red), ~100 μ m (blue), and ~60 μ m (green).

5.3.3 Effect of Aging on the Scattering Invariant and Peak Position

In Figure 5-6 (top), the patterns shown in Figure 5-5 are combined into one plot with a log scale in *q* to highlight the SAXS feature associated with porosity. This reveals that the wavevector of the peak maximum is relatively constant across a range of the largest scattering intensities; however, at lower scattering intensities it moves to larger wavevectors. Qualitatively, these regimes can be interpreted respectively as diffusion of pores—a reduction in pore volume fraction with little change in the shape of the pore size

distribution—and 'shrinking' of pores, whether by preferential loss of the largest pores or by changes in the size of individual pores.



Figure 5-6. SAXS/WAXS patterns from PIM-1 films aged for one day, shown in Figure 5-5, are combined into one plot (top). The integrand of the scattering invariant, q^2I , is also plotted with the same horizontal axis (bottom). There was little change in the corresponding scattering patterns measured again after two weeks (Appendix B).

To examine this aging behavior semi-quantitatively, the scattering invariant can be used as an indication of pore volume fraction and the maximum wavevector of the SAXS feature as an indication of pore sizes. In the lower half of Figure 5-6, the integrand of the scattering invariant is plotted versus q to illustrate the contributions from different scattering features. There is no maximum in q^{2I} corresponding to the SAXS maximum, although the weak high-q features related to the organization of spirocenters are evident. The maximum contribution to the invariant arising from porosity is obscured by these but lies somewhere in the range of 1.0 to 2.2 Å⁻¹. The corresponding real-space size scale of 3 to 6 Å is comparable to pore sizes measured by other techniques.

Figure 5-7 displays the partial scattering invariant—Equation 3-3 with integration limits of q = 0.1 to 0.5 Å⁻¹—for all scattering patterns collected as a function of sample thickness. These integration limits were selected to exclude parts of the scattering pattern dominated by the low-q upturn, or by high-q scattering that arises in part from local segmental order and persists even when porosity is largely eliminated under high simulated pressure (see Figure 3-2). This integration range may include some non-porous scattering and exclude some high-q scattering from very small pores, but the values reported in Figure 5-7 are comparable to one another.

The clearest general trend in Figure 5-7 is the lower pore volume fraction in films thinner than ~100 μ m, evident for all thermal histories. Differences in pore volume fraction between 100- and 240- μ m films aged near room temperature are negligible, but 100- μ m films aged somewhat faster at 75 °C. In most cases, there was little difference between patterns collected after one day of aging (open circles) and those collected after 13 additional days of aging at room temperature (filled circles) or a higher temperature (filled squares).

At each thickness, aging at higher temperatures during the first day resulted in lower pore volume fractions (Figure 5-7), with only a small additional decrease during the next two weeks (Appendix B). The exception to this was that $60-\mu m$ films aged to a greater extent during the first day at 75 °C than at 125 °C.



Figure 5-7. Partial scattering invariant—Equation 3-3 with integration limits of q = 0.1 to 0.5 Å⁻¹—calculated from PIM-1 SAXS patterns for a variety of thicknesses and thermal histories. Open circles represent films aged for one day at 30 °C (blue), 75 °C (orange), or 125 °C (red). Circles of the same color scheme filled with blue correspond to films subsequently stored for 13 days at ambient temperature. Filled squares represent films are not shown in above figures is also included; these patterns (SAXS only) are shown in Appendix B.

Figure 5-8 displays the peak positions for all patterns collected as a function of sample thickness. Although the position of this scattering maximum is not a direct indication of the size of pores, it may cautiously be interpreted as a relative indication of differences in the sizes of pores, especially for patterns whose pore volume fractions are similar. As discussed in Section 4.2, if pores are approximated as hard spheres with a constant pore volume fraction, a peak at lower q indicates larger pores; at a constant hard-sphere size, a peak at lower q indicates a lower pore volume fraction.

The small differences between patterns collected after one day and two weeks of aging, along with the remaining greater pore volume fraction in thicker films, suggest that the thinnest films may be able to age more fully at a given temperature: 60-µm films exhibited lower pore volume fractions than thicker films for each thermal history. However, when stored at room temperature, peak positions in 60-µm SAXS patterns were very similar to peak positions from thicker films aged at either room temperature or 125 °C (Figure 5-7).

When aged at 75 °C, 60- μ m films exhibited a maximum at higher *q*, which may indicate smaller pores. Taken together, these observations suggest that aging at different temperatures—and perhaps at different thicknesses—may occur by fundamentally different mechanisms. Figure 5-9 directly compares the peak maxima and partial scattering invariants for all patterns.



Figure 5-8. Position of the broad maximum in PIM-1 SAXS patterns for a variety of thicknesses and thermal histories. Error bars on q_{max} correspond to four times the error arising from a least-squares fit of a Gaussian peak, multiplied by four to allow for the somewhat arbitrary selection of a restricted q range near the maximum for peak fitting. As the SAXS maximum moves to higher q, error bars are very large due to the nearby WAXS peaks. Wavevector maxima from some films whose patterns are not shown in above figures are also included; these patterns (SAXS only) are shown in Appendix B.

Examining Figure 5-9, the peak maximum is relatively constant across a range of values of the pore volume fraction. Aging in this regime, highlighted in purple, is consistent with diffusion of free volume elements toward a free surface where they are lost. However, below some critical value of the pore volume fraction, the peak maximum begins to move to higher q as the pore volume fraction decreases. This regime, highlighted in green, could be explained by the shrinking of pores. Changing the upper limit of integration for calculating the invariant to 1.0 or 2.0 Å⁻¹ results in plots with this same characteristic shape, except that

films exposed to 125 °C deviate from the pattern (Appendix B). This may suggest that pore shrinking occurs more quickly relative to pore diffusion at elevated temperatures.



Figure 5-9. The wavevector of the SAXS peak maximum (Figure 5-8, vertical axis) plotted against the partial scattering invariant (Figure 5-7, vertical axis). Film thicknesses are not indicated in this figure; samples may be regarded as accessing different regions of an aging phase diagram through a combination of varied temperature and film thickness.

5.4 Conclusions

Changes in PIM-1 scattering patterns as a function of film thickness and storage temperature consistent with physical aging were observed: storing films at higher temperatures resulted in lower-intensity scattering patterns. Below a threshold of approximately 100 μ m, films were able to age more quickly and/or to a greater extent, resulting in lower pore volume fractions than observed in thicker films with equivalent thermal histories. The existence of a threshold value for film thickness dependence of aging behavior has been reported for other polymers [10], but the threshold thickness in PIM-1 is larger by a factor of 2 to 10.

Because the largest changes occurred during the first day of aging, experiments with

better time resolution to study the first few hours of aging would be useful. Some have been performed at the National Synchrotron Light Source (beamline X27C), but accurate data reduction has been complicated by the lack of a direct transmission measurement, as well as the competing effects of evaporation and aging immediately following removal from the swelling liquid. An advantage of the data reported in this chapter is the assurance of no residual alcohol after 24 hours under vacuum.

Comparing the dependence of pore volume fraction (quantified by the scattering invariant) and pore size (as roughly estimated by the peak maximum) on film thickness and thermal history suggests that more than one mechanism of aging may be possible. To investigate this possibility, the peak position was plotted against the partial invariant, regarding films of different thicknesses and thermal histories as accessing different portions of an aging phase diagram for this class of microporous polymer. Points on this plot fell into two distinct regimes: at high volume fractions, the peak position was nearly constant; below a threshold volume fraction, the peak moved to higher *q* as volume fraction decreased. These two regimes are interpreted respectively as diffusion and shrinking of pores during aging.

Chapter 6

PIM Scattering, Porosity, and Aging: Summary and Future Work

6.1 Summary and Conclusions

In this dissertation, extensive X-ray scattering studies of PIM-1 and related materials are reported. Due to their large free volume, these polymers form microporous films with potential applications in gas separation and storage, but their performance as membranes is impacted by physical aging: a slow increase in density over time affecting all glasses. Scattering methods offer a convenient method for studying the structure of PIM films with well-defined sample history; the challenge lies in understanding the features appearing in scattering patterns and extracting quantitative information from them.

To clarify the meaning of scattering features, PIMs of varied chemistries were studied experimentally. Simulations previously developed for PIMs were also used to examine contributions to scattering patterns from different parts of the polymer and to investigate the effect of eliminating porosity (at high simulated pressure) on simulated scattering patterns⁴. This investigation demonstrated that the weak high-*q* peaks observable with WAXS are related to the local organization of chain segments but do not correspond directly to pore sizes, as had been suggested previously [51, 52]. Instead, a broad feature whose peak is only observable in high-*q* SAXS patterns is strongly related to pore sizes, as discussed in Chapters 3 and 4.

Several models for extracting pore sizes from PIM film scattering patterns were explored in Chapter 4. While none fit the data well enough to yield a quantitative measurement of pore size distribution, the size scales of model parameters were sufficiently physically reasonable to constitute further support for the association of the broad SAXS feature with porosity. A particulate hard-sphere pore model, though not a realistic description of well-connected porosity, gave some intuitive understanding of the broad SAXS peak: its breadth may be related to polydispersity, and its location depends on both

⁴ In Appendix A, analogous complementary scattering studies and simulations on organic molecules with intrinsic microporosity are discussed.

pore size and concentration. A bicontinuous, nonparticulate model developed based on the thermodynamics of microemulsions did not fit the shape of the PIM SAXS peak well, but the range of fit parameters was of the approximate size scale expected for pores. The scattering invariant was chosen as an objective measure of changes in pore volume fraction, although it does not quantify pore sizes.

