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**Supporting information for article:**

**New Small-Angle X-ray Scattering Model for Polymer  
Spherulite with Limited Lateral Size of Lamellar Crystals**

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## S1. Contributions of Crystal Planes of Different Orientations to Small-Angle X-Ray Scattering at $q = 0.5 \text{ nm}^{-1}$ and Wide-Angle X-Ray Diffraction at $2\theta = 30^\circ$

To determine a scattering from a crystal plane, it needs the number of electrons  $N$  and the phase difference between adjacent electrons  $\phi$ :

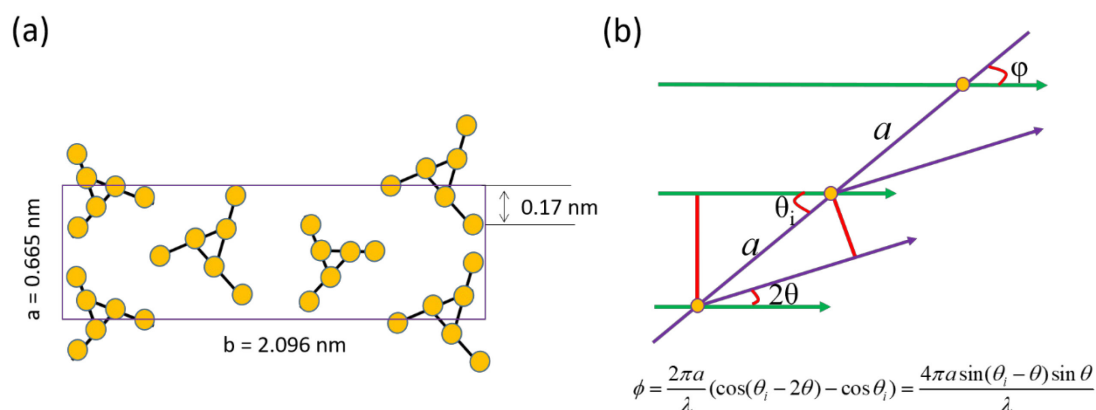
$$I_\phi = I_e \left( \sum_{n=0}^{N-1} \cos n\phi \right)^2 = \left( \frac{\sin \frac{N\phi}{2} \cos \frac{(N+1)\phi}{2}}{\sin \frac{\phi}{2}} \right)^2 I_e \quad (\text{S1})$$

Here  $I_e$  is the single-electron scattering intensity. The phase difference  $\phi$  can be determined by the following equation (See Fig. S1b):

$$\phi = \frac{4\pi a \sin(\theta_i - \theta) \sin \theta}{\lambda} \quad (\text{S2})$$

Here  $\theta_i$  is the intersection angle of the  $(00l)$  crystal plane with the incident X-ray, and  $a$  is the distance between adjacent electrons.

