Supporting Information

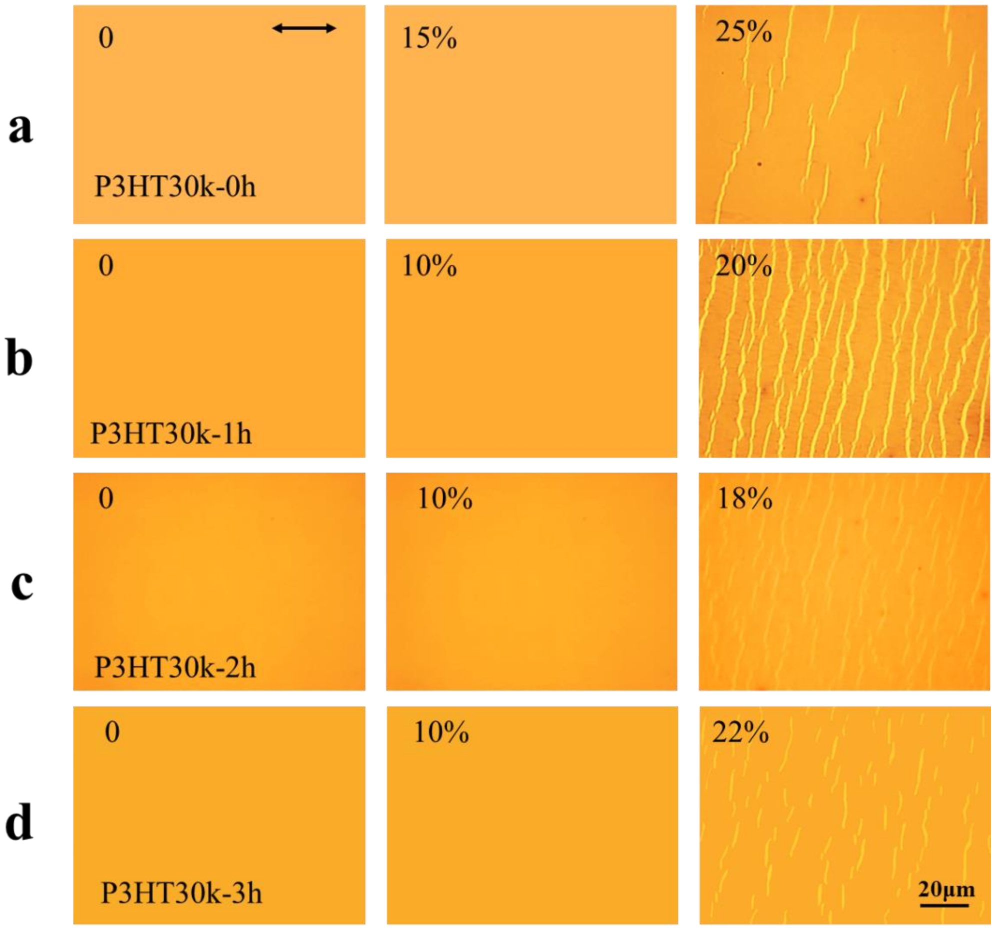

Figure S1. Optical microscopy images of P3HT30k films elongated under different strains. The samples were annealed by ODCB vapor for different time: (a) 0 h, (b) 1 h, (c) 2 h and (d) 3 h.

