



# Observation of molecular motions in polymer thin films by laboratory grazing incidence diffracted X-ray blinking

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## Abstract

Research on polymer surfaces has shown that the mobilities of polymer chains, which affect the aggregation state and thus the physical properties of the material, differ between the surface and bulk. However, the mobilities of the surface polymers have not been fully characterized. Therefore, we propose a time-resolved method for evaluating surface mobility. This measurement scheme is called grazing incidence diffracted X-ray blinking (GI-DXB) and can be used to evaluate the molecular motions occurring at polymer surfaces by continuously measuring X-ray diffraction patterns near the total reflection angle over small time periods. In this study, the crystallized polymer poly{2-(perfluorooctyl)ethyl acrylate} (PC<sub>8</sub>FA) was measured. The decay constants, which are indexes of molecular motions, were calculated to be  $3.98 \times 10^{-3} \text{ s}^{-1}$  for the fluoroalkyl groups in the side chains observed along the in-plane direction and  $3.36 \times 10^{-3} \text{ s}^{-1}$  for the lamellar structure observed along the out-of-plane direction when 2000 diffraction profiles of 500 ms were recorded and the incident angle was  $0.07^\circ$ . In contrast, transmission DXB indicated decay constants of  $2.63 \times 10^{-3} \text{ s}^{-1}$  for the side chains and  $2.87 \times 10^{-3} \text{ s}^{-1}$  for the lamellar structures. These results suggested that the PC<sub>8</sub>FA surface is mobile, because a larger decay constant indicates a higher mobility. GI-DXB can be used to measure surface dynamics. The authors contend that GI-DXB is a highly versatile tool because it allows the evaluation of local motions with a laboratory X-ray system, and these motions cannot be detected by conventional surface analyses. This measurement scheme may facilitate the development of high-performance polymers and discovery of new physical properties.

## Introduction

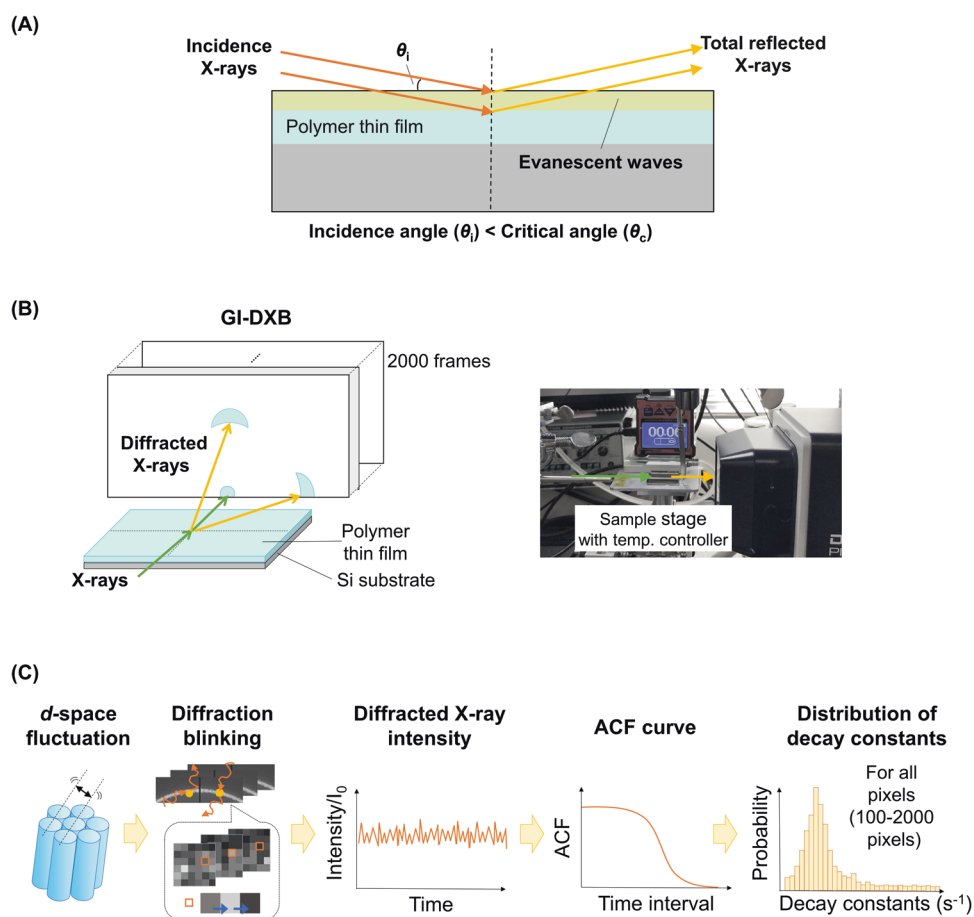
A vacuum or an air atmosphere results in behaviors at the surfaces of liquids and solids that differ from those in the interior (bulk). For example, wetting occurs on a solid surface [1, 2]. This is due to the excess energy associated with a surface composition in a nonequilibrium state. A polymer surface is no exception. Studies performed over the last 30 years have shown that polymer chains undergo different motions at the surface and in the bulk [3]. Analyses of polymer thin films on substrates with methods such as ellipsometry [4], scanning probe microscopy [5], X-ray reflectivity [6], neutron reflectivity [7], and grazing incidence X-ray photon correlation spectroscopy [8] have shown that the molecular mobilities of polymer chains at the surface are different from those in the bulk. However, the dynamics at the polymer surface, the associated aggregated molecular structures, and the mechanisms for the surface properties corresponding to these states are not fully understood. Therefore, novel time-resolved evaluation

