Electronic Supplementary Information

for

Linking microscopic structural changes and macroscopic mechanical responses in a near-ideal bottlebrush elastomer under uniaxial deformation

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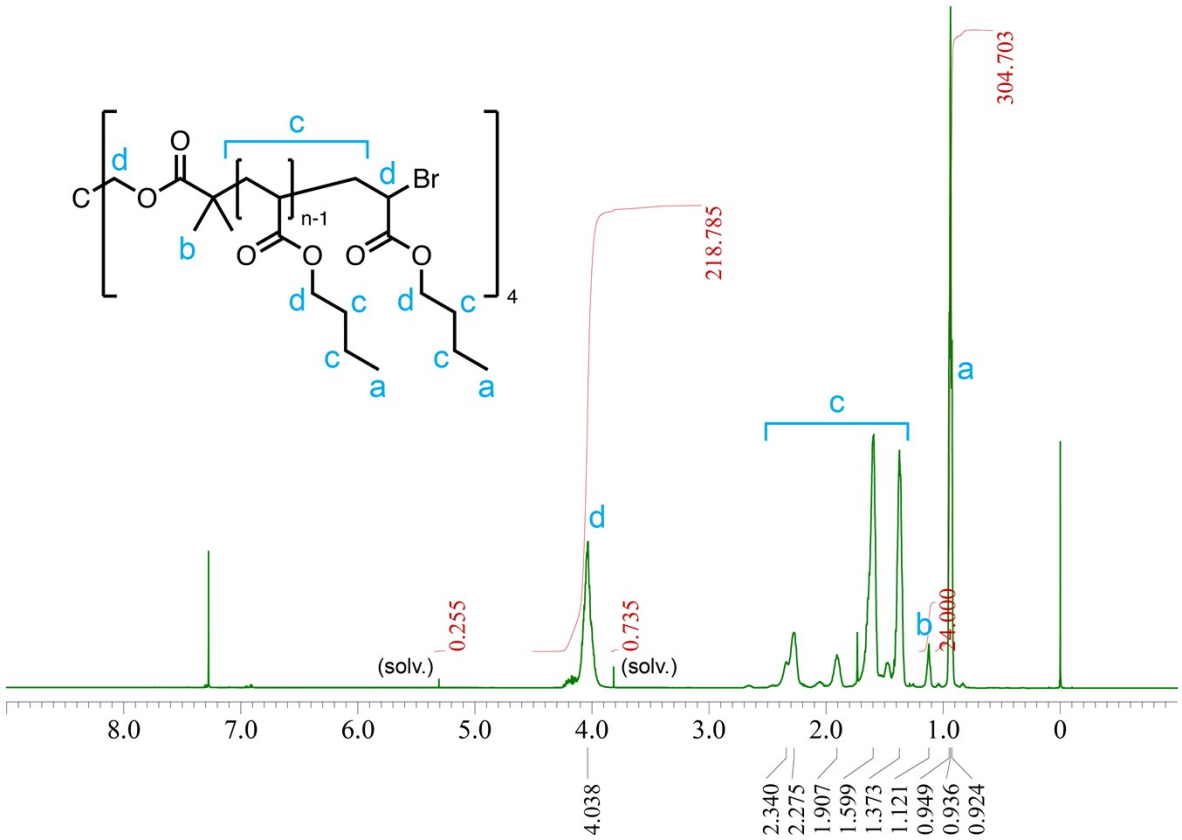
S1. Synthesis of star P*n*BA.