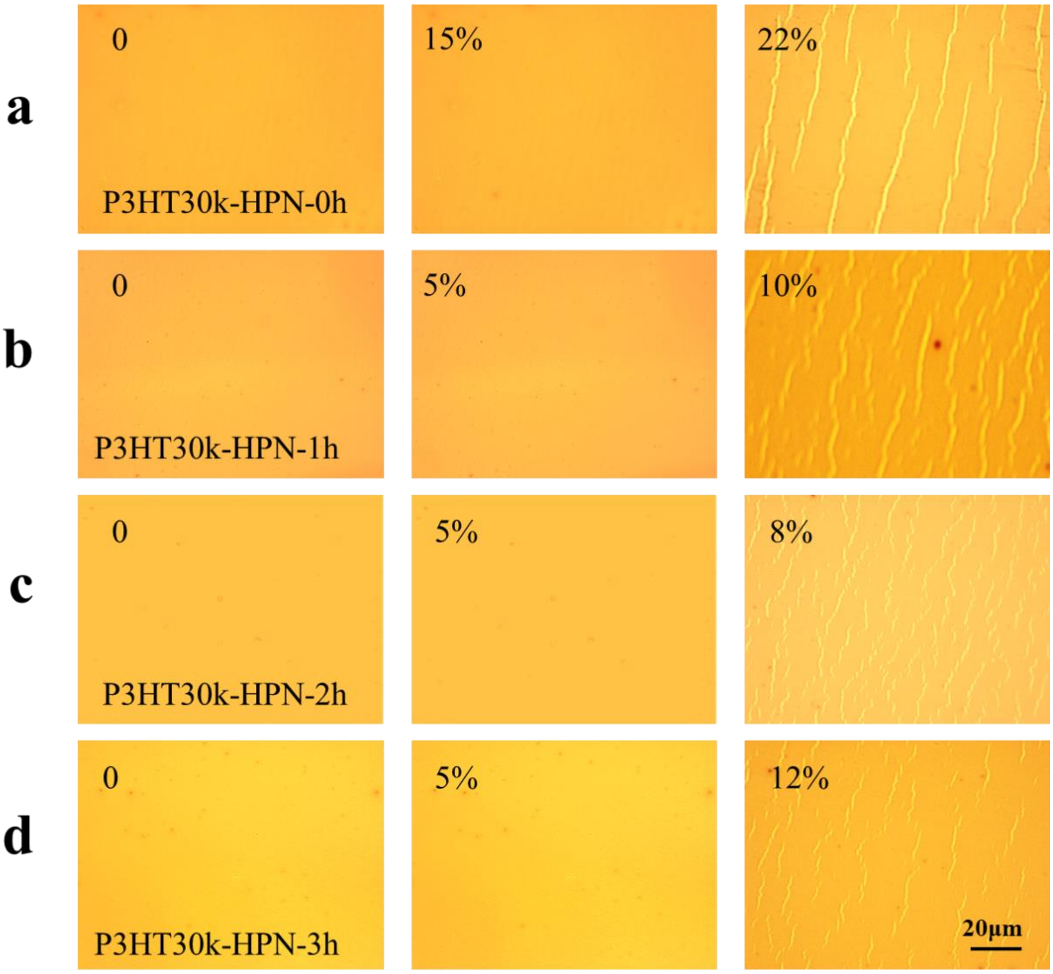

Figure S2. Optical microscopy images of P3HT30k-HPN films elongated under different strains. The samples were annealed by ODCB vapor for different time: (a) 0 h, (b) 1 h, (c) 2 h and (d) 3 h.

