

Lab 4 – Module γ_1

Short range order

OBJECTIVES

- ✓ Understand structure of amorphous materials
- ✓ Learn principles of x-ray scattering from amorphous materials

SUMMARY OF TASKS

- 1) Perform x-ray scattering measurements on semicrystalline polyethylene, and a series of amorphous methacrylate polymers
- 2) Determine the lattice parameters and average crystallite size for polyethylene
- 3) Interpret observed peaks in the scattering patterns for methacrylate polymers
- 4) Determine the average interchain distances for polyethylene and methacrylate polymers from x-ray scattering patterns
- 5) Determine approximate degree of crystallinity for PE sample

BACKGROUND

Diffraction from Crystalline Materials of Finite Crystal Dimension

For crystalline materials, we learned that the periodic arrangement of atoms gives rise to constructive interference of scattered radiation having a wavelength λ comparable to the periodicity d when Bragg's law is satisfied¹:

$$n\lambda = 2d \sin \theta \quad [1]$$

where n is an integer and θ is the angle of incidence. Bragg's law implies that constructive interference occurs only at the exact Bragg angle and the Intensity vs. 2θ curve exhibits sharp lines of intensity. In reality, diffraction peaks exhibit finite breadth, due both to instrumental and material effects. An important source of line broadening is finite crystal size. In crystals of finite dimensions, there is only partial destructive interference of waves scattered from angles slightly deviating from the Bragg angle.¹

This is illustrated in Fig. 1 below, which shows XRD patterns for two polycrystalline V_2O_5 films with different average crystal sizes.

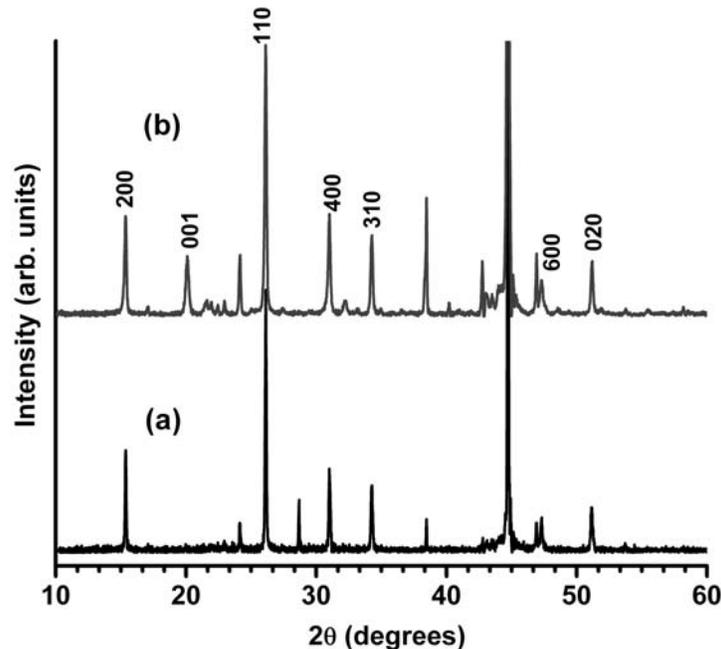


Figure 1. XRD patterns from V_2O_5 thin films with average crystallite sizes of a) 250 nm and b) 80 nm. Peak broadening is observed with decreasing crystallite size. (data courtesy S. C. Mui)

If we define the angular width of a particular peak as:

$$B = \frac{1}{2}(2\theta_1 - 2\theta_2) \quad [2]$$

where θ_1 and θ_2 define the angular bounds of the peak in radians, then the average crystal size can be estimated from the Scherrer formula as¹:

$$t = \frac{0.9\lambda}{B \cos \theta_B} \quad [3]$$

Based on this discussion, what might we expect to observe in XRD patterns of nanocrystalline systems like quantum dots?

X-ray Scattering from Amorphous Materials

Above it was established that as the crystal size gets smaller, diffraction peaks get broader. What happens in the extreme when there is no crystallinity? Whereas crystalline materials exhibit long range order, amorphous materials such as glassy polymers, metallic glasses and oxide glasses exhibit only *short range order*.² Their scattering pattern displays broad, low intensity peaks characteristic of the average local atomic environment, as shown in Fig. 2 for an amorphous zirconium phosphate³.