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**Fig. 1** Schematic image of evanescent waves (A), schematic image of GI-DXB (B) and a series of analyses on DXB (C)



methods must be developed to deepen our understanding of these surfaces.

Single-molecule measurements have been a remarkable development in the field of biotechnology in recent years and are making it possible to observe the behaviors of biomolecules, such as proteins, at high speed and with high accuracy. The authors proposed diffracted X-ray tracking (DXT) [9, 10] to capture the motion of an object with a time resolution below the microsecond scale and high spatial resolution at the picometer scale based on the motions of diffraction spots used as labels. However, the versatility of DXT is limited by the use of white X-rays. Therefore, the authors proposed diffracted X-ray blinking (DXB) [10–13], in which the mobility of an object is determined from the blinking intensities of the diffraction spots with monochromatic X-rays. DXB can be implemented with a special X-ray diffractometer installed in a synchrotron radiation facility as well as in a laboratory X-ray system. We also recently demonstrated that DXB measurements can be performed using commercially available colloidal gold as a label instead of gold nanocrystals [13] and that the diffraction patterns of crystalline proteins [13], crystalline inorganic material [12] and crystalline polymers [13] can be

analyzed without using labels. In our previous studies, the target samples were irradiated with X-rays, and the diffraction images were analyzed to observe the molecular motions. In principle, molecular dynamics information could be collected regardless of the geometry if X-ray diffraction occurs. Therefore, the authors reasoned that molecular motions could be observed by performing time-division measurements in the same way, such as by performing grazing incidence X-ray diffraction (GIXD) [14] measurements. In GIXD measurements, X-ray irradiation under total reflection conditions provides near-surface information (at scales of approximately 10 nm) where the evanescent light is localized (Fig. 1A).

Herein, we propose a surface analysis method named grazing incidence diffracted X-ray blinking (GI-DXB), which constitutes an adaptation of DXB to GIXD, and observe molecular dynamics at polymer surfaces. In this study, the high potential and diversity of DXB as an analytical method are demonstrated through the characterization of poly{2-(perfluorooctyl)ethyl acrylate} (PC<sub>8</sub>FA), which exhibits hydrophobicity. As the polymer is crystalline, surface molecular motions were measured by using GI-DXB without labels.

## Materials and methods

### Preparation of the PC<sub>8</sub>FA thin film

PC<sub>8</sub>FA was prepared by free radical polymerization. The number average molecular weight ( $M_n$ ), weight average molecular weight ( $M_w$ ), and molecular weight dispersity (MWD) of the polymer were measured by GPC as 28900 g/mol, 74500 g/mol, and 2.58, respectively (details can be found in the Supplementary Information). HCFC-225 is a mixed solvent comprising 3,3-dichloro-1,1,1,2,2-pentafluoropropane and 1,3-dichloro-1,1,2,2,3-pentafluoropropane.