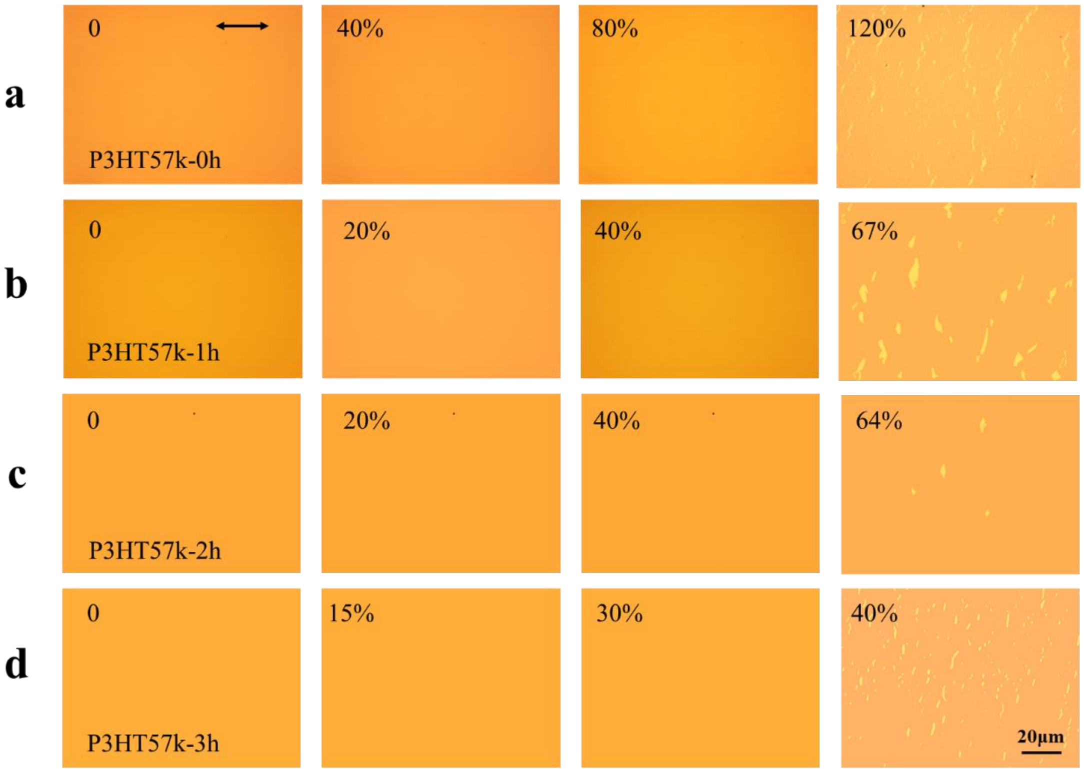

Figure S3. Optical microscopy images of P3HT57k films elongated under different strains. The samples were annealed by ODCB vapor for different time: (a) 0 h, (b) 1 h, (c) 2 h and (d) 3 h.

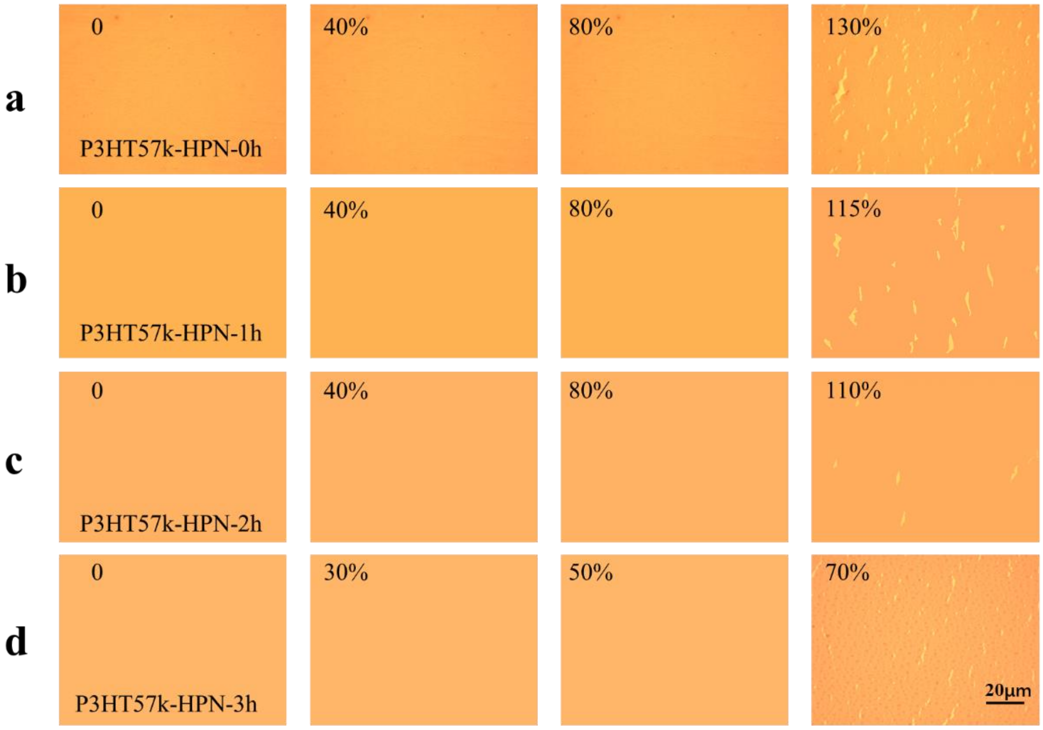

Figure S4. Optical microscopy images of P3HT57k-HPN films elongated under different strains. The samples were annealed by ODCB vapor for different time: (a) 0 h, (b) 1 h, (c) 2 h and (d) 3 h.