In Chapter 5, PIM scattering patterns were shown to depend on time, temperature, and film thickness in a manner consistent with the decrease in pore volume fraction during physical aging. Comparing pore volume fraction (quantified by the scattering invariant) to pore size (roughly estimated by the SAXS peak maximum) suggests that there may be two distinct mechanisms of aging in PIMs: pore diffusion at high pore volume fraction and pore shrinking at low pore volume fraction.

In addition to their applications in gas separation, PIMs constitute a useful model system for studying changes in porosity, closely related to free volume, during aging. However, this potential hinges on the degree to which they can be considered typical glasses. With no observable T_g , the reversal of PIM physical aging is accomplished through swelling in nonsolvent organic liquids. A preliminary investigation of alcohol adsorption and swelling using QCM and SANS is reported in Appendix C, but several experimental difficulties were encountered and the meaning of these results is not well understood. Several strategies for better understanding PIM structure and aging are suggested below.

6.2 Suggested Future Studies

6.2.1 Improved PIM Scattering Models

Available particulate and bicontinuous nonparticulate scattering models are inadequate to describe scattering that clearly arises from porosity (unoccupied volume) in PIMs. An accurate model would require an understanding of the nature of effective porepore interactions, or equivalently local correlations in the distribution of porosity. Porosity is simply the space not occupied by polymer segments, and to a first approximation, a PIM chain consists of rigid segments joined by sites of contortion with each connection having one of four possible angles frozen in during synthesis⁵. These major degrees of freedom in a chain's configuration are further apart (15-Å rigid segments) than typical for a polymer, but still close enough together that three consecutive segments can enclose a gap not easily filled by other chains. (PIM-7, with longer rigid segments than PIM-1, has lower permeability [26].) Perhaps an approach such as the polymeric reference site interaction model (PRISM), which has successfully described the local order and packing of polymer segments [56, 61], could be "inverted" to describe effective interactions between pores.

6.2.2 Thickness Dependence of PIM Aging Rate

In PIM-1, the aging rate—or at least the rate of decrease in scattered intensity differs significantly between films 60 and 100 µm in thickness. In glassy polysulfone, there is no apparent difference in aging rate between 36- and 61-µm films, but there is a small difference between 36- and 9-µm films [6]. The aging rate in ref [6] was quantified by film permeability, and a similar study of the effect of PIM film thickness on the rate of permeability decrease would confirm the dependence suggested by the scattering data reported in this dissertation. The theoretical investigation suggested in Section 7.2.1 might also reveal whether the unusual chain statistics described above give rise to atypically longrange correlations in the structure of PIM porosity, which could help explain the sensitivity of aging rate to film thickness in relatively thick PIM films. Finally, grazing-incidence scattering techniques—as opposed to the transmission geometry used through this work provide a better signal-to-noise ratio in thin films along with the possibility of depth profiling.

6.2.3 Interactions Between PIMs and (Nonsolvent) Organic Liquids

Large changes in PIM scattering patterns during aging may make PIMs a useful model system for investigating changes in the structure of porosity during aging. Improved

⁵ More realistically: in the bulk state, rigid segments exhibit limited flexibility at the dioxane bonds, and sites of contortion are somewhat flexible around the preferred angle of approximately 90°.

models for extracting physical parameters from scattering data—especially a measure of the size of pores—are required to fulfill that promise. Another complication is the lack of an observable T_g in bulk PIM-1 and necessity of swelling films in alcohols to reverse aging, in place of the standard practice of heating them above T_g .

A better understanding of interactions between PIM films and the nonsolvent organic liquids used to rejuvenate them would facilitate comparison with the existing body of work on physical aging in glasses. Improved versions of the preliminary adsorption and SANS studies described in Appendix C would help achieve this goal. Similar SAXS experiments using an adsorbed gas with high X-ray scattering contrast such as CS₂ could also be informative.

In particular, it is possible that immersion in nonsolvent liquids effectively lowers the T_g of PIMs, similar to the technique of solvent annealing. This lowered T_g might be observable with differential scanning calorimetry. However, it would likely be above the boiling point of any liquid used, requiring the use of a vapor environment.

Chapter 7

The Low-q Scattering Upturn in Amorphous Polymers

7.1 Introduction

An unexplained increase in scattered intensity from polymeric systems is frequently observed at the low-*q* limit of SAXS experiments. SAXS features that are well understood, such as a peak arising from aggregates in ionomers [62-68], appear superimposed on this low-*q* scattering. When quantitative models are applied to SAXS data, it is common either to effectively ignore the upturn or to include the low-*q* scattering as an additive power-law contribution, which was introduced in Section 3.4:

$$I(q) \propto q^{-\alpha} \tag{3-1}$$

Ultra-small-angle X-ray scattering is able to probe q ranges several decades lower than SAXS, encompassing size scales up to several microns. However, due to the optics necessary to resolve scattering at such small angles, the high intensity of a synchrotron source is required. As a result, most USAXS studies have been performed on systems in which either a fractal structure or phase separation at a scale of ~10 nm to several microns is expected. Examples include lamellar spacings in semi-crystalline polyethylene [69] and block copolymers [70], bubble formation in borosilicate glass [71], volume-phase transitions in hydrogels⁶ [72], particle interactions in colloidal solutions [73, 74], and particle size distributions in polymer nanocomposites [75]. Other applications of USAXS to soft materials are reviewed in ref [40]. These investigations do not constitute examples of the *unexplained* low-q scattering discussed in this chapter.

A low-*q* scattering upturn has been observed in a variety of ionomers, polymers in which either cations or anions are covalently bonded to polymer chains, and in which ionic groups frequently microphase separate into roughly spherical aggregates with liquid-like

⁶ The "volume-phase transition" arises from the sensitivity of network chain conformations to small changes in ambient conditions.

order [76]. These SAXS studies of ion-containing polymers also provide considerable evidence that low-*q* scattering is associated with ions. A slight increase in upturn intensity during heating has been interpreted as arising from a difference in thermal expansion between ion-rich and ion-poor regions [64]. Anomalous SAXS (ASAXS) experiments on nickel-neutralized sulfonated polystyrene (SPS) ionomers, examining the difference between two SAXS patterns taken at two different energies, suggest that the upturn is associated with ions rather than voids or impurities [77]. In manganese-neutralized SPS ionomers, the ionomer scattering peak appears during heating; at the same time, the intensity of the upturn decreases [62].

Explanations suggested for the low-*q* scattering observed in ionomers include variation in the number of ionic groups per chain leading to "spatial fractionation of polymer chains" [76] and several others discussed below. However, the phenomenon has also been observed in a number of amorphous homopolymers with no added ions, including polystyrene, polycarbonate, poly(ethylene terephthalate), poly(vinyl chloride) and poly(methyl methacrylate) [78, 79], as well as the glass-forming liquid orthoterphenyl [80]. Density fluctuations and 'clustering' in bulk amorphous materials, studied with both X-ray [81-84] and light scattering [85, 86], may be related in some way to the low-*q* scattering upturn. An explanation unifying all of these observations cannot be contingent on the presence of ions, although it is possible that ions could alter the scattering contrast.

7.1.1 Possible Sources of Low-q Scattering

Scattering measurements provide ensemble-averaged information: USAXS patterns given in this chapter were each collected over a period of 20 min from a scattering volume of approximately 1 mm³. Because the interaction of each photon with the material is virtually instantaneous compared to the time scales involved in molecular motion, dynamic fluctuations contribute to electron-density contrast. Both static and dynamic structures must therefore be considered as sources of low-*q* scattering.

Scattering contrast arises from differences in electron density. In a material with uniform composition, such as a homopolymer, contrast at the large length scales corresponding to low-q scattering can only arise from variations in the density of the

material (or the inclusion of foreign particles). In a material with multiple components, such as an ion-containing polymer, composition fluctuations must be considered as an additional potential source of scattering contrast.

7.1.1.1 Thermal Density Fluctuations

For a variety of polymers and other liquids above and below T_g , it has been shown that thermal density fluctuations from liquid molecular motion—which are frozen in below the glass transition—obey [82]

$$I(q) \propto e^{bq^2} \tag{7-1}$$

This can be extrapolated to the intensity at q = 0, which can then be related to the isothermal compressibility β_T [30, 87]:

$$I(0) \propto k_B T \beta_T \tag{7-2}$$

where *T* represents temperature in Kelvin and k_B is Boltzmann's constant. Figure 7-1 illustrates the contribution of thermal density fluctuations to scattering from atactic polystyrene (blue), which is clearly distinct from the excess low-*q* scattering attributed to "impurities" [30, 88]. Thermal density fluctuations therefore are *not* a viable explanation for the phenomenon investigated in this chapter.



Figure 7-1. Scattering from atactic polystyrene; the horizontal axis is given as s^2 , where $s = q/2\pi$. The scattering highlighted in blue is due to thermal density fluctuations, as given by Equation 7-1. Figure adapted from ref [88].

7.1.1.2 Clusters in Amorphous Polymers

Several theories have addressed other density variations in glasses or glass-forming liquids. "Fischer clusters" in liquids are described as transient solid-like and fluid-like regions, differing in density and short-range order, that form fractal aggregates [89]. An alternate mechanism in atactic homopolymer melts may be the aggregation of sequences of atypical tacticity into semicrystalline micelles [90].

