

## Electronic Supplementary Information (ESI)

### “Characteristic Smectic Structures of Main-Chain Liquid-Crystalline Polyimides Driven by a Microphase Separation between Aromatic Imide Mesogen and a Dimethyl Siloxane Spacer”

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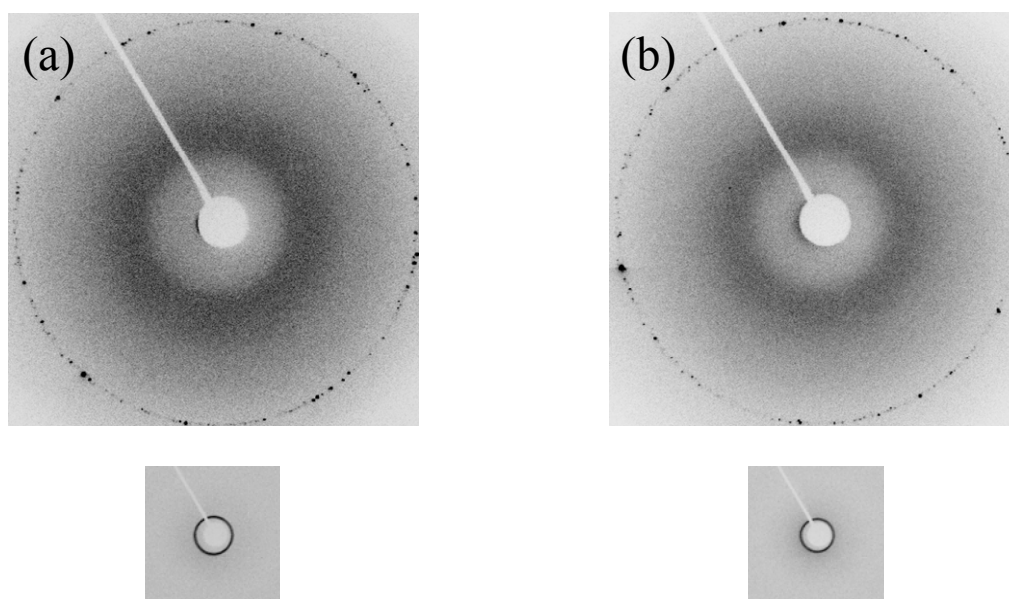


Figure S1. (a) The WAXD powder pattern observed at 170 °C in the  $S_C$  phase region and (b) observed at 230 °C in the  $S_A$  phase region. The photographs for the Debye-Scherrer ring of the inner sharp reflection are shown below those in wide angle region. The spacing of inner layer reflection was 31.1 Å at 170 °C and 35.7 Å at 230 °C, respectively. These values are absolutely same as those observed for the fiber specimen.

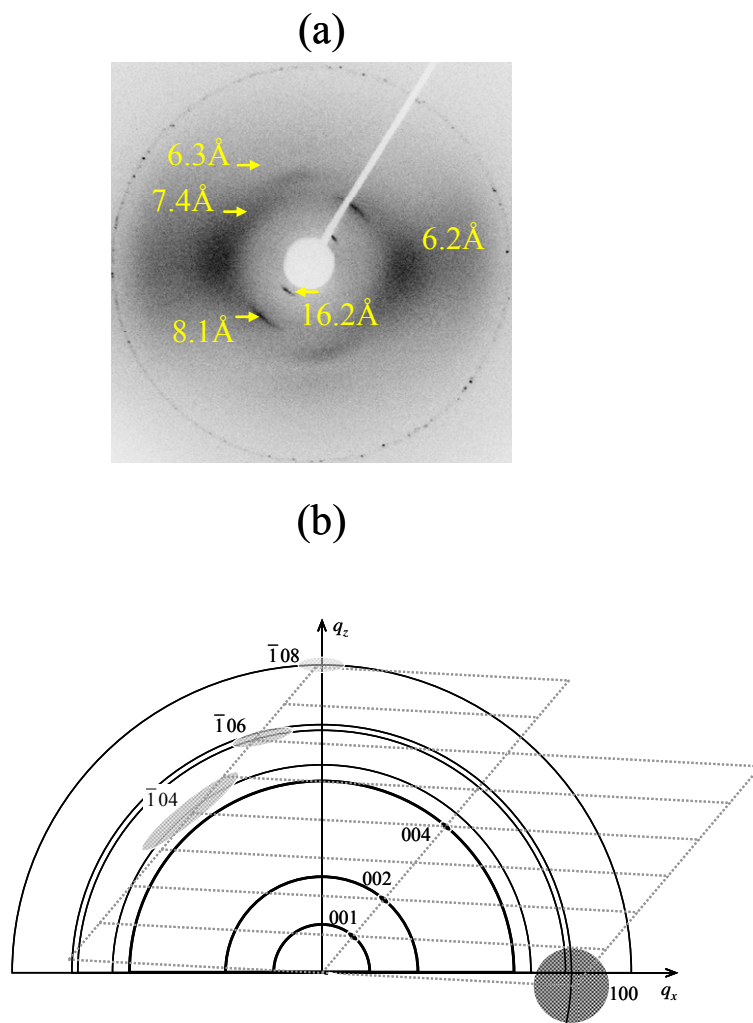


Figure S2. (a) The monodomain-like WAXD pattern for the  $S_C$  phase in the oriented film sample of BPDA/4SiO<sub>3</sub>-3Cl and (b) the two-dimensional reciprocal lattice satisfying the reflection positions.