The tetrafunctional initiator, pentaerythritol tetrakis(2-bromoisobutyrate) (4f-BiB) was synthesized according to the literature procedure[1]. *n*-Butyl acrylate (*n*BA; FUJIFILM Wako Pure Chemical Corp., Japan) was passed through a short column of activated alumina before use. Copper(I) bromide (CuBr; FUJIFILM Wako) was purified by washing in glacial acetic acid overnight and then in ethanol and diethyl ether and vacuum drying. All other reagents were used as received. In a 200 mL Schlenk flask, 1464 mg of 4f-BiB (2.00 mmol, 1 eq.) and 51.267 g of *n*BA (400.0 mmol, 200 eq.), 57.88 mg of *N*,*N*,*N*',*N*'',*N*''-pentamethyldiethylenetriamine (PMDETA, 0.334 mmol, 0.167 eq.), and anisole 16 mL were added and the mixture was degassed by three freeze-pump-thaw cycles. After the third pumping procedure, 57.00 mg of CuBr (0.3974 mmol; 0.199 eq.) was added onto the frozen solution under nitrogen flow, and the tube was evacuated once again. After melting the solution in nitrogen atmosphere, the polymerizataion was initiated by heating the tube in a 50 °C oil bath. The reaction was monitored by sampling the aliquots of the reaction mixture and analyzing it by ^{1}H NMR. After 5 h, the reaction was quenched by cooling in liquid nitrogen and exposing to air. The monomer conversion estimated from the ^{1}H NMR of the quenched reaction mixture was 46%. The solution was precipitated in 8:2 methanol/water mixture three times. The viscous polymer was dissolved in DCM and washed with water twice. After concentrating the DCM solution in air, the solution was precipitated in 8:2 methanol/water mixture twice, and the liquid polymer was washed with water two more times. The polymer was dissolved in DCM and passed through a cotton puff to remove dusts and then concentrated by a rotavapor. After drying in vacuo at r.t. for ~ 2 days, the polymer was obtained as slightly green clear viscous liquid. Yield = 23.8 g (45%). The ^{1}H NMR spectrum is shown in Fig. S1. M_n = 13.8 kDa. Size-exclusion chromatography (light scattering detector): M_n = 13.1 kDa, M_w/M_n = 1.06.



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40 Fig. S1. The ^{1}H NMR spectrum of star P*n*BA in $CDCl_3$.

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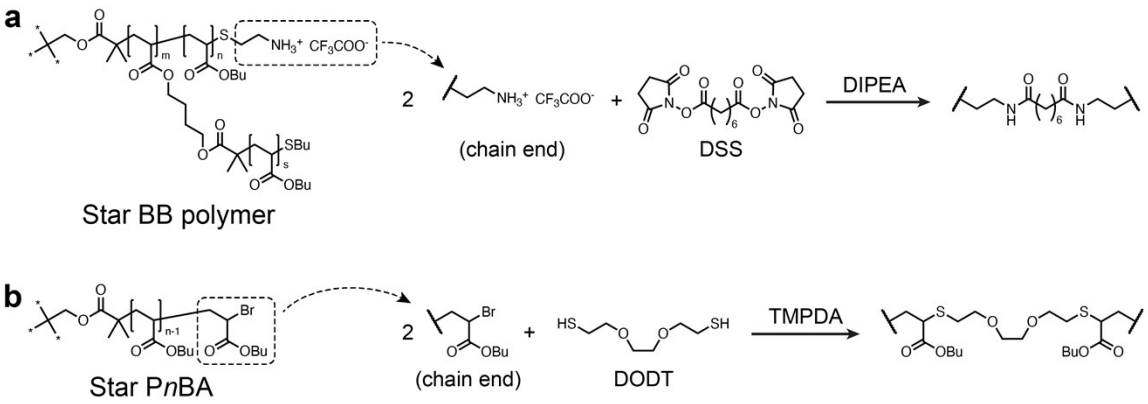

Fig. S2. Reactions scheme of the synthesis of (a) **B** and (b) **N**.