7.1.1.3 Heterogeneities Specific to Ion-Containing Polymers

Critical fluctuations in ion concentration are predicted to occur near room temperature in materials with a dielectric constant near 5 [91]; these would lead to large-scale dynamic fluctuations in composition. It has also been suggested that clusters of ions may behave like crosslinks [92], creating a fractal structure similar to a gel, or that ions may form large aggregates in the form of flexible strings or sheets.

7.1.1.4 Artifacts

Voids [64, 78], parasitic scattering from instrumentation [64, 93], and foreign particles or additives [64, 79] have all been suggested or examined as possible sources of low-*q* scattering. It is likely that in some experiments artifacts such as these do contribute to low-*q* scattering. However, experiments in which USAXS patterns can be superimposed on light-scattering patterns (Figure 7-2) suggest that the low-*q* scattering upturn is not purely an instrumental artifact. Any scattering contribution from voids or impurities is expected to vary from one experiment to the next, depending on sample source and thermal history. Thermal history is investigated as a contributing factor in this work.



Figure 7-2. USAXS scattering intensity combined with a comparable quantity from light scattering, S(q), for the liquid glass-former orthoterphenyl. Data were collected at room temperature from a supercooled sample with no crystalline component; T_g of orthoterphenyl is 243 K. Figure reproduced from ref [80].

7.1.2 Models for Low-q Scattering

By combining USAXS with a technique such as light scattering that can resolve scattering at even lower q, it is sometimes revealed that power-law scattering persisting to the lowest q accessible with USAXS transitions to flat scattering at even lower q [80, 94] (see for example Figure 7-3). In some studies, both well-understood USAXS features and unexplained power-law scattering at the low-q limit are observed, and the latter is explained by hypothesizing some larger structure [75, 95].

When scattering like that illustrated in Figure 7-3—flat at low q, power law at higher q—is observed in a particulate system, the power-law exponent is related to the shape of particles. For three-dimensional structures such as spheres, α (in Equation 3-1) is equal to 4; for two-dimensional objects such as disks, $\alpha = 2$; and for one-dimensional objects such as rods, $\alpha = 1$ [30]. Objects that are less compact give rise to power-law scattering related to their mass fractal dimension. For example, Gaussian polymer chains give rise to scattering with $\alpha = 2$ [30].



Figure 7-3. Combined USAXS and light-scattering data from precipitated silica in wet and dry states, reproduced from ref [94]. USAXS data reported in this dissertation does not extend below 10^{-4} Å⁻¹.

In a non-particulate system with two *randomly* distributed phases, it has been shown [54, 55] that scattering intensity follows the Debye-Bueche law:

$$I(q) = \frac{8\pi \langle \eta^2 \rangle \xi^3}{(1+q^2\xi^2)^2}$$
(7-3)

where $\langle \eta^2 \rangle$ is the average fluctuation in electron density and ξ is a "correlation length" representing the typical size scale of inhomogeneities. At low *q*, this functional form

corresponds to flat (q-independent) scattering, while the high-q limit is equivalent to the Porod law introduced in Section 3.4:

$$\lim_{q \to \infty} \frac{I(q)}{Q} = \frac{2\pi}{\varphi_1 \varphi_2} \frac{S}{V} \frac{1}{q^4}$$
(3-2)

where *Q* is the scattering invarient (Equation 3-3). Several attempts [67, 68, 77, 93] have been made to apply Equation 7-3 to unexplained low-*q* scattering in ionomers, but the fit is very poor: the flat low-*q* scattering is not observed, and power-law exponents vary widely. For example, the same group of authors have variously estimated ξ in zinc-neutralized SPS as 90 nm [93], 9 nm [68], and 12-15 nm [67]. In all of these cases, ξ in Equation 7-3 was not well specified because the (hypothetical) flat scattering at low *q* was not observed.

Fluctuations in concentration—as opposed to the inhomogeneities arising from two distinct phases described by Equation 7-3—also give rise to a correlation length, describing the length scale over which fluctuations remain correlated [30]:

$$I(q) = \frac{I_0}{1 + q^2 \xi^2} \tag{7-4}$$

This functional form describes scattering from systems such as miscible polymer blends [30] and was first shown to apply to mixtures of small molecules near the critical point by Ornstein and Zernike [96]; the critical ion fluctuations mentioned in Section 7.1.1.3 might be expected to produce such scattering. Like Equation 7-3, Equation 7-4 predicts a constant scattering intensity as q approaches zero, but in Equation 7-4 high-q intensity is proportional to q^{-2} . Applying Equation 7-4 to the combined light scattering and USAXS data from orthoterphenyl (Figure 7-2) produced an approximate correlation length of 86 nm [80], although the power-law exponent was 2.24 instead of 2.

7.1.2.1 Interpretation of USAXS Data in This Work

In most scattering experiments, scattering features corresponding to specific structures are expected to be observed and appropriate models can be chosen in advance.

In this work, the structure giving rise to the scattering feature of interest is unknown, and the goal is to uncover clues about its nature. The vast majority of USAXS measurements reported here include power-law scattering persisting to the lowest accessible q with widely varying exponents. Neither Equation 7-3 nor Equation 7-4 fits such data well, so simple power-law exponents are reported. Based on the discussion above, power-law exponents close to 4 indicate two well-defined phases, while exponents closer to 2 should be regarded as arising from a more continuous distribution of phases.

In several ion-containing polymers, cations were varied. It was hypothesized that scattering of larger intensity but the same functional form would be observed, indicating that the morphology remained the same but the electron-density contrast was enhanced with larger cations. However, Figure 7-4 illustrates an alternate possibility: a fundamental change in the morphology of the system leading to scattering patterns of a different shape.



Figure 7-4. Possible effects of changing cations on polymer structure and scattering.

7.3 Methods and Materials

7.3.1 Ultra-small-angle X-ray Scattering (USAXS)

Small-angle scattering methods including USAXS are described in Section 2.4. Backgrounds were subtracted from all patterns shown, including an air background for free-standing films and a Kapton background for films contained within Kapton windows. USAXS patterns are calibrated on an absolute-intensity scale [39, 40].

Of special note is that the data reduction process results in a high-q flat background of arbitrary intensity [97]. In addition, the minimum q in a reduced USAXS pattern is limited

by several factors. Sufficient intensity above the instrumental background is necessary, so samples with lower intensity at low q will also tend to have a higher q_{min} compared to higher-intensity samples measured during the same run. However, the intensity of instrumental background itself can vary from run to run depending, for example, on the cleanliness of the silicon crystals whose reflections are used to focus the beam to achieve high angular resolution [97]. The scattered intensity from the Si crystal rocking curves is proportional to q^{-2n} , where n is a large number of crystal reflections [39]. This contribution to USAXS patterns is subtracted along with the background, and the power-law exponent is too large to account for the low-q scattering discussed here.

Dr. Jan Ilavsky (Advanced Photon Source, Argonne National Laboratory) provided recommendations for USAXS data reduction and performed some USAXS measurements by mail-in service. Dr. Gregory Tudryn also assisted with some USAXS experiments. Dr. Andrew Allen (NIST) collected preliminary USAXS data for ionomers.

7.3.1.1 Wide-angle X-ray Scattering (WAXS)

Some samples in this part of the study were also characterized using wide-angle Xray scattering (WAXS). The method was the same as that described in Section 2.3, except that a 0.8 mm collimator was used, and transmissions measured during USAXS experiments on the identical samples were used for accurate background subtraction.

7.3.2 Poly(ethylene oxide)-based Ionomers

A series of poly(ethylene oxide)-based ionomers was chosen as the first model system for investigation of the low-q scattering upturn based on previous observations of the upturn in ionomers and the availability of different ion concentrations and counterions (Li, Na, Cs) (Figure 7-5). Other workers have extensively studied their structure and dynamics using broadband dielectric relaxation spectroscopy [98, 99], quasielastic neutron scattering [100, 101], SAXS [102, 103], and simulations [103, 104]. Synthesis of these materials is described in ref [105] and data such as T_g and M_n are reported in refs [103] and

[105]. Number-average molecular weights range from 3000 to 6000 g/mol and T_g ranges from 238 to 295 K.

A pertinent result of SAXS studies of these ionomers is the dependence of aggregation on cation type and temperature. At room temperature, ionomers with Li cations contain ionic aggregates, and the morphology changes little during heating up to 120 °C. Ionomers with Na or Cs cations contain primarily isolated ion pairs at room temperature, but at higher temperatures aggregates form due to the temperature-dependent decrease in the polymer's dielectric constant [102].



Figure 7-5. Chemical structures of poly(ethylene oxide)-based ionomers. Note that these are random copolymers of sulfonated and unsulfonated units. Varied sulfonation levels were only available for the 600 g/mol PEO spacer with Li and Na cations. In the discussion below, sample names follow the convention of [PEO spacer molecular weight] [cation] [x], e.g. "600 Na 11" is a copolymer with 11% sulfonated units, Na cations, and m = 13.