A PC<sub>8</sub>FA thin film was prepared by spin coating a 3-mass % PC<sub>8</sub>FA/HCFC-225 solution (2000 rpm, 30 s) onto a polyimide film (thickness = 12.5 μm) for transmission DXB measurements. The thickness of the polymer film on the silicon (Si) substrate, which was prepared under the same conditions as for the polyimide film, was approximately 400 nm, as indicated by ellipsometry. A polymer thin film on a Si substrate [15, 16] was prepared by spin coating a 1-mass % PC<sub>8</sub>FA/HCFC-225 solution for GI-DXB measurements. The average film thickness was determined to be approximately 95 nm by ellipsometry. The surface roughness of the thin film on the Si substrate was measured at the macroscopic and microscopic scales by using laser microscopy and atomic force microscopy, respectively (the measurement conditions are detailed in the SI). The spin-coated substrates were annealed at 120 °C for 10 min and cooled to room temperature to align the side chains above their softening point (75 °C).

### Transmission DXB and GI-DXB measurements

Both measurements were performed with a laboratory X-ray source (Rigaku Corp., Japan, Micro-Max-007HF: CuK $\alpha$ , wavelength ( $\lambda$ ) = 1.54 Å, 40 kV, 30 mA) in air. A wide diffraction range was obtained by using a two-dimensional photocounting PILATUS 3R 200K-A (Dectris Ltd., Switzerland) detector, and the camera length was 55 mm. The exposure time per frame was set to 500 ms, and 2000 diffraction profiles were measured for each exposure time.

Transmission DXB measurements were conducted on a Peltier cooling-and-heating stage 10048 L (Japan Hightech Ltd., Japan) to maintain the sample temperature at 20 °C. GI-DXB measurements were performed with a biaxial goniometer to control the incident angle. The Peltier cooling-and-heating stage 10021 (Japan Hightech Ltd., Japan) was placed under the sample to maintain the sample temperature at 20 °C. Incident angles of approximately 0.07° and 0.22° were used to obtain information on the surface and entire thin film, respectively. The incident angles were determined from the critical angle, which was estimated to be approximately 0.18° based on the density of C<sub>8</sub>FA [17] and previous GIXD reports [16, 18]. Note

that laboratory X-ray beams are not perfectly parallel and are not aligned with slits. Measurements performed at synchrotron radiation facilities in the future should show improved accuracy for the results. The smoothness of the sample was maintained by an alignment procedure and by measuring at the determinate temperature (the results of surface roughness are detailed in the SI). GI-DXB measurements were also made every 50 ms and 1 s (detailed in the SI).

### Autocorrelation function for DXB analysis

Figure 1 shows the scheme for GI-DXB (B) and the analytical procedure (C). Transmission DXB obtains bulk information on the sample by transmitting X-rays. In contrast, GI-DXB measures the surface mobility by reflecting the X-rays under total reflection conditions.

Within the analytical range, diffraction spots appeared and disappeared due to local motion. A DXB measurement takes thousands of diffraction images in sequence with a small time division to calculate the intensity changes derived from  $d$ -space fluctuation. The changes in the diffraction intensities for different pixels were extracted from 2000 frames with ImageJ. Approximately 100–2000 pixels were used for the analyses. The diffraction intensity for each pixel was corrected by dividing it by the direct beam intensity. The corrected intensity fluctuation for each pixel was calculated using the following autocorrelation function (ACF): [12, 13].

