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Abstract

As an important means of nanoscale structural characterization, small-angle X-ray scattering (SAXS) technology plays an indispensable role in the study of nanomaterial structures, and the introduction of synchrotron radiation SAXS technology has enabled a qualitative leap in both spatial and temporal resolution, providing strong technical support for the multiscale structural characterization of polymer materials. When X-rays pass through a material, the SAXS intensity is closely related to the electron density difference between the scattering phases in the material. If the electron density difference between scattering phases equals zero, SAXS technology cannot detect the structure of the scattering phase. To obtain accurate scattering intensity signals, before analyzing SAXS data, researchers typically perform preprocessing such as desmearing, normalization, and background subtraction on the relevant data, and then calculate the relevant structural parameters. These preprocessing steps mainly consider the possible effects of parasitic slit scattering, light source variations, and scattering from outside the sample, and seldom consider the possible influence of the Beamstop on SAXS intensity. This paper discusses the influence of the Beamstop during synchrotron radiation SAXS experiments and provides recommendations for avoiding its effects.

Full Text

Effects of Beamstop Scattering on Small-Angle X-ray Scattering Intensity

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Abstract

As an important technique for structural characterization at the nanoscale, small-angle X-ray scattering (SAXS) plays an irreplaceable role in the study of polymer material structures. The application of synchrotron radiation SAXS technology has achieved a qualitative leap in spatial and temporal resolution, providing robust technical support for the multi-scale structural characterization of polymer materials. When X-rays pass through a sample, the SAXS intensity is closely related to the electron density difference between the scattering phases in the sample. If the electron density difference between the scattering phases is zero, SAXS technology cannot detect the structure of the scattering phases. In order to obtain accurate scattering intensity signals, before analyzing SAXS data, one usually needs to preprocess the relevant data by desmearing, normalizing, and subtracting the background scattering, and then calculate the structural parameters of the sample. The above preprocessing mainly considers the possible effects of slit parasitic diffraction, light source changes, and scattering outside the sample, with little consideration given to the possible impact of beam blockers on SAXS intensity. The influence of Beamstop during the synchrotron radiation SAXS experiment was discussed for avoiding its impact in SAXS measurements.

Keywords: small angle X-ray scattering (SAXS), Beamstop, scattering intensity, metallocene polypropylene

Synchrotron radiation sources offer high brightness, broad wavelength coverage, excellent polarization, and continuous wavelength tunability, making them ideal tools for studying material structure and properties. Synchrotron radiation technology has brought revolutionary changes to the structural investigation and non-destructive testing of condensed matter[1-3]. Benefiting from the application of synchrotron radiation sources and improved experimental conditions, numerous disciplines have seen enhanced development, particularly in polymer structure research. In recent years, the development of high-brightness synchrotron radiation sources and sophisticated experimental techniques has created unprecedented opportunities for studying the structure-property relationships of polymer materials, as well as for fundamental understanding and potential applications of these materials[4-6].

Synchrotron radiation X-ray small-angle and wide-angle scattering are important experimental techniques for investigating polymer crystallization and other nanoscale ordered structures. The lamellar structures of crystalline polymers, microphase-separated structures of block copolymers, and structures of inorganic nanomaterials and polymer composites all fall within the scope of X-ray scattering techniques. Using synchrotron radiation X-ray scattering technol-

ogy, one can track and observe structural evolution during the processing of commercial and novel polymer materials, which has greatly inspired renewed understanding of polymer-related physicochemical problems[7,8]. Polymer processing still involves many physicochemical issues that remain to be clarified. Synchrotron radiation X-ray scattering technology offers unparalleled advantages for studying structure changes in polymer materials induced by external forces such as shear, pressure, and stretching, particularly during processing operations like spinning, injection molding, and extrusion. Related research has not only advanced the fundamental theory of non-equilibrium thermodynamics in polymer materials but also provided direct guidance for polymer material design and processing. Deep understanding of polymer crystallization processes is crucial for performance prediction and control during polymer material processing. During SAXS data acquisition, configuring a Beamstop in front of the detector is an important measure to prevent radiation damage to the detector from the direct X-ray beam, but it may also affect the recorded SAXS intensity[9-13]. However, the impact of Beamstop on scattering intensity has rarely been discussed. This paper addresses the influence of Beamstop during synchrotron radiation SAXS experiments and offers recommendations for avoiding its effects.

1.1 Sample Preparation

The experimental sample was metallocene-catalyzed high-isotacticity polypropylene (mPP). Gel permeation chromatography (GPC) measured the weight-average and number-average molecular weights as 6.3×10^5 $g \cdot mol^{-1}$ and 10^5 $g \cdot mol^{-1}$, respectively. High-temperature ^{13}C-NMR spectroscopy measured the isotacticity as [mm] = 97% and [mmmm] = 91%. The sample was pressed into 1 mm thick sheets using a hot press for subsequent testing.