Ionomer samples were provided by Prof. Ralph Colby's group at Penn State; Dr. Gregory Tudryn assisted with sample preparation. For USAXS measurements, samples were contained with aluminum cells 1 mm in thickness with Kapton film windows. Each sample was loaded into a cell with one window attached and then annealed in a vacuum oven at 40 °C for 6 days to minimize voids and water content. The second Kapton window was then attached and samples were stored in polyethylene bags with dessicant for several days until USAXS experiments were performed. Some samples, as indicated in figures and discussion below, were annealed for only 1 day at 40 °C or remeasured after an extended period of storage at ambient temperature.

7.3.3 Poly(vinyl methyl ether)-Perchlorate Complexes

Complexes of poly(vinyl methyl ether) (PVME) and lithium perchlorate (LiClO₄) have been previously studied using broadband dielectric relaxation spectroscopy [106]. PVME is amorphous and solvates alkali cations by the same mechanism as PEO: interactions with ether oxygens. Concentrations were therefore chosen to cover the range of cation to ether oxygen ratios spanned by the PEO-based ionomers (Table 7-1). In the discussion below, sample names are given as [cations per 100 ether oxygens] [cation], e.g. "0.8 Li".

PVME was purchased from Scientific Polymer Products, Inc. with a manufacturerreported M_w of 90,000 g/mol (by GPC) and T_g of -49 °C. LiClO₄ and NaClO₄ were purchased from VWR. Complexes of PVME/LiClO₄ and PVME/NaClO₄ were prepared by dissolving polymer and salt in methanol, stirring overnight, pouring the solution into Teflon dishes, and evaporating the solution in a vacuum oven at 70 °C for 24 hours. Samples for USAXS were then loaded into the sample aluminum/Kapton cells used for ionomers.

PEG spacer molecular wt. (g/mol)	Sulfonation %	Cations per 100 ether oxygens	
600	3.3	0.25	
600	5.6	0.43	
600	11	0.84	
600	17	1.3	
600	49	3.8	
1100	100	4.2	
600	100	7.7	
400	100	11	

Table 7-1. Cation to ether oxygen ratios corresponding to sulfonation levels available in PEO-based ionomers.

7.3.4 Homopolymers Without Added Ions

Several homopolymers were studied; Table 7-2 lists manufacturer-reported molecular weights and approximate glass transition temperatures. Poly(dimethyl siloxane), a liquid at room temperature, was dried at 45 °C for 1 day before being sealed an aluminum scattering cell with Kapton windows. Solid polymers were hot-pressed directly into

aluminum scattering cells with no windows, holding them at temperatures given in Table 1-2 for 10 minutes under 2.0 metric tons of pressure.

Samples described as "quenched" were immediately removed from the hot press and placed in thermal contact with a large metal block, bringing them to room temperature in less a minute. "Annealed" samples of polystyrene were placed in a vacuum oven at 120 °C for 1 day after quenching. Samples described as "slowly cooled" were left in the hot press with the heat turned off and removed when they reached room temperature after approximately 20 hours.

Prior to hot pressing, some samples of atactic polystyrene described as "filtered" were dissolved in toluene and pushed through a 0.2-µm polytetrafluoroethylene filter attached to a syringe. Toluene was allowed to evaporate and then the samples were dried in a vacuum oven at 80 °C for 1 day before hot pressing.

Sample name	Polymer	Mol. wt. (g/mol)	Est. T_g (K)	Polymer Source	Hot press temp. (K)
HDPE	high-density polyethylene		140-160ª	VWR	444
sPS	syndiotactic polystyrene	300,000	373ª	Scientific Polymer Products, Inc.	557
aPS, high MW	atactic polystyrene	125,000 to 250,000	378 ^b	VWR	527
aPS, low MW	atactic polystyrene	500 to 8,000	240-358c	VWR	527
PDMS	poly(dimethyl siloxane)	17,000	123-150ª	VWR	

Table 7-2. Homopolymers with manufacturer-reported molecular weights. Glass transition temperatures are estimated from ^a the Polymer Data Handbook [107], ^b differential scanning calorimetry by Chimaobi Ibeh, or ^c refs [108] and [109].

7.4 Results and Discussion

7.4.1 Repeatability and Effect of Sample Cell Window

In Figure 7-6, USAXS patterns from identical samples contained in cells with three different window types are compared. There was no significant difference between the patterns, suggesting that the low-*q* scattering was not related to the sample-window interface and did not represent imperfectly subtracted residual scattering from windows.



Figure 7-6. Three samples of a PVME-NaClO₄ complex in sample cells with different windows—Kapton, aluminum, and no window (air background)—were compared after subtraction of the appropriate background. As a reference for relative intensity, the USAXS pattern from the Kapton windows processed as a sample with air background subtracted is also shown.

Scattering patterns from the 0% sulfonated PEO copolymer (Figure 7-7) and other samples were highly repeatable across four sets of measurements at the same beamline between April 2008 and April 2009. Except at the highest ion content, low-*q* scattering from ionomers was also independent of thermal history.



Figure 7-7. Repeatability of USAXS patterns from the 0% PEO copolymer. Three samples (A, B, C) were measured in April, August and December of 2008, respectively. They were loaded into aluminum/Kapton cells after storage in a vacuum oven at 40 °C for 1 day (A) or 6 days (B and C). Sample B was measured again in April 2009 after storage in a polyethylene bag with dessicant at ambient temperature for 8 months.

7.4.2 Poly(ethylene oxide)-based Ionomers

A large variability in scattering patterns, depending on sample history, was observed for the 100% sulfonated Na PEO ionomer (Figure 7-8). A sample stored at 40 °C for only one day prior to measurement had larger low-q scattering than two different samples annealed for 6 days at 40 °C—the latter produced similar but not identical patterns.

Two of these samples were remeasured after aging for 12 months (1 day initial anneal) or 8 months (6 day initial anneal). The sample initially annealed for 6 days yielded a nearly identical scattering pattern, while the sample initially annealed for 1 day produced a pattern with lower intensity.



Figure 7-8. Variability in scattering patterns from the 100% sulfonated Na PEO ionomer. Three samples (A, B, C) were measured in April, August and December of 2008, respectively. They were loaded into aluminum/Kapton cells after storage in a vacuum oven at 40 °C for 1 day (A) or 6 days (B and C). Samples A and B were measured again in April 2009 after storage in a polyethylene bag with desiccant at ambient temperature.

The dependence of this variability in USAXS patterns on thermal history suggests that the large low-q scattering is associated with a non-equilibrium structure. As samples were annealed or aged for longer periods of time, the low-q scattering intensity decreased and a shoulder near 0.01 Å⁻¹ appeared—similar to the relationship reported between the low-q upturn and the appearance of the ionomer peak in MnSPS [62]. This was only

observed in the Na ionomer at the highest ion content. This shoulder was not observed in the Li or Cs ionomers at the same ion content (Figure 7-9), but Li and Cs ionomers were only measured once.



Figure 7-9. Effect of cation type on USAXS patterns from 100% sulfonated PEO-based ionomers incorporating a 600 g/mol PEO spacer. Two Na ionomers USAXS patterns with different sample histories are shown; all others were annealed at 40 °C for 6 days prior to ambient-temperature USAXS measurements.

USAXS patterns from ionomers with varied concentrations of Li and Na are compared in Figure 7-10. At relatively low ion concentrations, power-law slopes are approximately 2, but many patterns include a shoulder at high q or multiple power-law regimes. At the highest ion concentrations, larger slopes are sometimes observed, but especially in the fully sulfonated, 600 g/mol spacer Na ionomer, these may be sensitive to sample history.

Power-law slopes fitted to patterns that were well described by a sum of a low-q power law (Equation 3-1) and a constant term representing the flat background at high q are compared in Figure 7-11. At first glance, it appears that Na ionomers have power-law slope of approximately 2.5, and Cs ionomers approximately 3.5 (Figure 7-12), independent of ion concentration, and that in Li ionomers slopes may increase with ion content. When coupled with the result that at room temperature only Li ionomers include ionic aggregates [102], this suggests that the large structure giving rise to low-q scattering is related to ionic aggregates. However, this should be interpreted with great caution for two reasons: as noted in the table caption, a large number of patterns with more complex shapes are omitted from this chart. In addition, significantly different slopes were observed for the two different neutral polymers with PEG spacers of 400 and 600 g/mol. This suggest that some other variable may play a more important role.



Figure 7-10. Effect of cation concentration on scattering patterns from ionomers with either Li (left) or Na (right) cations.



Figure 7-11. Dependence of low-q power-law slope on cation type and concentration. The slopes given are best fits to the sum of a low-q power-law term (Equation 3-1) and a constant term representing the flat background at high q. Many USAXS patterns included a shoulder at high q, multiple power-law regimes, or a dependence on sample history. All of these are omitted from the plot above because the patterns were not well described by the sum of a power-law and flat background.



Figure 7-12. USAXS patterns from samples scattering with a $q^{-3.5}$ power-law dependence.

7.4.3 PVME/Perchlorate Complexes

Poly(vinyl methyl ether) films containing varying amounts of LiClO₄ or NaClO₄ were examined with both WAXS and USAXS. WAXS patterns (Figure 7-13, top) showed no evidence of crystallinity in PVME/LiClO₄ complexes with up to 10 Li per 100 VME units. However, beginning around 1 Li : 100 VME, the relative intensities of the two amorphous halos of PVME began to change, suggesting that the added ions altered the local polymer segmental organization. In simulations of PVME, an analysis of partial structure factors similar to that described in Section 3.3.1 indicates that the 1.0 Å⁻¹ peak represents the distance between adjacent backbone segments while the 1.5-1.6 Å⁻¹ peak represents the distance between adjacent —OCH₃ side groups [110]. In PVME/NaClO₄ complexes (Figure 7-13, bottom) there was no change in the relative intensities of the two amorphous halos, but somewhere between 0.5 and 0.8 Na per 100 VME the solubility limit of the salt was reached: at the two highest concentrations, several sharp peaks also observed in powder NaClO₄ appeared.