Applying the Scherrer formula to the peaks in this pattern, what is the calculated “crystal size” for this material? What do the peak positions represent?

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Figure 2. X-ray scattering pattern of amorphous zirconium phosphate synthesized using a non-ionic surfactant template.³

To better understand amorphous x-ray patterns, we can calculate the predicted intensity using the structure factor for amorphous materials. The structure factor is defined as²:

$$F(s) = \sum_{n=1}^M f_n \exp\left[2\pi i \vec{s} \cdot \vec{r}_n\right] \quad [4]$$

where \vec{s} is the scattering vector, f_n is the atomic scattering factor (proportional to atomic number), and \vec{r}_n is the atomic position vector for the n th atom. For a crystalline system, the summation in [4] is taken over the unit cell, and the total intensity is determined from the contribution of all unit cells.¹ For an amorphous material, there is no unit cell, since the atomic positions are not strictly periodic. Hence we take the summation in [4] over all atoms in the material.

Recalling the relationship between I_{coh} and F :

$$I_{coh} \propto F(s)F(s)^* = \sum_{m=1}^N \sum_{n=1}^N f_m f_n \exp\left[2\pi i \vec{s} \cdot \vec{r}_n\right] \exp\left[-2\pi i \vec{s} \cdot \vec{r}_m\right] \quad [5]$$

and letting $\vec{r}_{nm} = \vec{r}_n - \vec{r}_m$,

$$I_{coh} = \sum_{m=1}^N \sum_{n=1}^N f_m f_n \exp\left[2\pi i \vec{s} \cdot \vec{r}_{nm}\right] \quad [6]$$

Using the assumption that the material is isotropic, i.e., that its structure has radial symmetry, the exponential can be replaced by its angular average²:

$$\int_0^\pi \int_0^{2\pi} \exp(2\pi i r_{nm} s \cos \alpha) \sin(\alpha) d\alpha d\phi = \frac{\sin(qr_{nm})}{qr_{nm}} \quad [7]$$

$$I_{coh} = \sum_{m=1}^N \sum_{n=1}^N f_m f_n \frac{\sin(qr_{nm})}{qr_{nm}} \quad [8]$$

where $q = \frac{4\pi}{\lambda} \sin \theta = 2\pi s$ [9]

For simplicity, we consider the case where all atoms are of the same type:

$$I_{coh} = f^2 \sum_{m=1}^N \sum_{n=1}^N \frac{\sin(qr_{nm})}{qr_{nm}} \quad [10]$$

If we consider the interaction of each atom with itself,²

$$I_{coh} = f^2 N \left[1 + \sum_{n \neq m} \frac{\sin(qr_{nm})}{qr_{nm}} \right] \quad [11]$$

where the first term is individual atom scattering, obtained by letting $r_{nm} \rightarrow 0$. I_{coh} can be expressed in continuum form by substituting in the *radial distribution function*, $4\pi r^2 \rho(r)$:

$$I_{coh} = f^2 N \left[1 + \int_0^{\infty} 4\pi r^2 \rho(r) \frac{\sin(qr)}{qr} dr \right] \quad [12]$$

where $\rho(r)$ is the *atomic pair density function*,^{3,6} which gives the average density of atoms (number/volume) at a distance r from the center of a reference atom.^{2,4} The quantity $4\pi r^2 \rho(r) dr$ in eq. 12 gives the number of atoms within a shell of thickness dr around the reference atom, as shown in Fig. 3.

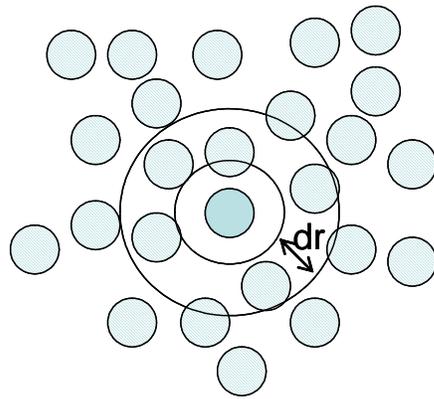


Figure 3. Schematic representation of atomic distribution within an amorphous material. The quantity $4\pi r^2 \rho(r) dr$ is the number of atoms in a shell of thickness dr around a reference atom.

