Electronic Supplementary Material (ESI) for Soft Matter.

# Electronic Supplementary Information (ESI)

# Structural and Morphological Transitions in Extension-Induced Crystallization of Poly(1-butene) Melt

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## A. DSC measurement

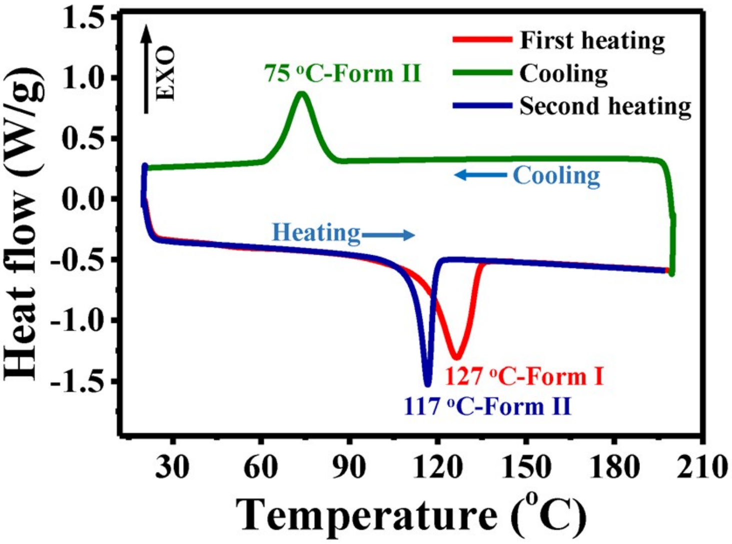

**Fig. S1** Thermal properties of PB-1 measured by differential scanning calorimeter (DSC, TA Instruments DSC 2920) with a heating/cooling rate of 10 °C/min. The initial PB-1 sample contains only stable Form I crystal, whose melting point is about 127 °C determined by the first heating procedure. Crystallization of Form II occurs during the subsequent cooling of melt and the crystallization temperature is about 75 °C. After Form II is completely crystallized, the sample is immediately heated again in order to avoid the transition of Form II to Form I. The second heating procedure shows that the melting temperature of Form II crystal is about 117 °C.