Figure 7-13. WAXS patterns from PVME films with varying amounts of $LiClO_4$ (top) or $NaClO_4$ (bottom). Sample names indicate the molar ratio of cations to 100 VME units. The

vertical scale of all patterns is arbitrary.

In general, USAXS intensity increased with increasing NaClO₄ content (Figure 7-14, right). LiClO₄ content had less effect on USAXS intensity (Figure 7-13, left). Although Li⁺ is a smaller ion than Na⁺ and expected to contribute less to scattering contrast, both contain large $ClO_{4^{-}}$ ions. For both cation types, there was a pronounced shoulder in the USAXS pattern corresponding to the concentration just below the onset of the changes in WAXS patterns noted above (1 Li : 100 VME, purple in Figure 8-10, left; 0.5 Na : 100 VME, brown in Figure 7-14, right).

Both of these observations suggest that increased low-*q* scattering intensity may be in some way related to interactions between cations and polar ether oxygens on the polymer backbone. If an amorphous polymer contains regions with different densities as postulated in Section 7.1.1.2, perhaps any added ions are more easily solvated by polymer segments in less dense regions. Larger power-law slopes were observed than in ionomers, especially at high salt content. Given the discussion in Section 7.1.2, this suggests that whatever large-scale structure gives rise to the scattering upturn may have more clearly defined boundaries in the polymer/salt system.



Figure 7-14. USAXS patterns from the same PVME films whose WAXS patterns are shown in Figure 7-12. Some power-law slopes are noted, color-coded to scattering patterns.

7.4.4 Homopolymers Without Added Ions

In semi-crystalline polymers, the degree of crystallinity depends on thermal history. Samples that are quenched rather than allowed to cool slowly are less crystalline, and the intensity of wide-angle scattering peaks associated with crystallinity is lower. Samples of syndiotactic polystyrene (sPS) and high-density polyethylene (HDPE) with varied thermal histories affecting the degree of crystallinity and/or crystallite sizes were examined; the high-q peaks labeled in Figure 7-15 give some indication of crystal size. All patterns include similar power-law slopes (1.7 or 1.8) at the lowest accessible q with no apparent dependence of slope or intensity on sample history. A similar lack of dependence of low-q scattering on crystallization time was reported for isotactic polystyrene and attributed to "foreign particles" [84].



Figure 7-15. USAXS patterns from crystallizable homopolymers including high-density polyethylene (right) and syndiotactic polystyrene (left). The labeled high-q peaks are likely an indication of crystalline lamellar spacing: crystal growth is kinetically limited and crystals grow larger in slowly cooled samples. However, the low-q scattering seems unaffected by this change in thermal history.

Figure 7-16 compares USAXS patterns from atactic polystyrene of two different molecular weights (125-250 kg/mol and 500-8000 g/mol) prepared under varied conditions. For the high molecular weight polymer, the intensity and power-law slope of 2.8 were independent of thermal history. However, the filtered high-MW aPS exhibited reduced

scattering intensity, suggested that impurities may contribute to low-q scattering. Patterns from syndiotactic polystyrene (~300 kg/mol) were of similar intensity. Low-molecular-weight aPS exhibited lower scattered intensity and with a lower power-law slope of 1.8.

Low-*q* scattering was observed in all polymers examined with the exception of poly(dimethyl siloxane) (PDMS). Due to its silicon content, the PDMS sample had an unusually low transmission—0.27, compared to at least 0.70 for other samples—which reduces the intensity of the raw scattering pattern (all patterns reported here are calibrated on an absolute scale including a correction for sample transmission). As noted in Section 7.3.1, the minimum *q* accessible is limited by the intensity of polymer scattering compared to the background intensity. In the case of PDMS, it is not the case that *flat* low-*q* scattering was observed, but that the pattern was truncated at 0.01 Å⁻¹. Because low-q scattering with a power-law slope of 4 has previously been reported for PDMS [111], this result is likely not significant.



Figure 7-16. USAXS patterns from atactic polystyrene (aPS) of two different molecular weights with varied preparation conditions. One syndiotactic polystyrene (sPS) pattern is included for comparison. Low-molecular-weight patterns are truncated due to the lower scattered intensity above background; below the q range reported, I(q) is unknown, not zero.

7.5 Conclusions

It seems clear that the strong low-*q* scattering observed in these polymers is not a trivial artifact. It was not influenced by the windows used in sample cells, suggesting that it is not an interfacial phenomenon and not an artifact of background subtraction. In most materials examined, it was not sensitive to thermal history or aging, which would very likely alter the void and water content of polymers. (The main exception—the fully sulfonated Na PEO-based ionomer—appears to have been out of thermal equilibrium during at least one measurement.) Because the power-law slope and intensity both depend on the material and the instrumental rocking-curve wings are known to have a power-law dependence with an exponent larger than any observed, it is unlikely to be an instrumental artifact.

In addition, low-*q* scattering is clearly influenced by ion content in both PEO-based ionomers and PVME/perchlorate complexes. The stronger association with cations than with anions in polymers whose chemistry renders them more likely to associate with cations suggests that the low-*q* scattering is in some way linked to changes in local segment organization. In addition, power-law exponents were generally larger in the polymer/salt system than in ionomers; following the discussion in Section 7.1.2, this suggests that whatever large-scale structure gives rise to the scattering upturn includes more sharply delineated phases in the polymer/salt system.

In homopolymers without added ions, the low-q scattering reported here was unaffected by crystallinity or thermal history. The reduced intensity in a filtered sample suggests that impurities may contribute to low-q scattering. However, a dependence on molecular weight was also observed, interesting in light of the fact that T_g depends on molecular weight and density fluctuations may be frozen in during the glass transition.

The data reported here demonstrate that an unexplained upturn in scattering intensity, generally following a power law, occurs in a wider variety of polymers than had previously been studied using USAXS. Although this scattering seems to be influenced by local interactions between polymer segments and ions, it also occurs in non-ionic homopolymers.

These observations may provide some clues about the source of the low-*q* scattering upturn widely observed in polymers. An ideal future experiment would be designed to

confirm some specific theory that makes predictions encompassing the range of different low-*q* power-law exponents observed in polymers. USAXS is a useful technique, but accessing a lower *q* range with light scattering to observe the transition to flat scattering would be extremely valuable in determining correlation length of inhomogeneities. Because an association with a critical phenomenon is suggested by power-law exponents close to 2, varying pressure to access different parts of the phase diagram could be useful. Highpressure sample cells are often more convenient to design for neutron-scattering instruments, and because the source of neutron scattering contrast is fundamentally different, SANS/USANS experiments could help determine the nature of the different phases.

Appendix A

Organic Molecules of Intrinsic Microporosity: Interpretation of Wide-Angle Xray Scattering Features

OMIMs are oligomeric model compounds with design principles similar to those underlying PIMs: they pack inefficiently due to their rigidity and concavity. OMIM-1 (Figure A-1) has a BET-equivalent surface area of approximately $600 \text{ m}^2/\text{g}$ [13, 112]. This molecule forms a glassy powder when precipitated from solution, though it can also form a crystalline structure when slowly cast from solution [112]. No T_g below the decomposition temperature has been observed in DSC experiments [112].



Figure A-1. Chemical structure and three-dimensional models of OMIM-1 (~1300 g/mol), reproduced from ref [13].

As part of a collaborative project [113], illustrated in Figure A-2, several methods of simulating OMIM-1 were investigated with the goal of developing a pre-synthesis screening procedure for OMIMs based on predicted surface areas and other properties. Comparison of experimental and simulated scattering patterns was the primary method of structure validation, revealing that the density was higher than expected—at least 1 g/cm³—and that despite the supposed rigidity of molecules, allowing for their flexibility in simulations is important for predicting material properties.

Even though the simpler simulation protocols proved inadequate for predicting material properties, comparing S(q) from simulations with different constraints was useful in formulating an interpretation of observed wide-angle scattering peaks. This interpretation was validated by two means: examination of partial scattering structure factors, using methodology similar to that described in Chapter 3 for PIMs, as well as comparison with experimental WAXS patterns from OMIMs of varied structures.
The data and discussion highlighted in red in Figure A-2 were omitted from ref [113] because complementary simulations were not performed. They are reported here for several reasons. Some WAXS patterns were available during the initial stages of the project and informed the interpretation of scattering peaks. Others were later obtained from newly synthesized materials and demonstrate one of the major outcomes of the study: with a clear interpretation of scattering features, WAXS becomes a powerful tool for understanding the packing of these small rigid molecules and its impact on their porosity.



Figure A-2. Diagram of an OMIM study involving both simulations and WAXS experiments, most of which is published in ref [113]. The data and discussion highlighted in red were omitted from the manuscript—no complementary simulations were performed—and are thus reported here.

A.1 Materials and Methods

Powder samples of OMIMs were provided by members of Prof. Neil McKeown's research group, including Grazia Bezzu, Mariolino Carta, Kadhum Msayib and Rupert Taylor. The synthesis of these materials has been described elsewhere [112]; powders were obtained by precipitation from solution. Their chemical structures are illustrated in Figures A-3 and A-4. WAXS data for OMIM-4 were originally collected by Rupert Taylor but are shown here incorporating the correction illustrated in Figure 3-5.