1.2 Characterization

Synchrotron radiation SAXS experiments were conducted at the 1W2A beamline of Beijing Synchrotron Radiation Facility (BSRF) and the BL10U1 beamline of Shanghai Synchrotron Radiation Facility (SSRF)[14,15]. The experimental parameters for the two beamlines were as follows: at 1W2A, the X-ray wavelength was 0.154 nm, using a Pilatus 1M detector with a sample-to-detector distance of 3240 mm; at BL10U1, the X-ray wavelength was 0.124 nm, using an Eiger 4M detector with a sample-to-detector distance of 27500 mm.

2 Results and Discussion

First, at the 1W2A beamline, the mPP sample was heated to 210 °C. After complete melting, it was cooled at a rate of 10 °C/min. During cooling, SAXS/WAXS techniques were used to observe structural changes in the sample, with the WAXS and SAXS results shown in [Figure 1: see original paper]. Figure 1(a) indicates that during cooling, mPP formed both α-crystals and γ-crystals.

It is well known that high-isotacticity PP typically forms only α-crystals upon melting and crystallization, β-crystals can form in stressed melts or solutions, and γ-crystals form only under high pressure. The sample used in this experiment was metallocene-catalyzed high-isotacticity PP, but due to isotacticity defects in the molecular chains, γ-crystals could form under normal pressure. The SAXS intensity shown in Figure 1(b) exhibits two distinct scattering signals: a scattering peak between q values of 0.2–0.5 nm^{-1} related to sample crystallization, and a scattering peak below q values of 0.1 nm^{-1} that persists continuously, with both position and intensity varying with temperature.

[Figure 1: see original paper] shows the WAXS (a) and SAXS (b) profiles during cooling from melting of mPP obtained from Beamline 1W2A at BSRF. To further analyze the SAXS data, we processed the data from Figure 1(b) as shown in [Figure 2: see original paper]. In Figure 2(a), the SAXS intensity (ordinate) is plotted on a logarithmic scale. The elevated scattering intensity (scattering peak) in the high q region (~0.3 nm^{-1} and above) is caused by crystallization, while the scattering peak in the low q region (~0.1 nm^{-1} and below) persists throughout. To better observe changes in the low-q scattering peak, the abscissa range was reduced to $q < 0.1$ nm^{-1}, as shown in Figure 2(b). The results demonstrate that during cooling, the intensity of this scattering peak gradually decreases while the peak position qpeak gradually increases, with the corresponding correlation length decreasing from 165.3 nm to 125.6 nm. Unless the polymer possesses self-assembled structures, it is difficult to form structures of such large dimensions in melts and crystals, and no reports of self-assembled structures have been seen in polyolefin homopolymers. If isotacticity defects exist within the same chain, it is also impossible to form structures of such large dimensions. Could the difference in isotacticity between [mm] and [mmmm] lead to phase separation in different molecular chains? To further verify the scattering peak near low q values, ultra-small-angle SAXS (USAXS) experiments were conducted on the crystallized sample at room temperature at the Shanghai Synchrotron Radiation Facility, with the USAXS intensity shown in [Figure 3: see original paper].

[Figure 2: see original paper] shows (a) the logarithm of the ordinate of SAXS profiles shown in Figure 1(b), and (b) the abscissa range of Figure 1(b) reduced to less than 0.1 nm^{-1}. Figure 3 indicates that the scattering peak in the low-q region appears near 0.027 nm^{-1}, corresponding to a real-space structural dimension of 232.6 nm. If the low-q scattering peak were related to sample structure, the scattering entity size at room temperature should not be larger. It is well known that synchrotron radiation is electromagnetic radiation emitted when electrons are accelerated to near-light speeds. Facilities for generating synchrotron X-rays include: electron accelerator (gun), high-vacuum storage ring (where pulsed electron beams are injected), and magnetic devices (such as bending magnets, wigglers, and undulators for adjusting and directing emitted light to beamlines). Additionally, synchrotron experimental stations require slits, mirrors, monochromators, and Beamstop devices to select wavelengths and spot sizes for testing. Therefore, we believe that the scattering intensity

at the low-q end is susceptible to Beamstop scattering effects, as illustrated in [Figure 4: see original paper].

[Figure 3: see original paper] shows the SAXS profile obtained from Beamline BL10U1 at SSRF. [Figure 4: see original paper] illustrates the SAXS measurement schematic. As can be seen from Figure 4, the X-ray beam emitted from the source point is not an ideal parallel beam but actually has a certain divergence angle α. The existence of this divergence angle causes scattering at the Beamstop edge, affecting the low-q SAXS intensity. For an incident X-ray beam with certain divergence, theoretically only an infinitely large Beamstop could completely eliminate the influence of Beamstop scattering on low-q SAXS intensity. However, the effective minimum q value (qmin) determines the maximum measurable real-space size (dmax) in SAXS. Considering the effective measurement range, Beamstop size should generally not be too large in practical applications, but the impact of Beamstop scattering on SAXS must be fully considered.