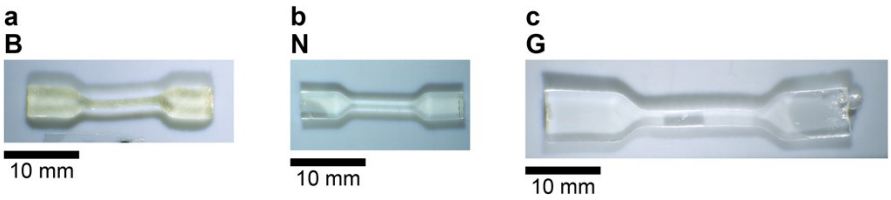

Fig. S3. Photographs of the test pieces of (a) **B**, (b) **N**, and (c) **G**.

Fig. S4. Photographs of the tensile-SAXS set-up.

S2. Verification of normal incidence geometry and sample incompressibility from X-ray absorbance in tensile-SAXS.

Fig. S5 (open symbols) plots the X-ray absorbance ($A = -\ln \tau$ where τ is the transmittance) against stretch ratio (λ) for the three network samples. A decreases with increasing λ due to thinning by stretching. For a normal incidence geometry, A obeys a Beer-Lambert law $A = \mu l$ where μ is the linear absorption coefficient and l is the sample thickness. μ usually depends solely on the atomic composition and the physical density and hence is invariant against stretching provided that the material is incompressible. Incompressibility also leads to $l \propto \lambda^{-1/2}$. Therefore, $A\lambda^{1/2}$ should be constant independent of λ. The results of such correction are plotted in closed symbols in Fig. S5, indeed showing independence on λ. Therefore, the normal incidence of the X-ray beam and the incompressibility of the samples are verified. The result further suggests that l, which is required for thickness correction in SAXS data reduction, is obtained simply as $l = l_0\lambda^{-1/2}$ where l_0 is the thickness before stretching. The scattered intensity reported in the present paper has been corrected for the thickness estimated by this method.

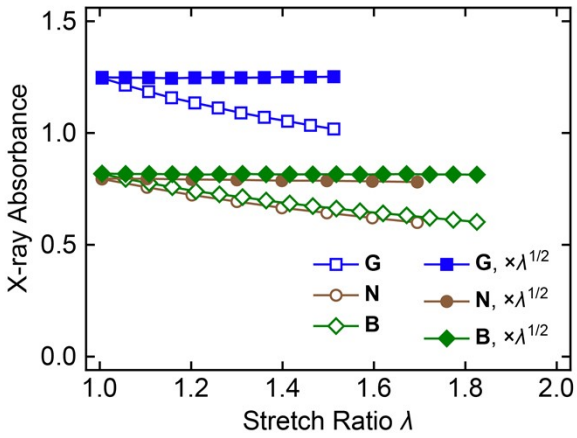

Fig. S5. X-ray absorbance during uniaxial tensile tests. Open symbols are the observed absorbance and close symbols are the absorbance corrected for the expected thickness reduction by stretching an incompressible material.

S3. Polarization correction in SAXS.

The scattered intensity I_{obs} from an isotropic material shows anisotropic scattered intensity if the beam is polarized and is described as[2]

$$I_{obs} = I_{corr}\left[P(1 - \cos^2\beta\sin^2 2\theta) + (1 - P)(1 - \sin^2\beta\sin^2 2\theta)\right] \qquad (S1)$$

where I_{corr} is the intensity expected when the polarization effect is absent, P is the fraction of the horizontally polarized component of the incident beam, and β is the azimuthal angle of the scattered X-ray with $\beta = 0$ being the horizontal direction. The two terms of Equation S1, each of which represent the contribution from the horizontally and vertically polarized components in incident beam, can be obtained by letting I' = 1 (horizontal polarization) and −1 (vertical polarization) in Equation 12 in ref. 2, respectively. The equation means that a horizontally polarized incident beam (P > 0.5) leads to reduction of the scattered intensity along the equator ($\beta =$ 0° and 180°). Fig. S6a shows the sector averaged 1D profiles of scattered intensity from an isotropic glassy carbon standard (SRM3600, NIST, USA) collected by using the same setup used for the tensile-SAXS measurements. Close examination of the profiles at the high q region (Fig. S6b) reveals slight reduction at around $\beta =$ 0° and 180°, indicating that the incident beam is horizontally polarized. To quantify the extent and the direction of polarization, the intensity in the range 8.0° $\leq 2\theta \leq$ 8.2° was integrated to get the azimuthal intensity profile (Fig. S6c, closed symbols). The azimuthal profile was then fitted with the slightly modified equation.