Immediately prior to scattering measurements, all samples were degassed in a vacuum oven at 120-130 °C for at least 24 h. The effect of immersing OMIMs in methanol prior to this degassing step to assist in removing residual adsorbed species was also investigated, but unless otherwise noted data shown are from untreated powders.



Figure A-3. Chemical structures of OMIMs with varied end groups. Molecules whose scattering patterns have not been previously published are highlighted in red.



Figure A-4. Chemical structures of OMIMs with altered core nitrile groups.



Figure A-5. An illustration of the correction for particulate power-law scattering using SAXS and WAXS data from OMIM-3. The particulate power-law contribution was fit (gray line) to SAXS data (green open circles) from 0.02 to 0.17 Å⁻¹ and subtracted from wide-angle X-ray scattering (WAXS) pattern (red line) to give corrected WAXS data (blue line). Figure reproduced from ref [113], supporting information.

Small- and wide-angle X-ray scattering patterns were obtained from degassed powders using instruments at Penn State and data reduction methods described in Chapter 2. Low-*q* power-law scattering was observed with a larger intensity and higher-*q* onset for all powder samples compared to PIM films. In powders, this power-law scattering can be attributed to the particulate nature of the material. To facilitate comparison with simulated non-particulate samples, this power-law scattering was subtracted as shown in Figure A-5.

A.2 Results and Discussion

A.2.1 Effect of Methanol Treatment Before Degassing

Treating PIM films with methanol can remove residual adsorbed species [24] and can affect PIM scattering patterns (Chapters 3–5). The effect of immersing OMIM powders in methanol just prior to degassing was also examined (Figure A-6). Larger OMIMs appeared to be insoluble in methanol, and their scattering patterns were unaffected by this procedure. OMIM-1, however, appeared to be slightly soluble in methanol. The procedure

changed the OMIM-1 powder sample into a brittle, flaky film yielding a more ordered WAXS pattern (Figure A-7).



Figure A-6. Methanol treatment of powder OMIM samples. Powders were stirred in methanol for 24 hours and then allowed to settle for two days (top row). OMIM-1 and methanol formed a phase-separated solution. The volume of the yellow phase (top left) was much larger than the initial powder volume, and unlike OMIMs 2 and 3 (top middle and right), no particles remained suspended in the bulk methanol phase. Excess methanol was then decanted and samples were dried under vacuum at 120 °C for 24 hours (bottom). OMIM-1 formed a brittle, flaky film while OMIMs 2 and 3 formed powders similar to the original materials.



Figure A-7. Scattering patterns from powder OMIM-1 (not methanol treated) and a flake of methanol-treated OMIM-1.

Because this ordered OMIM 'film' not did not correspond to the simulated structure or scattering pattern and a uniform procedure was desired, the methanol treatment step was omitted from the sample preparation procedure for all data shown below. A detailed analysis of OMIM crystal diffraction patterns is beyond the scope of this work, but it is important to note that some OMIMs may be able to form either a crystalline or an amorphous structure depending on sample history, and that OMIM solubilities may vary with molecule size even when molecular chemistry is very similar.

A.2.2 OMIM-1 WAXS Peak Assignment

An interpretation of characteristic OMIM WAXS features (Table A-1) was established by a process described in detail in ref [113]. Experimental WAXS patterns from OMIMs with varied end-group sizes (OMIMs 1, 2, 3 and 4) were considered along with simulated OMIM-1 WAXS patterns from simulations under different conditions. For example, in OMIMs with bulkier end groups, peak A shifted to lower *q* in experimental data. In addition, when simulated molecules were constrained to be rigid, only peak A could be reproduced accurately; peaks B and C could not be reproduced at any density unless molecules were allowed to be flexible. It was thus hypothesized that peak A represented an intermolecular distance rather than any intramolecular feature, and that peaks B and C were related molecular conformations achieved during packing.

Peak	q (Å-1)	d (Å)	Peak assignment		
А	0.34-0.38	16.7–18.6	Separation between nearest-neighbor molecules		
В	0.76-0.95	6.6-8.3	Separation between end-group centers		
С	1.33-1.43	4.4-4.7	Separation between outer end-group atoms		

Table A-1. Experimental scattering peak positions and interpretations (also given in ref [113]).

These peak assignments were validated in ref [113] by examining partial simulated structure factors, the same method developed in Chapter 3 of this dissertation. Below, this result is tested by application to additional OMIMs with varied end groups, OMIMs with varied core chemistries, and a dendrimer with intrinsic microporosity (DIM).

A.2.3 OMIM WAXS Patterns

WAXS patterns from OMIMs whose structures are given in Figures A-2 and A-3 are shown in Figures A-8 through A-12. Wavevectors and equivalent Bragg spacings for the peaks in these patterns are summarized in Table A-2 and plotted versus molecular weight in Figures A-13 through A-15, along with a detailed discussion in light of the peak assignments given above. Here, additional features such as differences in relative peak intensities and breadths are noted.

Figure A-8 shows amorphous OMIMs with varied end groups. Some variation in the wavevector of peak A is evident. Peak B is of significantly larger intensity in two of the larger molecules, OMIM-3 and "Cy6-OMIM-1. However, it is either nearly nonexistent or merged with peak C in OMIM-4, which is of a comparable molecular weight.



Figure A-8. WAXS patterns from OMIMs with end groups of varying sizes (structures given in Figure A-3).

In Figure A-9, scattering from a mixed OMIM ('MOMIM') is compared with patterns from the two related 'pure' OMIMs. Peak A appeared at a lower wavevector than in either pure OMIM, and peak B was broad and asymmetrical, likely bimodal.



Figure A-9. WAXS pattern from a mixed OMIM (MOMIM) with two different end groups. 'Pure' OMIMs with each of the two end groups are shown for comparison. (Chemical structures in Figure A-3.)

Cy6-OMIM-1 and "Cy6-OMIM-1 are isomers (Figure A-3). The arms of Cy6-OMIM-1 are more symmetrical, and its scattering pattern suggested that it was semi-crystalline. The strongest peak is presented as peak A in Table A-2, but there were also several weaker peaks closer to the usual location of peak A.



Figure A-10. WAXS pattern from a semi-crystalline OMIM (Cy6-OMIM-1, red). Two other OMIMs with large end group are shown for comparison, including an asymmetrical isomer, uCy6-OMIM-1.

Altering the nitrile group of the core of OMIM-1 produced smaller changes in scattering patterns (Figure A-11) than altering its arms.



Figure A-11. WAXS patterns from OMIMs with varied core chemistries (chemical structures in Figure A-4).

One molecule of more complex architecture, a dendrimer with intrinsic microporosity (DIM), was examined. In Figure A-12, its WAXS pattern is compared with that of an OMIM with identical end-group chemistry. Above 1 Å⁻¹, the patterns were identical. Peak A was clearly not observed at the same wavevector as in the OMIM. However, subtraction of the low-*q* particulate power-law scattering (illustrated in Figure A-5) was not as simple as for the smaller molecules; there was some excess scattering below 0.3 Å⁻¹. A peak is not conclusively reported here, but investigation of additional DIMs might reveal a scattering feature similar to peak A.



Figure A-12. WAXS pattern from a first-generation dendrimer of intrinsic microporosity (DIM) compared with an OMIM with the same t-Bu end groups. Chemical structures are given in Figure A-3.

Table A-2. Wavevectors and equivalent Bragg spacings for OMIM WAXS peaks appearing in Figures A-8 through A-12. (Table A-1 gives peak interpretations.) Peaks annotated with an asterisk (*) were very broad and likely a combination of multiple peaks. For the semicrystalline OMIM indicated with a double asterisk (**), the strongest peak is given. In Figures A-13 through A-15, these Bragg spacings are plotted versus molecular weight.

Malanda	Peak A		Peak B		Peak C		Mol. wt.
Molecule	q (Å-1)	d (Å)	q (Å-1)	d (Å)	q (Å-1)	d (Å)	(g/mol)
OMIM-1	0.376 ± 0.002	16.7 ± 0.1	0.95 ± 0.02	6.6 ± 0.1	1.33 ± 0.03	4.7 ± 0.1	1348
OMIM-2	0.37 ± 0.02	17 ± 1	0.91 ± 0.01	6.81 ± 0.06	1.37 ± 0.1 (*)	4.6 ± 0.3 (*)	1582
OMIM-3	0.338 ± 0.004	18.6 ± 0.2	0.76 ± 0.02	8.3 ± 0.2	1.43 ± 0.03	4.4 ± 0.1	2238
OMIM-4	0.31 ± 0.01	20.5 ± 0.5	merged with C		1.22 ± 0.05	5.1 ± 0.2	1911
^u Cy6-OMIM-1	0.31 ± 0.02	20.3 ± 1.4	0.95 ± 0.02	6.6 ± 0.2	1.4 ± 0.1	4.5 ± 0.3	2215
MOMIM	0.34 ± 0.04	19 ± 3	0.77 ± 0.1 (*)	8±1(*)	1.45 ± 0.05	4.3 ± 0.2	1786
Cy6-OMIM-1 (**)	0.41 ± 0.01	15.3 ± 0.4	multiple peaks (semi-crystalline)				
OMIM-1-Py	0.35 ± 0.04	18 ± 2	0.92 ± 0.04	6.8 ± 0.3	1.34 ± 0.08	4.7 ± 0.3	1285
OMIM-1-CF ₃	0.37 ± 0.03	17 ± 2	0.96 ± 0.03	6.8 ± 0.2	1.41 ± 0.06	5.2 ± 0.2	1419
t-Bu-DIM-1	no clear peak		merged with C		1.22 ± 0.05	5.1 ± 0.2	4846