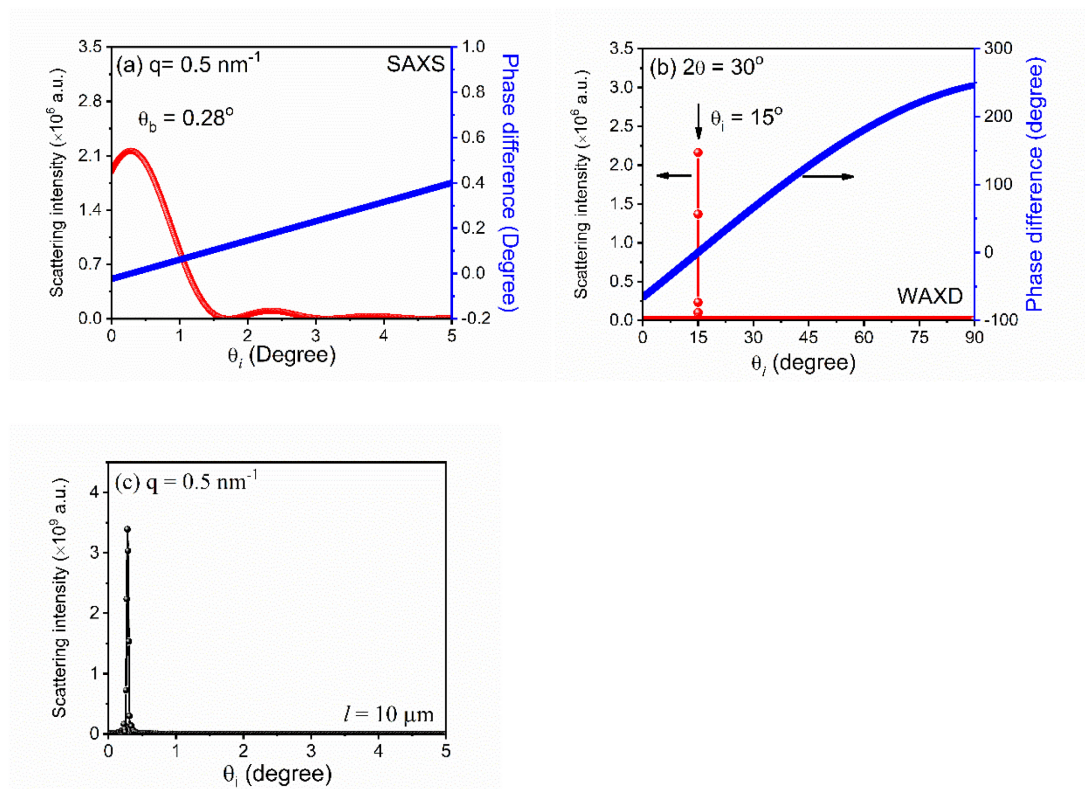
Estimating with the unit cell of  $\alpha$  crystal of iPP, the average distance between adjacent electrons is 0.17 nm (see Fig. S1a). Therefore, for an iPP crystal plane parallel to incident X-ray ( $\theta_i = 0$ ), phase difference of adjacent electrons is  $-0.024^\circ$  for  $q = 0.5 \text{ nm}^{-1}$ , and  $66^\circ$  for  $2\theta = 30^\circ$ . Phase differences at various incident angles were also determined at fixed  $q$  or  $2\theta$ . The wave vector  $q$  in Fig. S2a is fixed to be  $0.5 \text{ nm}^{-1}$ , while  $2\theta$  is fixed to be  $30^\circ$  in Fig. S2b. When  $q$  is fixed to be  $0.5 \text{ nm}^{-1}$  (corresponding scattering angle  $\theta = 0.28^\circ$ ), the phase difference increases from  $-0.024^\circ$  to  $0.4^\circ$  when the incident angle increases from  $0$  to  $5^\circ$ . While  $2\theta$  is fixed to be  $30^\circ$  (corresponding  $q = 26.2 \text{ nm}^{-1}$ ), the phase difference increases from  $-66.1^\circ$  to  $246.7^\circ$  when the incident angle increases from  $0$  to  $90^\circ$ .



**Figure S1** (a) A unit cell of  $\alpha$  crystal of iPP. (b) Determination of the phase difference between adjacent electrons on a crystal plane having an intersection angle  $\theta_i$  with the incident X-ray.

Scattering intensity from a crystal plane was also determined at fixed  $q$  or  $2\theta$  employing Eq. S1. In Fig. S2a and S2b, the electron number on the crystal plane was assumed to be 1471, since its corresponding lateral size is 250 nm, which is the typical size of a lamella. When  $q$  is fixed to be  $0.5 \text{ nm}^{-1}$  (corresponding scattering angle  $\theta = 0.28^\circ$ ), it can remain strong scattering in a broad range of  $\theta_i = 0 - 1^\circ$  because of small phase difference. While  $2\theta$  is fixed to be  $30^\circ$  (corresponding  $q = 26.2 \text{ nm}^{-1}$ ), it only can form strong scattering at  $\theta_i = \theta = 15^\circ$ . This is because large phase difference exists in adjacent electrons. Only at  $\theta_i = \theta = 15^\circ$ , the scatterings of the electrons have the same phase, forming fully constructively interference. This is so-called Bragg condition.

A scattering of a crystal plane with large lateral size was also determined. The lateral size was assumed to be  $10 \mu\text{m}$ . Under larger lateral size, scattering intensity concentrates in narrow range similar to Bragg scattering (see Fig. S2c).



**Figure S2.** Scattering intensities and corresponding phase differences between adjacent electrons on a crystal plane at various incident angles under fixed  $q$  or  $2\theta$ . In (a) and (c),  $q$  is fixed to be  $0.5 \text{ nm}^{-1}$ , while in (b)  $2\theta$  is fixed to be  $30^\circ$ . The lateral size in (a) and (b) was assumed to be  $250 \text{ nm}$ , and the lateral size in (c) was assumed to be  $10 \mu\text{m}$ . The average distance between adjacent electrons and the wavelength of X-ray in (a-c) were assumed to be  $0.17 \text{ nm}$  and  $0.124 \text{ nm}$ , respectively.