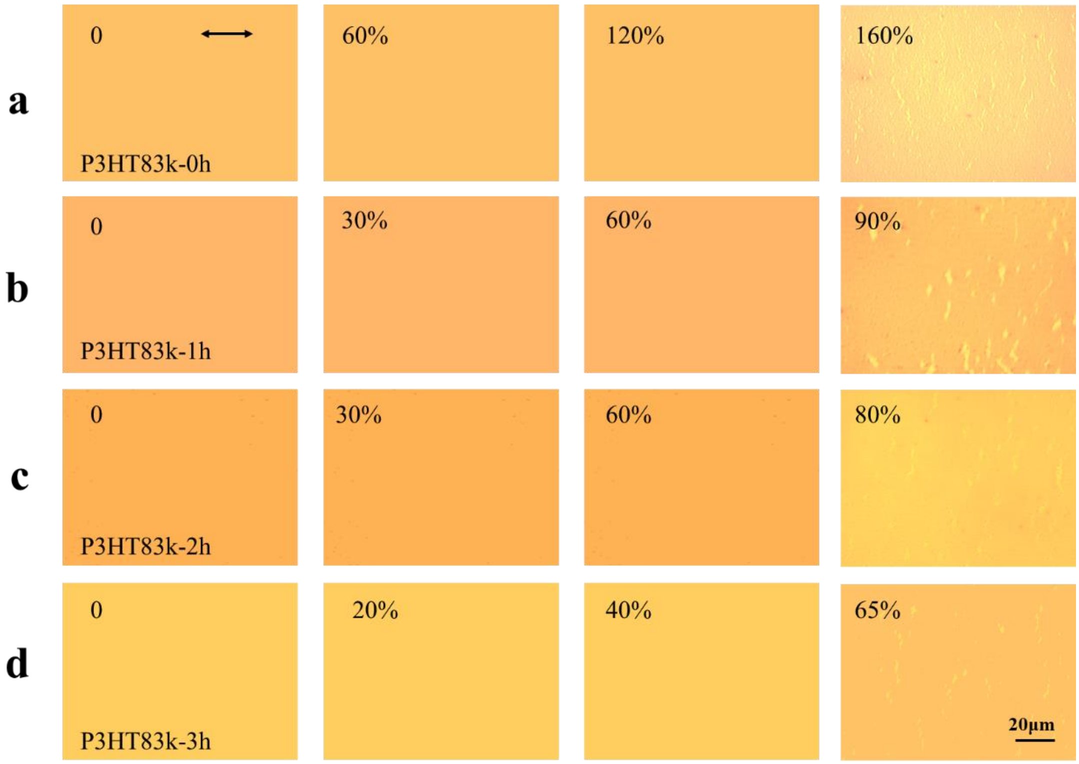

Figure S5. Optical microscopy images of P3HT83k films elongated under different strains. The samples were annealed by ODCB vapor for different time: (a) 0 h, (b) 1 h, (c) 2 h and (d) 3 h.