## B. Relative crystallinity of Form II

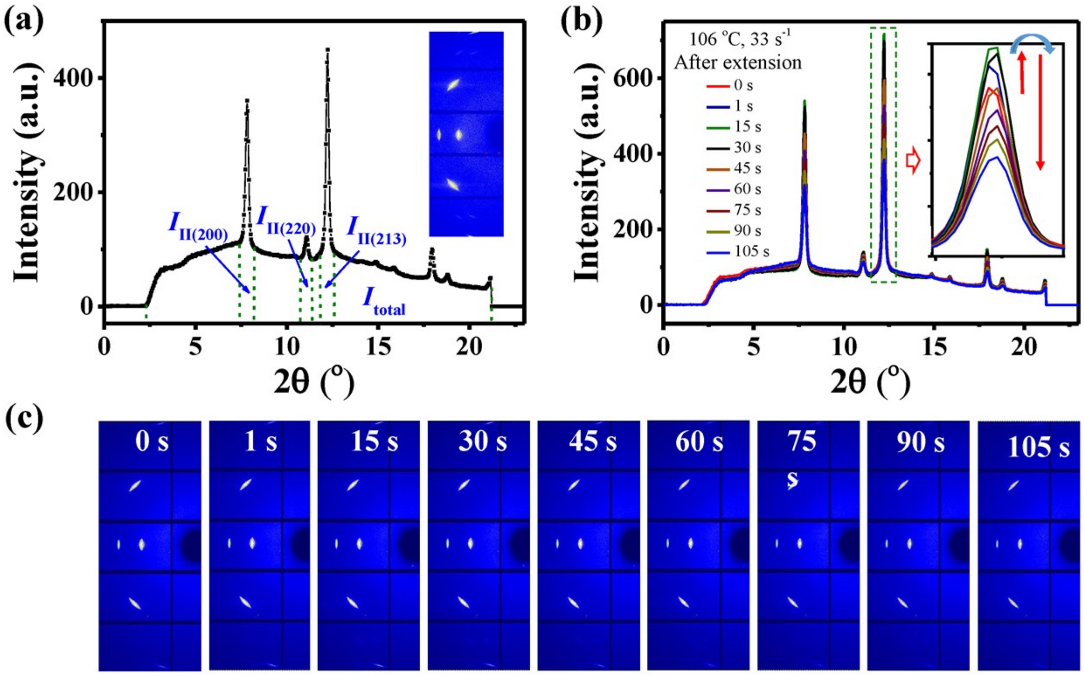

**Fig. S2** (a) Selected 1D WAXD curve of the crystallized sample. (b) A series of 1D WAXD curves of sample after subjected to extension at 106 °C with strain rate of 33 s$^{-1}$. The insertion shows an enlargement of Form II (213) diffraction. (c) The corresponding 2D WAXD patterns. The flow direction is vertical.

Due to the incompletion of 2D WAXD patterns (see Fig. S2a), the crystallinity of sample is unable to be precisely calculated through the standard method of multiple peak fitting. We use a simplified treatment to obtain the relative crystallinity of Form II after extension. The contribution of Form II to total diffraction intensity ($I_{total}$) of sample is approximately calculated by direct intensity integration over the corresponding 2θ ranges, namely 7.4 ~ 8.2° for $I_{II(200)}$, 10.7 ~ 11.3° for $I_{II(220)}$ and 11.7 ~ 12.6° for $I_{II(213)}$. Then the relative crystallinity of Form II is expressed as

$X_c = [I_{II(200)} + I_{II(220)} + I_{II(213)}]/I_{total}$, which is further corrected by defining $X_c = 0$ for pure melt. This simplified calculation can reflect the variation trend of the real crystallinity of sample. Figure S2b presents a series of 1D WAXD curves of sample after extension at 106 °C with strain rate of 33 $s^{-1}$. The corresponding 2D WAXD patterns are shown in Fig. S2c, which indicate that crystal orientation keeps almost constant in the whole process. The insertion in Fig. S2b shows an enlargement of Form II (213) diffraction, which clearly presents a non-monotonic evolution of diffraction intensity with time, namely increasing from 0 to 15 s followed by decreasing from 15 to 105 s. Meanwhile, an opposite trend exists in the diffraction intensity of amorphous melt although the overall intensity changes little, indicating that the sample thickness is invariant during isothermal holding. By using the above simplified method, the calculated relative crystallinity (see Fig. 3a in the paper) can clearly reflect this trend, demonstrating its reliability on characterizing the crystallization and melting processes of Form II crystal after extension.

## C. Shish length

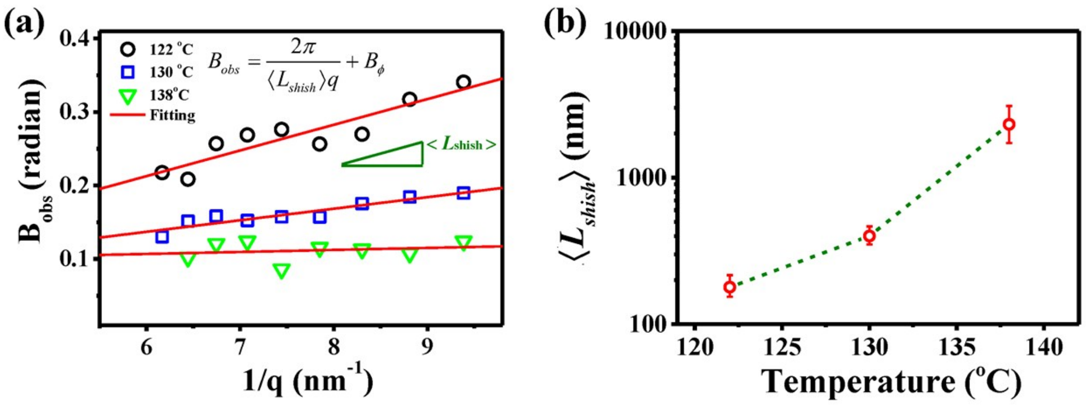

**Fig. S3** (a) Plots of the azimuthal integral width ($B_{obs}$) vs the value of $1/q$ from the equatorial streak in SAXS patterns at strain of 3 with strain rate of 33 $s^{-1}$. (b) The calculated average shish length $\langle L_{shish}\rangle$ as a function of extension temperature.