$$I_{obs} = I_{corr}\left[P(1 - \cos^2(\beta + \beta_{corr})\sin^2 2\theta) + (1 - P)(1 - \sin^2(\beta + \beta_{corr})\sin^2 2\theta)\right] \qquad (S2)$$

where β_{corr} accounts for a slight tilt of the polarization axis. The fitting result is shown in Fig. S6c as a solid curve. The optimized parameters are $P = 1.00$ and $\beta_{corr} =$ 4.8°. The azimuthal profile after correction by Equation S2 using the optimized parameters is shown as open symbols in Fig. S6c, in which an isotropic intensity distribution is seen. Fig. S6d shows the 2D plot of I_{obs}/I_{corr} calculated by using Equation S2 with the above optimized P and β_{corr} values. The polarization correction was performed by dividing the observed intensity by the values in Fig. S6d. The scattered intensities reported in the main text (Fig. 3-6) are those after the correction.

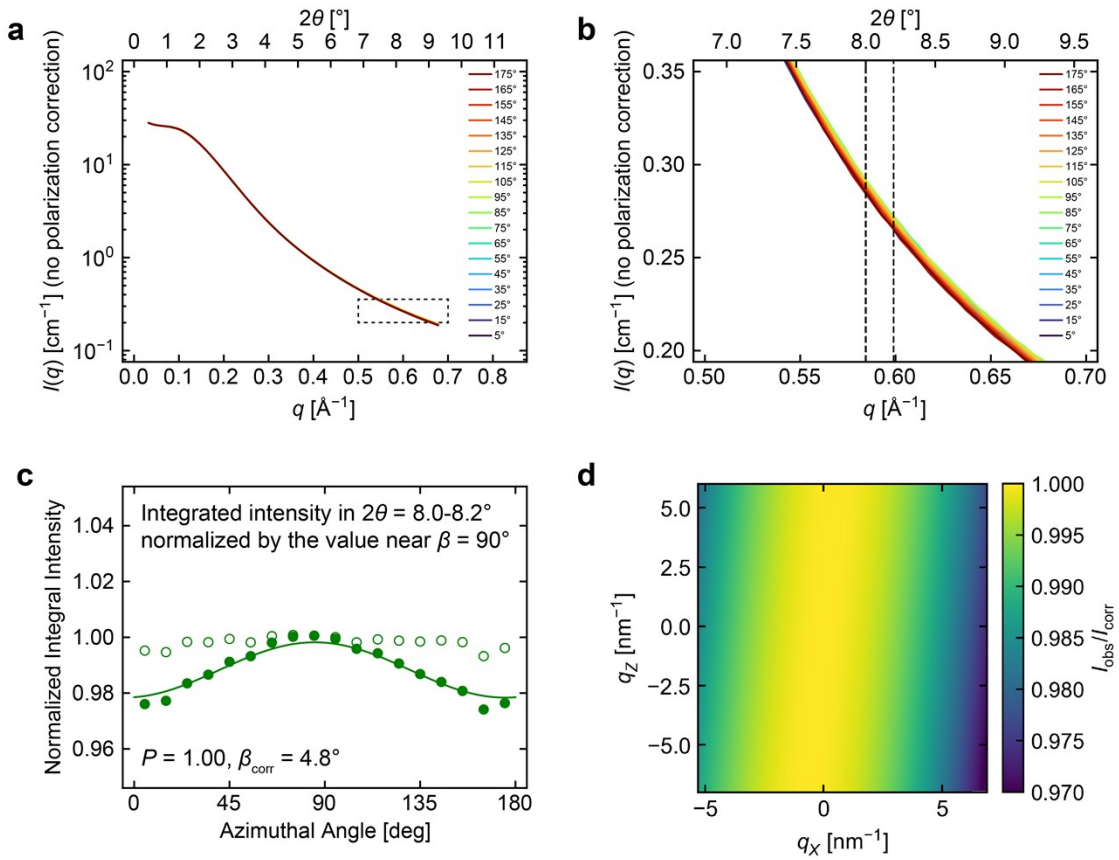

Fig. S6. (a) 1D profiles of the scattered intensity from an isotropic glassy carbon sample at each azimuthal angle β indicated. (b) Enlarged graph showing the region marked by dashed lines in panel a. (c) Azimuthal intensity profile (closed symbol) obtained by integrating the intensity in the region marked by dashed vertical lines in panel b. The integrated intensity has been normalized by the maximum value. The solid curve is the fitting result using Equation S2. Open symbols show the result of the polarization correction. (d) 2D plot of the polarization factor calculated by using Equation S2 with the optimized parameters ($P = 1.00$ and $\beta_{corr} = 4.8°$). The values lower than unity show the effect of the polarized incident beam.