A.2.4 Re-evaluation of WAXS Interpretation

As the size of the arms attached to an OMIM core increased, the nearest-neighbor peak A generally moved to lower wavevectors (Figure A-13, blue series). The OMIM with mixed arms also fit this trend (green), and the increased peak breadth may be related to the molecular heterogeneity. Changing the nitrile group of OMIM-1 had a much smaller effect (red); larger nearest-neighbor distances in OMIM-1-Py and OMIM-1-CF₃ could be related to the absence of attractive dipole-dipole forces between nitrile groups, but these differences may not be significant. In the dendrimer, this feature was either absent or appeared at a much smaller wavevector. All of these observations support the interpretation of this scattering feature as an intermolecular distance, and some additional insight may be derived from closer examination of exceptions to the 'rule'. One of the central conclusions of ref [113] was the importance of choosing end groups that push molecules further apart without filling the space that they create. Although OMIM-3 and "Cy6-OMIM-1 have very similar molecular weights, molecules appeared to pack more closely in OMIM-3, which has a more compact architecture. Cy6-OMIM-1 is a more symmetrical isomer of "Cy6-OMIM-1; if its strongest peak is interpreted as a nearest-neighbor distance, these molecules were able to pack even closer together in a very regular structure.



Figure A-13. Peak A equivalent Bragg distances.

Peak B has been associated with the distance between end groups close together in space, which may reside on either the same or different OMIM molecules. Unlike peak A, peak B appeared at nearly constant wavevector with a few exceptions. The Bragg spacing was larger in OMIM-3, which has very compact arms relative to its molecular weight. In the MOMIM, a hybrid of OMIMs 1 and 3, this peak also appeared at a lower wavevector and likely consisted of two poorly resolved peaks arising from structural heterogeneity.

The intensity of peak B was highest in two of the highest molecular weight amorphous OMIMs (OMIM-3 and "Cy6-OMIM-1), which is consistent with the association of this scattering feature with distances between adjacent end groups. In OMIM-4 and t-Bu-DIM-1, which both feature arms identical to OMIM-1 with short alkyl chains attached, a single peak was observed between the usual locations of peaks B and C. It is possible that these substituent groups occupy the space between adjacent end groups, so that the two end groups interpenetrate and the distinction between center-to-center and edge-to-edge is blurred.



Figure A-14. Peak B equivalent Bragg distances.

Peak C is attributed to distances between atoms at the edges of adjacent end groups on OMIMs. Variability in the apparent maximum of this feature was smaller (Figure A-15), although in many patterns it may be a collection of poorly resolved peaks.



Figure A-15. Peak C equivalent Bragg distances.

A.3 Conclusions

The additional data reported here support the OMIM WAXS feature interpretations developed in ref [113]. Examining peak A may be especially useful in understanding which

large substituent groups can keep neighboring molecules far apart without filling in the space that they create. Comparing the MOMIM with OMIMs 1 and 3, as well as comparing "Cy6-OMIM-1 with Cy6-OMIM-1, suggests that a reduction in molecular symmetry may result in poorer packing than would otherwise be expected for a given molecular weight or architecture.

However, the utility of peaks B and C is less clear. The structural origin of peak C is somewhat trivial, while the causes underlying significant changes in peak B are unclear. It is possible that a feature analogous to peak A appears in DIMs, but examination of a wider variety of DIMs with very careful SAXS/WAXS data reduction is needed.

Appendix B

PIM-1 Aging SAXS/WAXS Patterns

This appendix contains the scattering patterns discussed in Section 5.3.3. Summary data computed from these patterns, including the partial scattering invariant and peak position, are reported in Figures 5-6, 5-7 and 5-8.

A sample-to-detector distance of 0.5 m was used; other details are given in Section 2.4.1. All SAXS patterns were collected at room temperature and were calibrated to absolute intensity; it is important to note that this included normalization by sample thickness. WAXS patterns were scaled to overlap SAXS patterns.



Figure B-1. SAXS (open circles) and WAXS (filled circles) patterns from PIM-1 films aged at 30 °C for 1 day after removal from ethanol.



Figure B-2. SAXS (open circles) and WAXS (filled circles) patterns from PIM-1 films aged at 75 °C for 1 day after removal from ethanol.



Figure B-3. SAXS (open circles) and WAXS (filled circles) patterns from PIM-1 films aged at 125 °C for 1 day after removal from ethanol.



Figure B-4. SAXS (open circles) and WAXS (filled circles) patterns from PIM-1 films aged at 30 °C for 1 day (after removal from ethanol) and then for 13 days at ambient temperature in an evacuated Desi-Vac container.



Figure B-5. SAXS (open circles) and WAXS (filled circles) patterns from PIM-1 films aged at 75 °C for 1 day (after removal from ethanol) and then for 13 days at ambient temperature in an evacuated Desi-Vac container.



Figure B-6. SAXS (open circles) and WAXS (filled circles) patterns from PIM-1 films aged at 125 °C for 1 day (after removal from ethanol) and then for 13 days at ambient temperature in an evacuated Desi-Vac container.



Figure B-7. SAXS (open circles) and WAXS (filled circles) patterns from PIM-1 films aged at 75 °C for 14 days (after removal from ethanol).



Figure B-8. SAXS (open circles) and WAXS (filled circles) patterns from PIM-1 films aged at 125 °C for 14 days (after removal from ethanol).



Figure B-9. Combined SAXS/WAXS patterns for films measured after two weeks (top) and contribution to the scattering invariant (bottom), analogous to Figure 5-6.



Figure B-10. SAXS/WAXS wavevector maxima plotted versus the scattering invariant with alternate upper integration limits of 1.0 Å⁻¹ (top) and 2.0 Å⁻¹ (bottom).



Figure B-11. SAXS/WAXS wavevector maxima plotted versus the scattering invariant with three different upper integration limits, normalized by the maximum value of the invariant. Deviations from the behavior highlighted in Figure 5-7 occur only in films exposed to temperatures of 125 °C (red symbols) and only with invariant upper integration limits of 1.0 or 2.0 Å⁻¹ (green border).

Appendix C

Preliminary SANS/QCM Study of PIM-1 Swelling and Vapor Adsorption

C.1 Motivation and Experimental Considerations

Because X-rays interact with atomic electrons, the chemistry of a material determines its X-ray scattering length density and therefore the scattering contrast between multiple phases in a sample. Neutrons, however, interact with atomic nuclei in a way that depends on their allowed spin states [30], which vary across isotopes. In particular, there is a large scattering length difference between hydrogen and deuterium, and deuteration of organic materials is often used to negate or enhance the contrast between two phases in small-angle neutron scattering (SANS). In porous materials, contrast matching enables the measurement of porosity accessible to a fluid [114], while contrast enhancement provides information about the degree of swelling [115] (Figure C-1).



Figure C-1. Applications of SANS contrast variation, commonly achieved by deuteration of one phase, in porous materials. If a porous material is filled with a contrast-matched fluid (bottom), any scattering observed arises from inaccessible pores. If a high-contrast fluid is used (top), the interfacial surface area and degree of swelling can be determined.

In a gas adsorption experiment (Section 1.2.2), the relative pressure⁷ of a gas is increased through a set of discrete values, and the quantity adsorbed (mass or volume) is measured at each pressure. Pore size distributions may be calculated using the assumption that smaller pores fill at lower pressures (Figure C-2). However, hysteresis is observed in adsorption isotherms, indicating that polymer swelling occurs during the process of adsorption [13]. A series of SANS measurements on PIMs exposed to adsorbent gases at a variety of partial pressures, repeated under varied contrast conditions, could potentially provide a pore size distribution in a context directly comparable to other measurements of internal surface area and pore sizes, reconciled with an understanding of the structural changes accompanying gas adsorption.



Figure C-2. As a microporous material is exposed to an adsorbate vapor at increasing relative pressures, pores of increasing size are filled. The smallest pores fill first due to interactions with multiple pore walls.

PIM adsorption isotherm measurements are performed exclusively on precipitated powder samples due to the slow kinetics of adsorption in films. While a SAXS peak clearly related to porosity is observed in PIM films, in powder samples this feature is overwhelmed by power-law scattering arising from the particulate nature of powders. A film PIM sample is therefore required for SANS adsorption experiments, and the slow kinetics of adsorption in films constitute an experimental challenge.

Adsorption kinetics are faster in thinner films, but in transmission-geometry scattering experiments, relatively thick films are required to achieve an acceptable signal-

⁷ Relative pressure (partial pressure) is the ratio p/p^0 of a gas vapor pressure to its saturated vapor pressure at the temperature of interest.

to-noise ratio. Stacking multiple thinner films together is generally an acceptable strategy, but in an adsorption experiment, stacked films must be spaced so that both sides of each film are exposed to vapor flow. The total sample thickness within a vapor environment sample cell is also limited by its design, limiting the number of films that can be stacked while maintaining vapor flow.