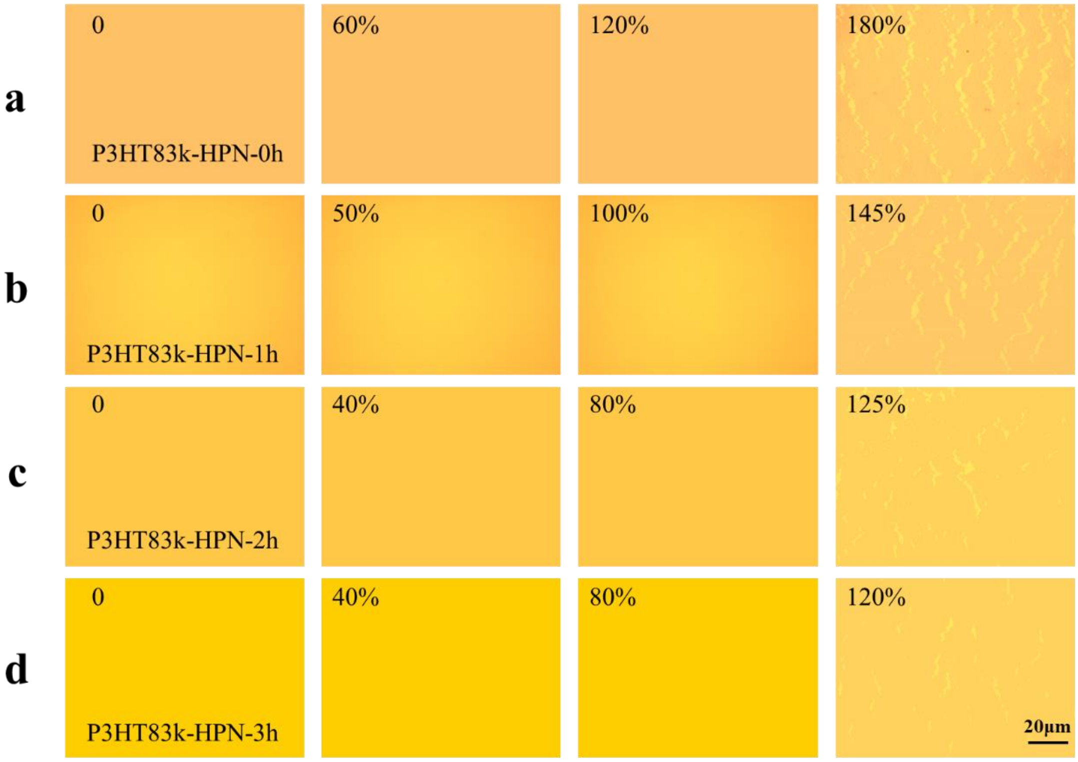

Figure S6. Optical microscopy images of P3HT83k-HPN films elongated under different strains. The samples were annealed by ODCB vapor for different time: (a) 0 h, (b) 1 h, (c) 2 h and (d) 3 h.

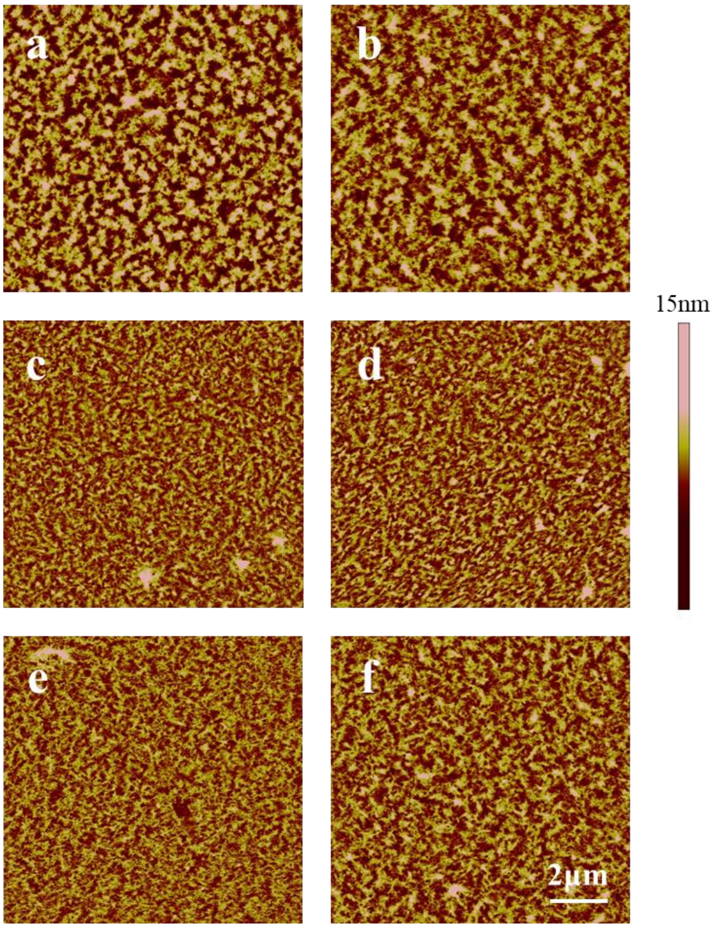

Figure S7. AFM height images of P3HT with and without HPN-68L: (a) P3HT30k, (b) P3HT30k-HPN, (c) P3HT57k, (d) P3HT57k-HPN, (e) P3HT83k and (f) P3HT30k-HPN.