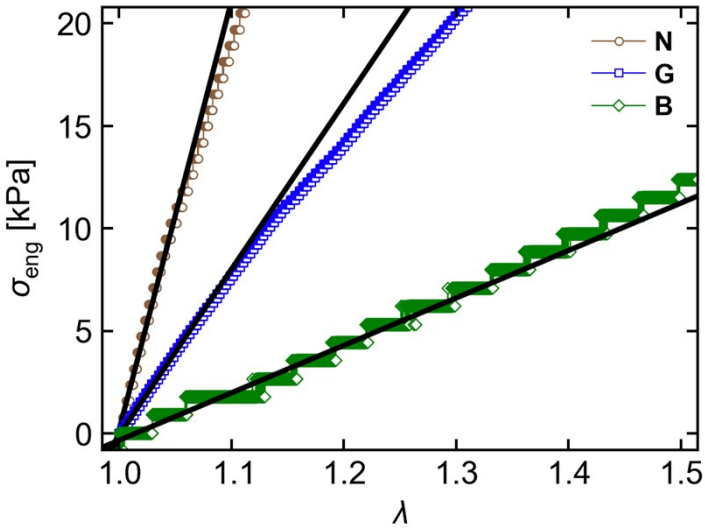

Fig. S7. Results of linear fitting to obtain Young's modulus (E_Y). Black solid lines indicate the fitted lines.

S4. Estimation of the diameter of BB polymer and P*n*BA.

The volume of a repeat unit (v_u) of P*n*BA (0.128 kg mol^{-1}) is calculated to be 0.20 nm^3 using the physical density of P*n*BA (1090 kg m^{-3})[3]. The length of a fully extended P*n*BA chain per repeat unit (l_u) is roughly $2l_b sin(\theta_b/2)$ where l_b is the backbone bond length and θ_b is the bond angle. We assume standard C-C bond length $l_b = 0.154$ nm and the tetrahedral angle $cos(\theta_b) = -1/3$ ($sin(\theta_b/2) = (2/3)^{1/2}$), leading to $l_u = 0.25$ nm. If a P*n*BA chain is seen as a simple cylinder, its cross section is $v_u/l_u =$ 0.20 nm^3/0.25 nm = 0.80 nm^2 which then lead to the diameter of ~ 1.0 nm.

The star BB polymer had M_n = 86.7 kDa. The molar mass of one arm is 86.7/4 = 21.7 kDa. Assuming that the star polymer in the melt state has the physical density identical to that of P*n*BA (1090 kg m^{-3}), the volume of one arm is 21.7/1090/N_A = 33 nm^3. The polymerization degree of the backbone per one arm is 9.3 (polymerization degree of the part of the backbone chain grafted with the side chains), and its fully extended length is roughly $9.3 \times 2 \times l_u = 2.3$ nm using the same assumption and the l_u value in the previous paragraph. Considering an arm as a simple cylinder, its cross section is 33 nm^3/2.3 nm = 14 nm^2, leading to the diameter of 4.2 nm.