The average shish length $\langle L_{shish}\rangle$ is calculated based on Ruland streak method.[1] Starting from the scattering of rod-like structure in polymer, the experimentally measured azimuthal integral width of SAXS streak is demonstrated to be contributed by both scatterer length and misorientation. The shish morphology in polymer melt is supposed to be rodlike, making it feasible to obtain $\langle L_{shish}\rangle$ by analyzing the equatorial streak in SAXS.[2] Two forms of equation are employed to fit the experimental data. If all the azimuthal distributions along $q$ can be described by a Gaussian profile, it follows:

$$B_{obs}{}^{2}=\frac{4\pi^{2}}{\langle L_{shish}\rangle^{2}q^{2}}+B_{\phi}{}^{2} \tag{1}$$

If a Lorentzian profile is proper to model the azimuthal distribution, the relationship becomes:

$$B_{obs} = \frac{2\pi}{\langle L_{shish} \rangle q} + B_{\phi} \tag{2}$$

Here $B_{obs}$ is the integral width of azimuthal intensity profile extracted from the equatorial streak at scattering vector $q$ and $B_{\phi}$ derives from the misorientation of shish. In this study, all the azimuthal distributions are better fit with Lorentz function, indicating that equation (2) is preferred. On the basis of equation (2), $\langle L_{shish} \rangle$ and $B_{\phi}$ equal to the reciprocal of slope and the intercept for the plot of $B_{obs}$ vs $1/q$, respectively. By performing azimuthal intensity integration on the equatorial streak in SAXS patterns collected at strain of 3 with strain rate 33 s$^{-1}$, Figure S3a shows the plots of $B_{obs}$ vs $1/q$ at different temperatures of 122, 130 and 138 $^{o}$C where the linear fitting is implemented. The calculated $\langle L_{shish} \rangle$ are presented in Fig. S3b, which indicates that high temperature enhances flow-induced shish length.

## D. Crystallization within 600 s after extension

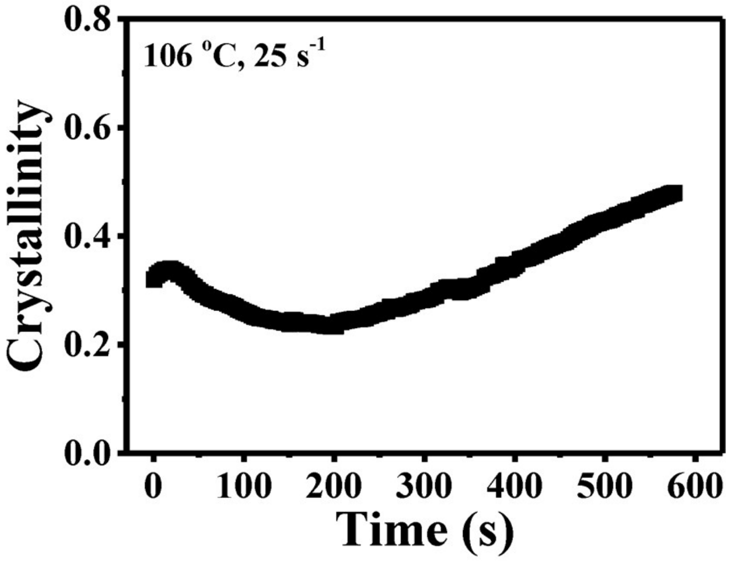

**Fig. S4** Time evolution of the relative crystallinity of Form II during isothermal holding of sample after extension at 106 °C with strain rate of 25 $s^{-1}$.

## References

1 R. Perret and W. Ruland, *J. Appl. Crystallogr.*, 1970, **3**, 525-532.
2 J. K. Keum, F. Zuo and B. S. Hsiao, *Macromolecules*, 2008, **41**, 4766-4776.