$$ACF = \frac{\langle I(t)I(t + \tau) \rangle}{\langle I(t)^2 \rangle}$$

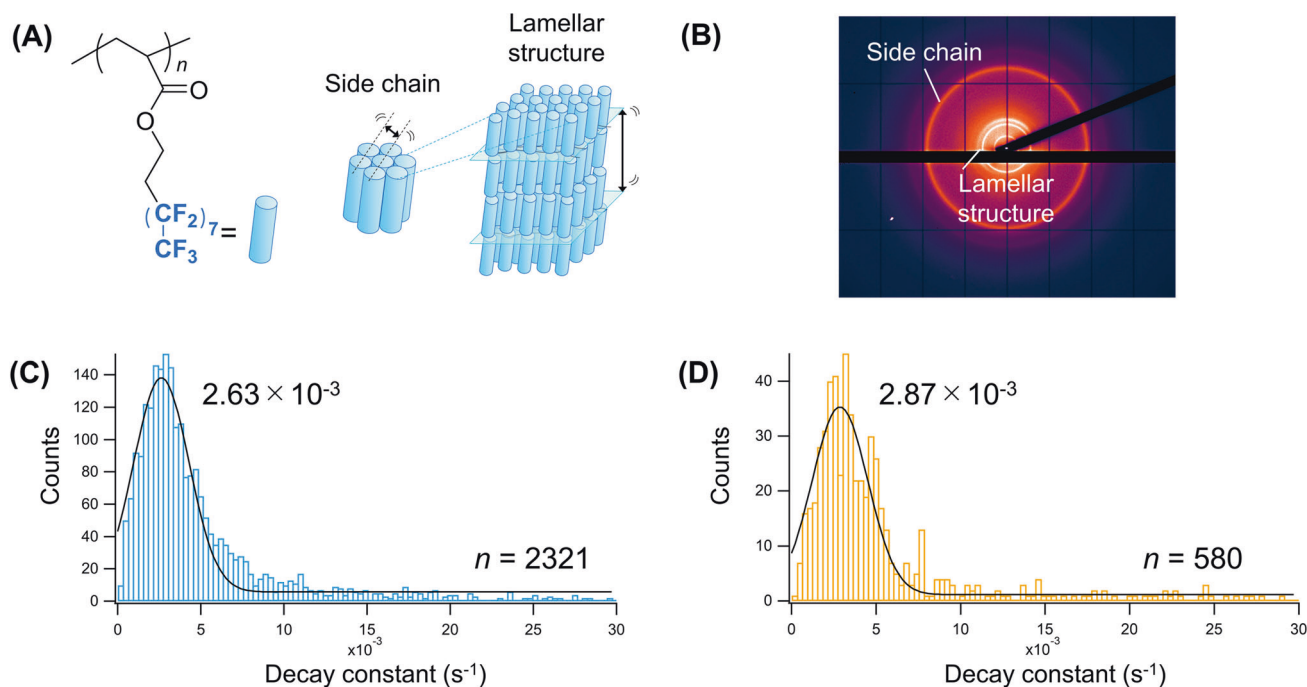
where the brackets  $\langle \rangle$  indicate a time average,  $I(t)$  denotes the diffraction intensity, and  $\tau$  denotes the delay time. The ACFs were fitted using the following exponential curve:

$$f(t) = y_0 + A \exp(-T * t)$$

where  $y_0$  is a constant,  $A$  is the amplitude, and  $T$  is the decay constant. The fitting parameters  $y_0 > 0$ ,  $A > 0$  and  $T > 0$  were used to obtain the averaged ACF curves. The motion characteristics were evaluated with the distribution of the decay constants, and a larger decay constant indicated faster molecular motion since the constant represents the speed of decay. The curves were fitted using the weighted least-squares method. The distributions of the decay constants for all of the pixels were fitted with a Gaussian curve.

## Results and discussion

Figure 2A shows the chemical structure of PC<sub>8</sub>FA, and Fig. 2B shows the two-dimensional transmission X-ray



**Fig. 2** Schematic chemical structure of PC<sub>8</sub>FA and the aggregated structure of the Rf groups on the side chains and the lamellar structure (A). Two-dimensional XD pattern for bulk PC<sub>8</sub>FA obtained by

integrating 2000 frames of 500 ms (B). Distributions of the decay constants for the Rf groups on the side chains (C) and for the lamellar structure (D)