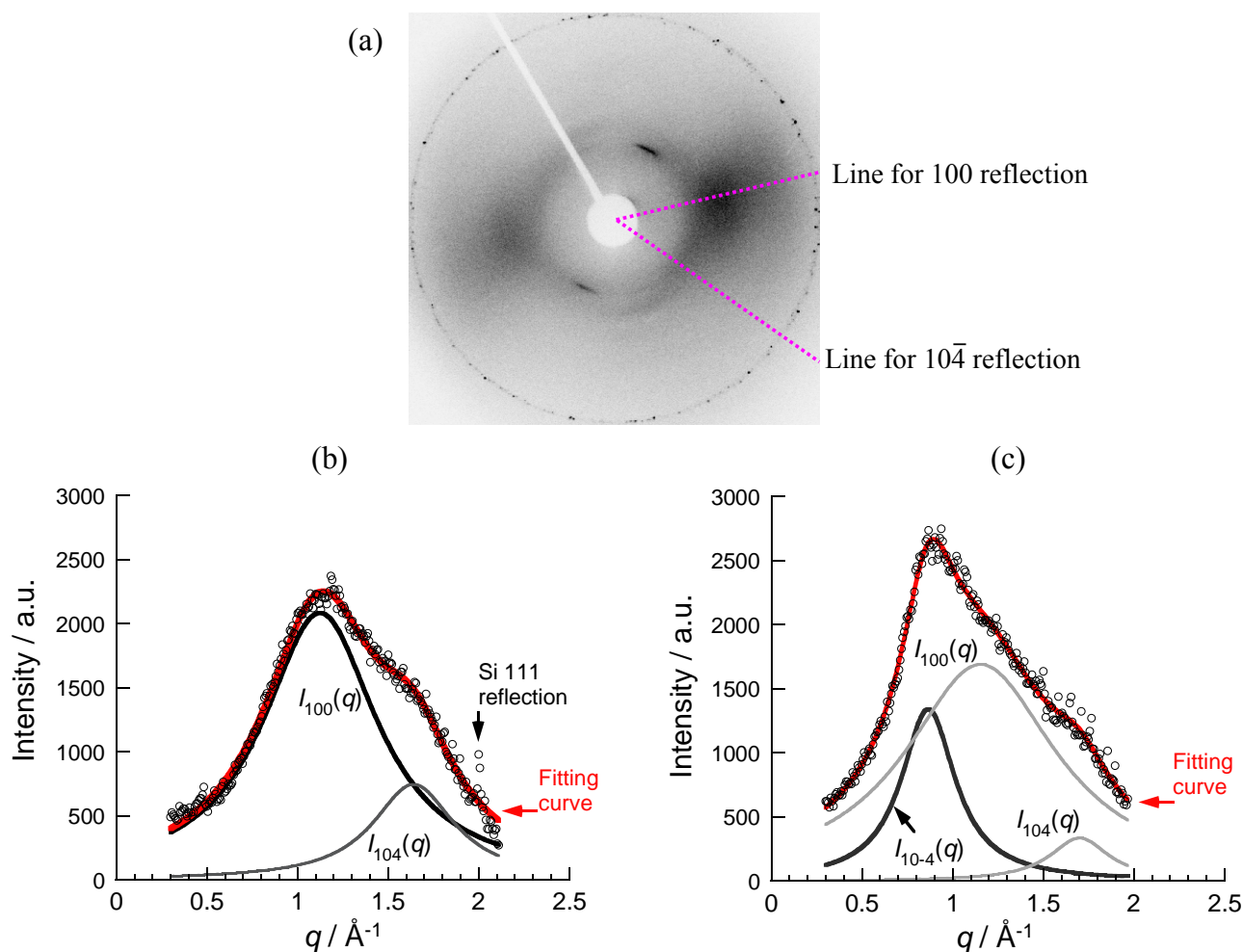


Figure S3. (a) The WAXD patterns of the monodomain-like films in the  $S_C$  phase. The line intensity profiles for the 100 and  $10\bar{4}$  reflections are obtained on the pink dotted lines on the WAXD pattern. The profiles with fitting curves (red solid line) for the 100 (b) and  $10\bar{4}$  (c) reflections are shown below the photograph. The profiles were fitted with sum of several Lorentz type functions because a broad reflection (most likely 104 reflection) was overlapped on the 100 reflection, and 100 and the broad reflection (104 reflection) were overlapped on the  $10\bar{4}$  reflection, respectively. The instrumental broadening of x-ray beam was neglected for the estimation of  $\xi$ , because the broadening estimated from the Si 111 reflection was too narrow compared with the width of those broad reflection and did not affect on the value of  $\xi$ .