For the SANS experiments reported here, methanol was chosen as the adsorbate for several reasons. With a liquid adsorbate, a room-temperature isotherm is possible, and a small adsorbate molecule is preferable for characterizing the size of small pores. Methanol is available in several deuterated varieties, d4, d1, and d3⁸ (although d3 is prohibitively expensive). In addition, the interaction between methanol and PIM-1 is of interest given the use of alcohols to reverse physical aging in PIM films.

Prior to SANS experiments, quartz crystal microbalance (QCM) experiments were performed to determine relative pressures of interest and to determine the film thickness representing the best compromise between scattering signal-to-noise and equilibration time for each relative pressure. Due to the kinetics observed and the sample thickness limitations of the vapor SANS environment, the extensive adsorption experiments discussed above were not performed. The experiments reported here represent only preliminary work, and many possible improvements are noted.

C.2 Methods and Materials

C.2.1 Quartz Crystal Microbalance (QCM) Experiments

A PIM-1 film was spin-cast onto a silicon-coated QCM sensor substrate, using a concentration of approximately 4 mg/ml in chloroform and a spin rate of 1200 rpm. The film was dried for 5 minutes on a hot plate at 40 °C and then placed in a Q-Sense E4 QCM-D instrument (Biolin Scientific, Inc.). Using a total flow rate of 500 standard cubic centimeters per minute (sccm) over the film surface at a temperature of 25 °C, the relative pressure of methanol was varied by volumetrically mixing dry nitrogen gas with saturated methanol

⁸ Methanol-d1 is CH₃OD, methanol-d3 is CD₃OH, and methanol-d4 is CD₃OD, where D indicates the replacement of hydrogen with deuterium.

vapor. After equilibration at each relative pressure, the resonant frequencies were measured, and the mass uptake Δm was calculated from the shift in resonant frequencies Δf using the Sauerbrey equation [116]:

$$\Delta m = -C \frac{1}{n} \Delta f \tag{C-1}$$

where *n* is the overtone number and C = 17.7 ng/cm²s. Resonant frequency shifts were relative to the dry polymer-coated substrate; the polymer mass was calculated by comparison with resonant frequencies measured from the same QCM sensor prior to spin-casting of the polymer film.

The PIM-1 film did not uniformly coat the QCM substrate; an imprint of the grooves in the spin-coater's chuck was visible on the film surface. Because the QCM sensor substrate was very thin and chloroform (the best solvent for PIM-1) has a relatively low boiling point, heat transfer through the substrate may have affected the rate of evaporation.

A nonuniform film violates one of the assumptions underlying Equation C-1. As a result, the adsorbed mass reported is not meaningful on an absolute scale, but the shape of the isotherm can still be discerned. Because non-uniform coating of the substrate tends to result in underestimates of adsorbed mass, the masses reported are the average of the overtones yielding the largest masses (n = 7 and n = 9).

After the methanol isotherm was completed, the film was dried on a hotplate at 40 °C for 5 min and placed under dry nitrogen flow for 7 minutes. The adsorption experiment was then repeated using ethanol. Dr. Brandon Rowe and Dr. Christopher Soles (National Institute of Standards and Technology) assisted with QCM experiments.

C.2.2 Vapor-environment SANS Experiments

SANS patterns were collected at beamline NG-3 of the NIST Center for Neutron Research using a sample-to-detector distance of 1.865 m, neutron wavelength of 5.1 Å, circular pinhole collimator, and ³He proportional counter detector. Dr. Ronald Jones and Dr. Chad Snyder (NIST) assisted with SANS experiments.

Two samples of PIM-1 were studied: a $100-\mu m$ film cast onto a glass substrate, and a stack of $\sim 20-\mu m$ films cast onto a mica substrate (both cast from chloroform solution). Although other PIM-1 films studied throughout this dissertation were cast onto glass, the mica substrate facilitated casting of relatively thin films of a consistent thickness and appropriate size.

An in situ vapor SANS cell [117] with quartz windows was used; background scattering including the contribution from these windows was subtracted from scattering patterns. For each sample, a SANS pattern was collected in the dry state. To approximate saturation with vapor (i.e. $p/p^0 = 1$) while circumventing the slow kinetics of adsorption in films, liquid methanol-d4 (VWR) was then added to the cell. Excess liquid was removed and another SANS pattern was recorded with the sample under 10 sccm flow of saturated methanol-d4 vapor to prevent evaporation. Additional SANS patterns were collected for liquid methanol-d4 and for the stack of films while immersed in methanol-d4.

C.3 Results and Discussion

C.3.1 Alcohol Adsorption Isotherms

QCM adsorption isotherms for methanol and ethanol on PIM-1 are shown in Figure C-3. Because the polymer film did not uniformly coat the polymer substrate, mass uptake is not accurate on an absolute scale. Points on the isotherms are from a mix of adsorption and desorption curves; some amount of hysteresis was evident but was not accurately captured in this experiment.

Nitrogen adsorption isotherms at 77 K [13, 23] have been collected for PIM-1 powders. All of these have the shape of type 1 isotherms (Figure 1-5), with rapid adsorption beginning at very low values of p/p^{0} . Type 1 isotherms are strongly characteristic of microporous materials in which adsorbate molecules are subject to attractive forces from multiple pore walls [12]. The alcohol adsorption isotherms above exhibit a very different shape most closely resembling a type III isotherm (Figure 1-5). The small amount of adsorption at low relative pressures can be attributed to weak adsorbate-adsorbent interactions, with cooperative or multilayer adsorption increasing the amount adsorbed at

higher relative pressures [12]. This suggests that PIM-1 interacts more weakly with alcohols than with nitrogen.



Figure C-3. Adsorption isotherms of methanol and ethanol on a PIM-1 film at 25 °C. Mass uptake is not accurate on an absolute scale.

C.3.2 SANS Experiments

SANS patterns from both dry films exhibited a broad scattering maximum at ~0.38 Å⁻¹, a larger wavevector than the 0.22–0.30 Å⁻¹ typical for SAXS patterns⁹. There is some precedent for differences between SANS and SAXS patterns above ~0.03 Å⁻¹ that are specific to microporous materials: the electron density in pores may not truly be zero, related to the overlapping surface potentials that give rise to enhanced adsorption in micropores. If so, X-ray scattering contrast between pore and matrix is reduced, but neutron scattering contrast is unaffected [118].

The broad SANS peak for either sample was not affected by immersion in methanol –d4 (Figure C-4). If this is the same scattering feature attributable to porosity in X-ray scattering experiments described in earlier chapters, this suggests that methanol-d4 did not fill most pores. Comparing the patterns from the stack of films immersed in methanol-d4 and while under vapor flow after the removal of excess liquid suggests that not all bulk methanol-d4 was successfully removed: the pattern from the immersed stack could be a

 $^{^9}$ PIM-1 films that have been aged above room temperature may exhibit a SAXS maximum above 0.35 Å $^{-1}$ (Figure 5-7).

linear combination of the pattern from the dry stack and the pattern from liquid methanold4 (Figure C-5). In the 100- μ m film under vapor flow, a second broad, weak peak appears near 0.1 Å⁻¹. This does not appear to be an artifact from the presence of bulk liquid methanol and may be indicative of swelling, although some pore filling would be expected to accompany swelling.



Figure C-4. SANS patterns from a 100- μ m film (solid lines) and a stack of 20- μ m films (circles) under several conditions: dry (black), immersed in methanol-d4 (red, stack only), and under 10 sccm flow of saturated methanol-d4 vapor following immersion and removal of excess liquid methanol-d4 (orange). While intensity units are arbitrary, the relative intensities of the two 100- μ m patterns are comparable to one another, as are the relative intensities of the three patterns from the stack of 20- μ m films.



Figure C-5. SANS pattern from bulk methanol-d4 (quartz background subtracted).

C.4 Conclusions

Some differences between methanol and ethanol isotherms are evident, such as the apparent onset of methanol adsorption at a lower relative pressure than ethanol adsorption. Adsorption experiments using higher-quality films might be able to relate this to the apparent greater effectiveness of methanol in rejuvenating PIM films, as quantified by SAXS intensity (Figure 3-3).

Before more extensive SANS experiments are attempted, it should be verified that the SANS peak at ~0.38 Å⁻¹ is the same porosity-linked scattering feature as the broad SAXS peak discussed throughout this work. Expanding the wavevector range to higher q could be useful for that purpose, revealing whether the weak high-q peaks appearing in WAXS patterns also appear in neutron scattering patterns at the same wavevectors. However, collecting a full adsorption isotherm from film thick enough to scatter strongly in transmission geometry is inherently challenging. Reflectometry experiments would allow the use of thinner films with the added possibility of depth-resolved structural information, but designing an appropriate vapor sample cell could be more complicated for that geometry.

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VITA

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Amanda McDermott was born November 28, 1984, in New Jersey and relocated at the age of five to Botetourt County in southwest Virginia. She attended Lord Botetourt High School as well as a half-day program at the Roanoke Valley Governor's School for Science and Technology. At the University of Virginia she majored in physics, took language and linguistics classes for fun, and studied the mechanical properties of amorphous steels in Joe Poon's research group. She also enjoyed spending a summer working in Bob Shaw's group at Oak Ridge National Laboratory and decided to apply to graduate programs in materials science. During her prospective visit to Penn State, she was surprised by Jim Runt's invitation to join his polymer-focused group despite her lack of chemistry background. She is now very grateful for this introduction to the field of polymer physics.