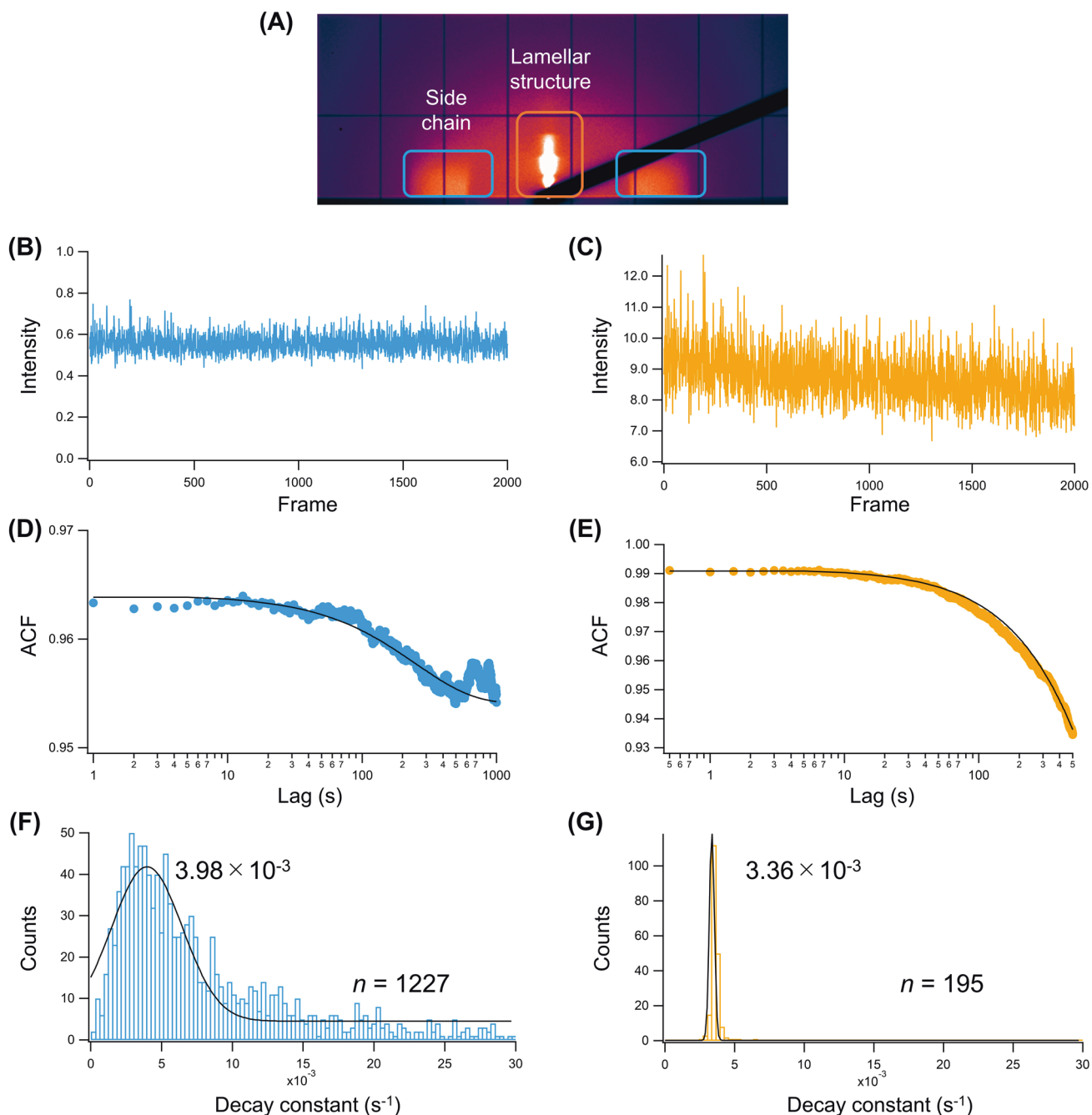
profiles with integration 2000 frames of 500 ms. The outer diffraction ring ( $2\theta = 18^\circ$ ,  $d = 0.5$  nm) indicated hexagonal packing of the fluoroalkyl (Rf) side chains. The diffraction peak near the center ( $2\theta = 5.5^\circ$ ,  $d = 1.6$  nm) corresponded to the lamellar structure. Notably, the primary diffraction profile of the lamellar structure was hidden behind the beam stopper and could not be observed directly, so the profile was observed from the second diffraction peak onward. The intensity changes and the ACF curves are presented in Supplementary Fig. S6. The decay constants were  $2.63 \times 10^{-3} \text{ s}^{-1}$  for the side chains and  $2.87 \times 10^{-3} \text{ s}^{-1}$  for the lamellar structure, as shown in Fig. 2C and D, respectively. Thus, if there are two or more different diffraction profiles within one X-ray diffraction (XD) profile, molecular motions can be calculated from each diffraction profile.