[Figure 5: see original paper] provides a schematic illustration of Beamstop scattering effects on SAXS intensity. The intensity distribution after primary scattering by the sample is shown by the blue line. After secondary scattering by the Beamstop, the intensity distribution is shown by the purple line. The final SAXS intensity distribution obtained on the detector is shown by the red line. From this schematic optical path in Figure 5, it can be concluded that in SAXS measurements, the influence of Beamstop scattering on SAXS intensity always exists. To minimize the impact of Beamstop scattering on SAXS intensity, the divergence of the incident X-ray beam should be reduced as much as possible. To make the effective minimum q value (qmin) as small as possible, the sample-to-detector distance should be increased as much as possible, i.e., adopting USAXS measurement mode. To make the effective maximum q value (qmax) as large as possible, the sample-to-detector distance should be shortened as much as possible, i.e., adopting WAXS measurement mode. For given SAXS test conditions where the incident X-ray beam divergence, spot size, SAXS camera length, Beamstop size, detector effective area, and pixel size are all fixed, one may consider adjusting the Beamstop center position to moderately deviate from the incident beam center position, so that the SAXS intensity on one side of the detector is overly affected by Beamstop scattering while the other side is minimally affected.

Beamstop scattering consists of two components: first, the direct transmitted beam through the sample being scattered by the Beamstop edge; and second, the primary scattered beam from the sample being scattered again by the Beamstop edge. The first case is the main source of Beamstop scattering, while the second case can be neglected due to the greatly reduced intensity of the primary scattered beam. For the first case, with the Beamstop center aligned with the incident beam center, assuming the incident X-ray intensity is 1, the Gaussian normal distribution function can be used to calculate the incident X-ray intensities that are blocked (Id) and not blocked (Is) by Beamstops of different sizes (D), as shown in .

shows the calculated blocked or not blocked intensity of incident X-rays by Beamstops with different sizes according to the Gaussian normal distribution function, for 1FWHM, 2FWHM, 3FWHM, 4FWHM, and 5FWHM. The calculation results show that when the Beamstop size (D) is 4 times the size of the original incident beam on the detector (FWHM), the unblocked portion of the intensity is reduced by 5–6 orders of magnitude. When the Beamstop size (D) is 5 times the size of the original incident beam on the detector (FWHM), the unblocked portion of the intensity is reduced by 7–8 orders of magnitude.

With the advancement of synchrotron radiation technology and the continuous development of X-ray detectors, SAXS technology is increasingly widely applied to determine material structures and probe related structure formation processes. Metallocene-catalyzed polyolefins have attracted much attention as new materials with excellent performance, high added value, but high technical barriers due to their narrow molecular weight distribution and high isotacticity. The experimental sample in this study is metallocene-catalyzed polypropylene, which differs from Ziegler-Natta-catalyzed isotactic polypropylene in that it can form γ-crystals upon melting under normal pressure, whereas the latter requires high pressure, copolymerization, or low molecular weight to form γ-crystals. The isotacticity measured by high-temperature ^{13}C-NMR for the sample used in this experiment differs between [mm] and [mmmm]. Polymer materials are typically described by chemical structure and molecular weight distribution. Branching is an important feature affecting polymer material properties besides chemical structure and molecular weight distribution. The presence of small amounts of short-chain branches can dramatically change polymer crystallization behavior, while long-chain branching directly relates to the hydrodynamic and rheological properties of polymer solutions and melts. Commercial polymer materials can undergo phase separation due to differences in branching content[16,17]. The SAXS results in Figures 1(b) and 2 suggest that intensity variations near low-q values may indicate phase-separated structures, as otherwise such large-scale structures could not exist in homopolymer materials. Potential causes for phase separation in the test sample include: high isotacticity and low isotacticity existing in different metallocene polypropylene molecular chains leading to phase separation, or different branching contents in different metallocene polypropylene molecular chains causing phase separation. However, the USAXS results in Figure 3 indicate that the intensity variations near low-q values in Figures 1(b) and 2 are the result of Beamstop scattering. The SAXS measurement schematic in Figure 4 illustrates the influence of Beamstop on scattering intensity. Further analysis and calculations of Figure 5 yielded the effect of Beamstop on incident X-ray intensity, with calculation results shown in Table 1. Meanwhile, the schematic in Figure 5 demonstrates that Beamstop scattering affects scattering intensity near low-q values. Currently, the theory regarding Beamstop effects on SAXS scattering intensity is not yet mature. To avoid this issue when using SAXS to study polymer structures, it is generally recommended to select a Beamstop size that is 4–5 times the size of the original incident beam on the detector. If the scattering signal from the sample structure may appear near

or overlap with the Beamstop scattering signal, the reliability of experimental data may be compromised. If the scattering q value related to the maximum structure size of the sample to be measured is between 0.04–0.06 nm^{-1}, it is best for the effective qmin value of SAXS to reach 0.01 nm^{-1} to avoid the influence of Beamstop scattering on SAXS intensity as much as possible.

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