## S2. Determination of Critical Total Reflection Angle on the Amorphous/Crystalline Interface of isotactic Polypropylene

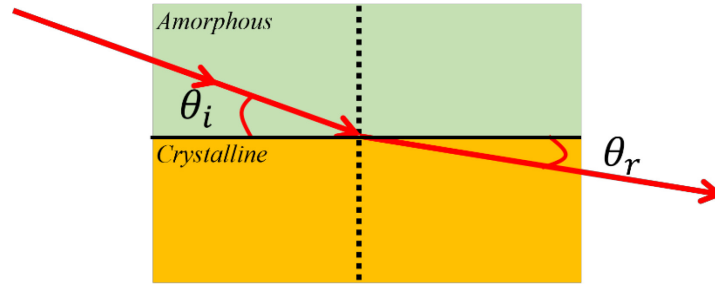
The critical total reflection angle on the amorphous/crystalline interface can be determined with Fresnel Equation. As is known, for two mediums with refraction indices  $n_i$ ,  $n_r$ , respectively, the incident angle ( $\theta_i$ ) and the refracted angle ( $\theta_r$ ) satisfy the following relationship: (Born & Wolf, 1999)

$$n_i \cos \theta_i = n_r \cos \theta_r \quad (\text{S3})$$

Let the amorphous layer be the incident medium, while the crystalline layer as the refractive medium, the refracted angle  $\theta_r$  will be smaller than the incident angle  $\theta_i$ . This is because amorphous polymer has a higher refraction index than crystalline polymer, which can be seen from the following equation:(Jeu, 2016)

$$n = 1 - \delta + i\beta = 1 - \frac{\lambda^2}{2\pi} r_e \rho + i \frac{\lambda}{4\pi} \mu \quad (\text{S4})$$

where  $r_e$  is Thompson scattering length of a single electron,  $\lambda$  is the wavelength of X-ray and  $\mu$  is the linear absorption coefficient. From Eq. S4, it can be found that the higher the density, the lower the refraction index. Evidently, crystalline polymer ( $\rho_c$ ) has a higher density than amorphous polymer ( $\rho_a$ ), therefore, it has a lower refraction index.



**Figure S3.** Refraction of X-ray on the amorphous/crystalline interface.

When  $\theta_r = 0$ , the incident angle is the critical angle for total reflection  $\theta_c^{ac}$ . The Fresnel

Equation becomes as:

$$\cos \theta_c^{ac} = \frac{n_r}{n_i} \quad (\text{S5})$$

Since  $\theta_c^{ac} \ll 1$ ,  $\cos \theta_c^{ac}$  can be estimated as  $1 - \frac{(\theta_c^{ac})^2}{2}$ . Meanwhile, estimating with Eq. S4,

the refraction indices  $n_a$ ,  $n_c$  are roughly equal to  $1 - r_e \rho_a \lambda^2 / 2\pi$  and  $1 - r_e \rho_c \lambda^2 / 2\pi$ ,

respectively. Therefore, the critical total reflection angle can be estimated as:

$$\theta_c^{ac} = \sqrt{\frac{r_e \lambda^2}{\pi} (\rho_c - \rho_a)} \quad (\text{S6})$$

It was reported that the critical total reflection angle  $\theta_{ap}$  on the vacuum/iPP interface was  $0.12^\circ$  for X-ray with  $\lambda = 0.124$  nm, which was obtained with the following equation:(Sakai *et al.*, 2005)

$$\theta_c^{ap} = \sqrt{\frac{r_e \lambda^2}{\pi} \rho_c} \quad (\text{S7})$$

Combining Eq.S7, Eq. S5 can be written further as:

$$\theta_c^{ac} = \varphi_c^{ap} \sqrt{\frac{\rho_c - \rho_a}{\rho_c}} \quad (\text{S8})$$

As is known, the amorphous density of iPP is around 92% of crystalline density.(Piccarolo *et al.*, 1992) Thus, the critical total reflection angle on the amorphous/crystalline interface  $\theta_c^{ac}$  is around 0.034°.

## References

- Born, M. & Wolf, E. (1999). *Principle of Optics*. Cambridge: Cambridge University Press.
- Jeu, W. H. d. (2016). *Basic X-ray scattering for soft matter*. Oxford: Oxford University Press.
- Piccarolo, S., Saiu, M., Brucato, V. & Titomanlio, G. (1992). *Journal of Applied Polymer Science* **46**, 625-634.
- Sakai, A., Tanaka, K., Fujii, Y., Nagamura, T. & Kajiyama, T. (2005). *Polymer* **46**, 1717-1717.