Figure 3A shows the two-dimensional GIXD profiles with integration 2000 frames of 500 ms for an X-ray incident angle of  $0.07^\circ$ . The penetration depth at this angle was approximately 10 nm, which provided information derived only from the surface aggregation state. The GIXD profile consisted of diffraction patterns for the in-plane and out-of-plane directions. Powder XD [15] (Supplementary Fig. S5) and previous GIXD results [16, 18] were used to determine the types of aggregation structures that produced the different diffraction patterns. The in-plane diffraction pattern was produced by a two-dimensional aggregated structure consisting of an Rf side chain oriented perpendicular to the substrate, whereas the out-of-plane diffraction pattern was created by a

two-dimensional aggregated structure comprising two layers, which corresponded to a lamellar structure.

Figure 3B and C show the intensity changes for the Rf side chain and lamellar structure, respectively. Figure 3D and E are ACF curves calculated from the intensity changes. The distributions of the decay constants are shown in Fig. 3F, G, and the peak locations were at  $3.98 \times 10^{-3} \text{ s}^{-1}$  for the side chain and  $3.36 \times 10^{-3} \text{ s}^{-1}$  for the lamellar structure. The poor signal-to-noise ratio associated with the intensity change shown in Fig. 3C was probably due to the low number of pixels used in the analysis. The distribution of the decay constants shown in Fig. 3G was narrower than that of the side chain in Fig. 3F and indicated a periodic lamellar structure.

Figure 4A and B indicate the distributions of decay constants determined at an incident angle of  $0.22^\circ$ , which was larger than the critical angle (approximately  $0.18^\circ$ ). Figure 4C and Supplementary Fig. S7 provide a comparison of the decay constants for transmission DXB and GI-DXB at incident angles of  $0.07^\circ$  and  $0.22^\circ$ . The value of the decay constant determined at an incident angle of  $0.07^\circ$  was the largest. These results indicated that the local motions of the PC<sub>8</sub>FA thin film surface were greater than those of the bulk or the entire thin film. This was consistent with previous studies showing that polymer surfaces exhibit greater motion than the bulk [3–8]. Interestingly, the results of differential scanning calorimetry (Supplementary Fig. S2), lateral force microscopy (Supplementary Fig. S4) and



**Fig. 3** A two-dimensional GIXD pattern for PC<sub>8</sub>FA obtained by integrating 2000 frames of 500 ms at an incident angle of 0.07° (A). Intensity changes divided by the direct beam intensity (B and C). ACF curves are shown in D and E, and the distributions of decay constants