The atomic pair density function is related to the pair distribution function $g(r)$, by:^{2,4}

$$g(r) = \frac{\rho(r)}{\rho_o} \quad [13]$$

where ρ_o is the bulk atomic density of the material (atoms/volume). For amorphous materials and liquids, $g(r)$ has a form such as that shown in Fig. 4.⁵ *How would this function look for a crystalline system?*

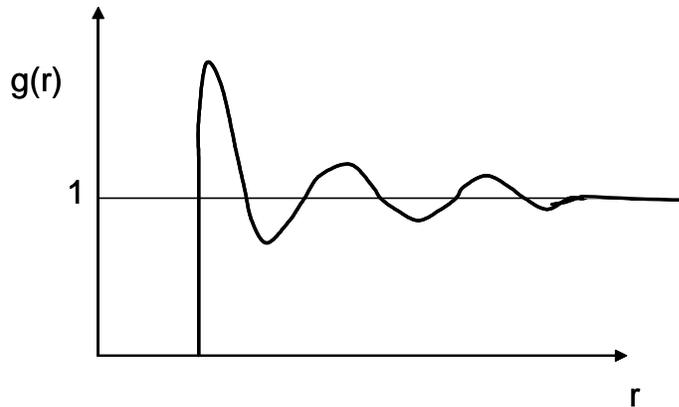


Figure 4. Schematic illustration of the pair distribution function for amorphous materials. The maxima correspond to distances where there is a higher probability of finding a neighboring atom.

The oscillatory behavior of $g(r)$ gives rise similar oscillations in the scattering patterns from amorphous materials. From eq. [12] we can expect that the scattering intensity from an amorphous material will behave as a damped oscillatory function whose features depend on the average local spacing between atoms in the structure (Fig. 5).

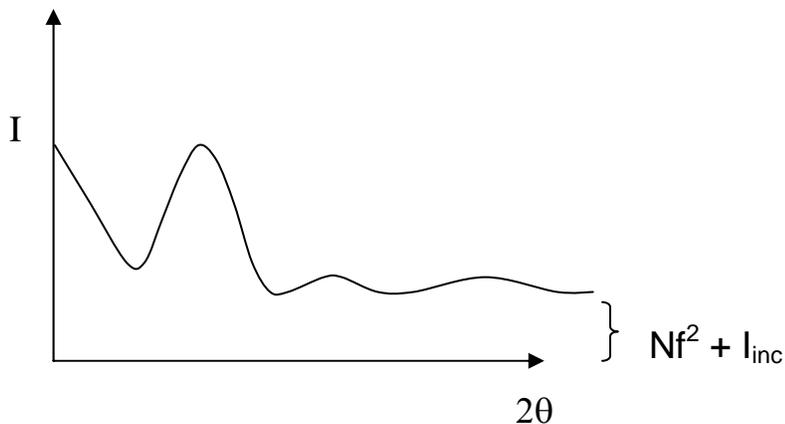


Figure 5. Schematic of X-ray scattering pattern for an amorphous material.

For systems that are partially crystalline, the amorphous and crystalline contributions to the scattering can be deconvoluted to determine the degree of crystallinity in the sample. The areas under the crystalline and amorphous peaks are proportional to their volume fraction in the sample,⁶ as shown for the PP/P(E-co-VA) blend in Fig. 4.⁷

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Figure 6. X-ray scattering pattern from blend of polypropylene and poly(ethylene-co-vinyl acetate). The total scattering pattern is deconvoluted into amorphous and crystalline contributions.⁷

Structure of polymers

In this laboratory we will investigate the structure of polymers by X-ray scattering. Polymers are covalently bonded long chain molecules composed of repeating units made of carbon and hydrogen, and sometimes oxygen, nitrogen, sulfur, silicon and/or fluorine. The covalent bonding in polymers imposes directionality on their spatial arrangement into periodic structures. Polymer chains exhibit weak intermolecular forces due to van der Waals attractions. The ability of polymer chains to pack into an ordered array depends greatly on the stereoregularity of their pendant groups. For example, depending on the method of polymerization, polystyrene may exhibit isotactic, syndiotactic or atactic structure, as shown in Fig. 7. Atactic polystyrene is entirely

amorphous due to the random arrangement of the pendant phenyl groups, while syndiotactic and isotactic polystyrene, having more regular structures, exhibit crystallinity.