S5. Orientation parameter.

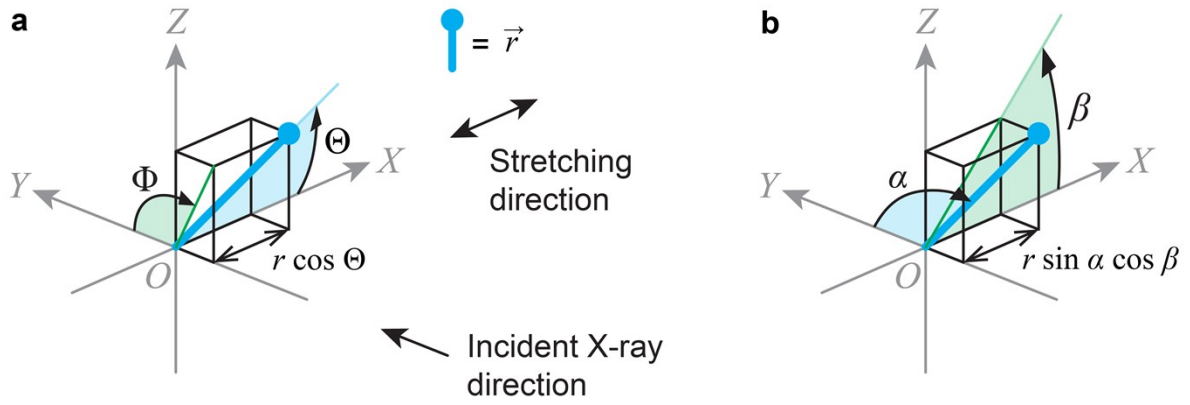

Fig. S8. Geometry for discussion of pole orientation. (a) Definition of the polar coordinate O-$r\Theta\Phi$. (b) Definition of the polar coordinate O-$r\alpha\beta$.

Suppose a distribution of poles $D(\vec{r})$ in a Cartesian coordinate O-XYZ. The number of poles in a volume element at $\vec{r}$ is $D(\vec{r})d\vec{r}$. We set the stretching direction parallel to the X axis. For the sample being stretched, $D(\vec{r})$ is axisymmetric around the X axis and mirror-symmetric about the YZ plane. Thus $D(\vec{r})$ is conveniently written in a spherical coordinate O-$r\Theta\Phi$ where r is the distance from the origin, Θ is the angle from the symmetry axis, and Φ is the azimuthal angle in the YZ plane, as depicted in Fig. S8a. The number of poles in a volume element defined by the intervals $[r,r+dr]$, $[\Theta,\Theta+d\Theta]$, and $[\Phi,\Phi+d\Phi]$ is $D(r,\Theta,\Phi)r^2\sin\Theta dr d\Theta d\Phi$. From the symmetry $D(\vec{r})$ is independent on Φ. Furthermore, by focusing only on the poles with a prescribed length r_0, the r-dependence is represented by a Dirac delta function $\delta(r-r_0)$:

$$D(r,\Theta,\Phi) = D(\Theta)\delta(r-r_0) \qquad (S3)$$

The orientation of the pole, with respect to the symmetry axis, is often measured by the average of $\cos^2\Theta$, $\langle\cos^2\Theta\rangle$.

$$\langle \cos^2 \Theta \rangle = \frac{\int_0^{\infty} dr \int_0^{\pi} d\Theta \int_0^{2\pi} d\Phi \left[\cos^2 \Theta D(\Theta) \delta(r - r_0) \sin \Theta \right]}{\int_0^{\infty} dr \int_0^{\pi} d\Theta \int_0^{2\pi} d\Phi \left[D(\Theta) \delta(r - r_0) \sin \Theta \right]}$$

$$= \frac{\int_0^{\pi} d\Theta \left[\cos^2 \Theta D(\Theta) \sin \Theta \right]}{\int_0^{\pi} d\Theta [D(\Theta) \sin \Theta]} \qquad (S4)$$