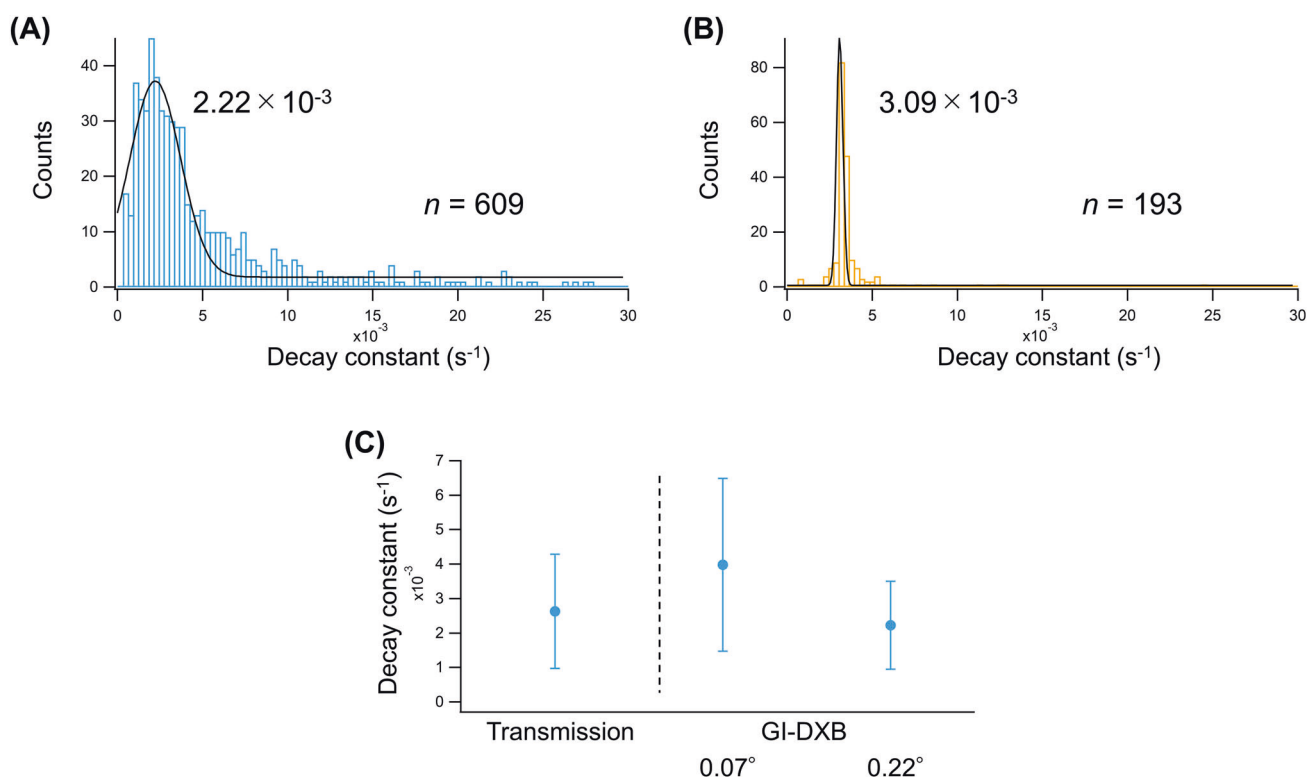
are shown in F and G. The side chain results are shown on the left side, drawn in blue, and those of the lamellar structure are on the right side, drawn in orange

dielectric relaxation [19] did not show any characteristic features at approximately 20 °C. These results suggest that GI-DXB can measure local fluctuations in neither  $\alpha$  relaxation nor  $\beta$  relaxation. The GI-DXB measurement method has the possibility of elucidating local motions.

A total of 2000 diffraction profiles were obtained at 50 ms and at 1 s to calculate the decay constants of the side chains from the in-plane diffraction pattern (Supplementary

Fig. S8). The calculation was performed in the same way as that for 500 ms. These results showed that the molecular motions were easily evaluated over a wide range of time scales by using a laboratory X-ray system. Furthermore, the use of a temperature control unit enabled observations of the temperature dependence of molecular thermal motions.

In this report, we present the first measurement of thermal motions in thin films by using the DXB method based



**Fig. 4** Distributions of the decay constants measured at an incident angle of 0.22° (A) for the side chains and (B) for the lamellar structure.

on the total reflection of X-rays. An ACF analysis was used to calculate 2D diffraction images for PC<sub>8</sub>FA with low time resolution to observe the dynamics of the side chains and the lamellar structure. GI-DXB is able to observe the surface motions of polymers, which cannot be determined by transmission DXB methods. The proposed measurement scheme constitutes a very important analytical method for demonstrating that various properties of polymer thin films are governed by thermal motions. It may be possible to perform detailed assignments of the molecular motions contributing to specific physical properties by calculating the dynamics of individual structures from a single type of image. In addition, the proposed method is very simple and versatile because the molecular dynamics can be observed with a laboratory X-ray system, as demonstrated in this study. The surface motions of polymers used as structural materials may affect their performance during use. Therefore, the proposed measurement method is expected to be effective for all fields in which polymers are used. Thus, this method will contribute to the advancement of material design and characterization and the realization of novel functions. The authors expect GI-DXB to be an important measurement tool in polymer science and other fields.

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The value of the decay constant determined via transmission DXB and GI-DXB (C) for the side chain

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## Compliance with ethical standards

**Conflict of interest** The authors declare no competing interests.

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