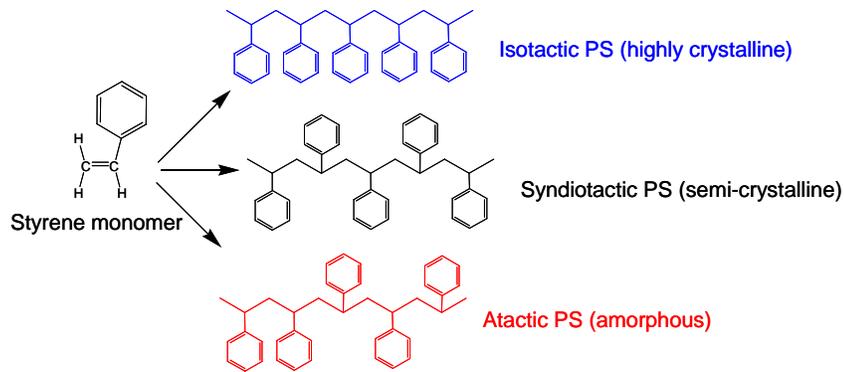


Figure 7. The three stereoisomers of PS: isotactic, syndiotactic, and atactic. Atactic polystyrene does not crystallize, due to the random placement of its side groups.

Polymers form into thin lamellar crystallites through a chain folding process, with their backbones oriented along one of the crystal axes, typically the c-axis. Chains may pack with zig-zag (all trans) or helical conformations of the backbone. Polyethylene, the largest volume commercial thermoplastic, arranges into an orthorhombic crystal with chains aligned along the c-axis in a zig-zag conformation (Fig. 8).⁶

unit cell of polyethylene

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PE crystallite formed by
chain folding

Figure 8. Crystal structure of polyethylene. (Images from http://www.tu-darmstadt.de/fb/ms/student/fs/german/lab/w2/31012_6.htm).

For orthorhombic crystals, the d-spacing for a set of planes (hkl) is related to the lattice parameters through:¹

$$d^{-2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

Knowing the structure for PE, how can we determine the interchain distance from the x-ray diffraction data?

For amorphous polymers, the scattering patterns show broad peaks representative of average characteristic distances between atoms in the structure. Most polymers exhibit a short range order maximum at a q value of 1.4 \AA^{-1} ,^{8,9} as seen for several polymers in Fig. 9 below.

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Figure 9. Normalized x-ray scattering intensity from 4 molten polymers. The peak at 1.4 \AA^{-1} is characteristic of the interchain van der Waals distance for C-C in amorphous hydrocarbon polymers. Oscillations at higher wavevectors are related to intrachain C-C distances.⁸

In this laboratory, we will compare the scattering patterns of a series of methacrylate polymers that have increasing side chain lengths. The general structure of these polymers is shown in Fig. 10. The length of the side chain influences the packing of these polymer chains in the melt or glassy state. As the side chain becomes longer, the average interchain distance increases.¹⁰ This increased spacing between chain backbones results in a decrease in the glass transition temperature, the temperature at which chains begin to exhibit backbone mobility, transforming from the glassy to the rubbery state.

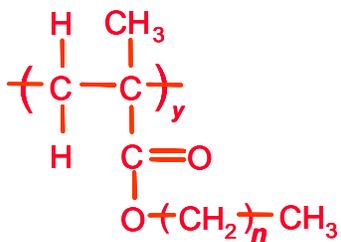


Figure 10. Monomer structure for methacrylate polymers.

Based on our X-ray scattering studies of various methacrylates, we will estimate the interchain spacing for the series of methacrylates, to correlate with glass transition values.

MATERIALS

polymethyl methacrylate ($T_g \sim 110^\circ\text{C}$)

polyethyl methacrylate ($T_g \sim 65^\circ\text{C}$)

polypropyl methacrylate ($T_g \sim 35^\circ\text{C}$)

poly(n-butyl methacrylate) ($T_g \sim 20^\circ\text{C}$)

polyethylene

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