The explicit form of $D(\Theta)$ is usually unknown, but it may be expanded as a spherical harmonic series[4]. For a low orientation degree, it may suffice to use the zeroth and second order terms only, which are proprtional to the associated Legendre polynomials of $\cos \Theta$.

$$P_0(\cos \Theta) = 1 \qquad (S5)$$

$$P_2(\cos \Theta) = \frac{1}{2}(3\cos^2 \Theta - 1) \qquad (S6)$$

Linear combination of these two terms simplifies to

$$D(\Theta) = a_0 + a_2 \cos^2 \Theta \qquad (S7)$$

where a_0 and a_2 are some real coefficients. Let us evaluate $\langle \cos^2 \Theta \rangle$ for this pole distribution. The normalization factor is

$$\int_0^{\pi} d\Theta [D(\Theta) \sin \Theta] = \int_0^{\pi} d\Theta \left[\left(a_0 + a_2 \cos^2 \Theta \right) \sin \Theta \right] = 2a_0 + \frac{2}{3} a_2 \qquad (S8)$$

The numerator is

$$\int_0^{\pi} d\Theta \left[\cos^2 \Theta D(\Theta) \sin \Theta \right] = a_0 \int_0^{\pi} d\Theta \left[\cos^2 \Theta \sin \Theta \right] + a_2 \int_0^{\pi} d\Theta \left[\cos^4 \Theta \sin \Theta \right]$$

$$= \frac{2}{3} a_0 + \frac{2}{5} a_2 \qquad (S9)$$

Combining Equations S8 and S9 into S4,

$$\langle \cos^2 \Theta \rangle = \frac{5a_0 + 3a_2}{15a_0 + 5a_2} \qquad (S10)$$

$\langle \cos^2 \Theta \rangle$ becomes 1/3 for $a_2 = 0$ (isotropic, no preferential orientation), as expected. Hermann's orientation parameter (*f*) is further calculated as

$$f = P_2(\langle\cos\Theta\rangle) = \frac{1}{2}\left(3\langle\cos^2\Theta\rangle - 1\right) = \frac{1}{2}\left(\frac{15a_0 + 9a_2}{15a_0 + 5a_2} - 1\right) = \frac{2a_2}{15a_0 + 5a_2} \qquad (S11)$$

Note that Equation S11 may be used only for a moderate degree of orientation.

Next, we relate the pole distribution to the observed scattered intensity. The scattered intensity at the scattering vector $\vec{q}$ is proportional to the pole distribution function at $\vec{q}$. Suppose that the incident X-ray points in $+Y$ direction and the scattered X-ray is observe by a two-dimensional detector parallel to XZ plane. For convenience let us define another coordinate $O\text{-}r\alpha\beta$ as in Fig. S8b. In this way, the azimuthal angle (β) matches the azimuthal angle on the detector plane. The angle from the $+Y$ axis (α) is related to the scattering angle 2θ as $\alpha = \pi/2 + \theta$. It is easily found from Fig. S8 that $\cos\Theta = \sin\alpha\cos\beta$. Thus $D(\Theta)$ is rewritten as

$$D(\alpha,\beta) = a_0 + a_2\sin^2\alpha\cos^2\beta \qquad (S12)$$

For small angle scattering, $\theta \ll \pi/2$ so $\alpha \approx \pi/2$ and $\sin^2\alpha \approx 1$. Therefore, we can fit the observed azimuthal intensity profile with

$$I(\beta) = a_0 + a_2\cos^2\beta \qquad (S13)$$

and insert the optimized coefficients to Equation S11 to evaluate the orientation function.

References

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