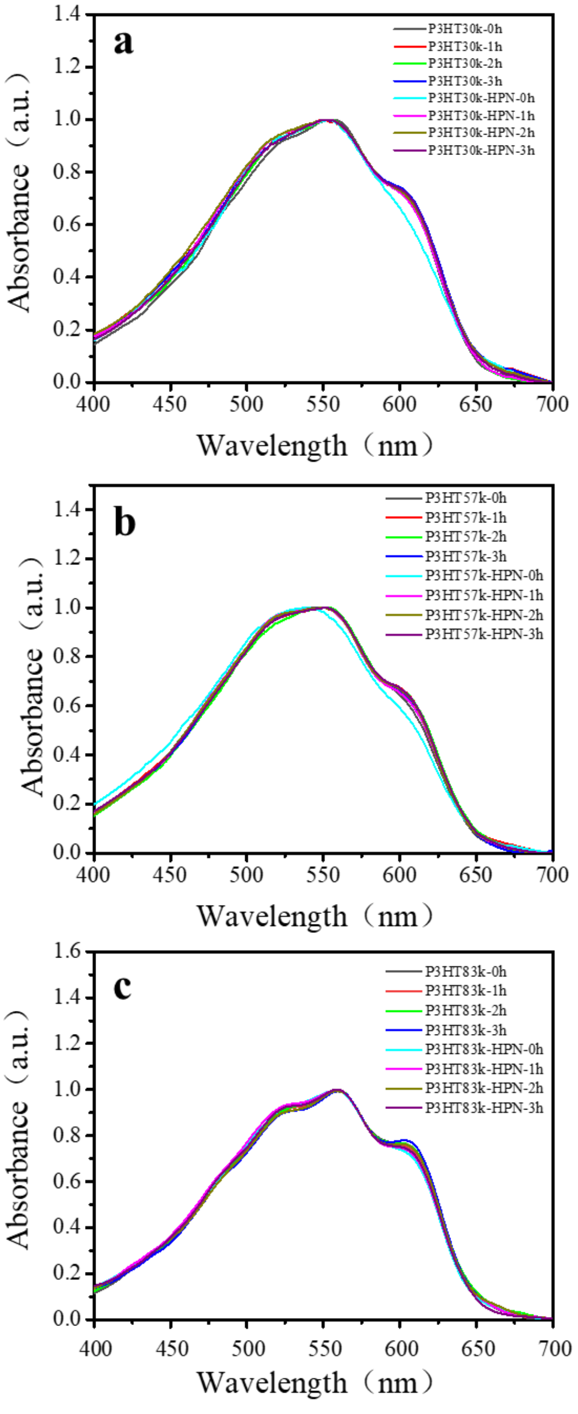

Figure S8. UV-vis absorption spectra of (a) P3HT30k and P3HT30k-HPN, (b) P3HT57k and P3HT57k-HPN and (c) P3HT83k and P3HT83k-HPN annealed by ODCB vapor for different times.

The calculation of the tie chain fraction (f_{TC})

The Huang-Brown model was used to quantify the probability of tie chains formation of P3HT with and without HPN-68L.[1,2] The Huang-Brown model assumes Fischer's solidification scheme[3], namely, the characteristic size of polymer chains in the melt is preserved on rapid crystallization. It is known that P3HT crystallizes rapidly. Here we assumed that the solidification of P3HT is consistent with Fischer's solidification scheme.[1,2,4]

The Huang-Brown model assumes that polymer chains form tie chains only when the end-to-end distance is greater than, or equal to the distance between adjacent crystallites. Huang and Brown argued that the probability of forming a tie chain spanning two neighboring crystalline domains that are a critical distance, d_c. The probability distribution $P(M)$ is described by[4]

$$P(M) = \frac{\int_{d_c}^{\infty} r^2 \exp\left(-\frac{3r^2}{2Nl_k^2}\right) \mathrm{dr}}{\int_{0}^{\infty} r^2 \exp\left(-\frac{3r^2}{2Nl_k^2}\right) \mathrm{dr}} \qquad (1)$$

This probability distribution $P(M)$ assumes Gaussian chain statistics where N is the number of effective Kuhn segments and l_k is the Kuhn length (l_k=2xL_p, where L_p is the persistence length of P3HT as 2.9 nm)[5]. When the molar mass M of P3HT is above 1200 g/mol, the contour length of P3HT is greater than its persistence length, Gaussian chain statistical behavior is valid. In this work, the molar mass of P3HTs are all above the critical molar mass.

In order to determine the critical distance d_c, we estimate the crystalline domain thickness (l_c) and the characteristic distance between crystalline domains (l_a). l_c is given by[6,7]

$$l_c = c \times \frac{bT_m - aT_m^0}{T_m^0 - T_m} \qquad (2)$$

where a and b are constants ($a = -5.4$, $b = -1.6$), the equilibrium melting temperature (T_m^0) of P3HT is 545±6K, [7] and c represents the repeat distance of the thiophene (0.39 nm). [8] The melting temperature (T_m) can be measured by DSC.

Then l_a can be estimated by [9]

$$l_a = l_c \times \frac{\rho_c(1 - X_c)}{\rho_a X_c} \qquad (3)$$

where ρ_c is the crystalline density of P3HT (1.13 g/cm^3) and ρ_a is the amorphous density of P3HT (1.094 g/cm^3).[10] X_C is the crystallite-size corrected crystallinity and can be calculated by[6]

$$X_c = \frac{\Delta H_f}{\Delta H_u} \frac{T_m^0}{T_m} \qquad (4)$$

where the enthalpy of fusion (ΔH_f) can be measured by DSC, and the enthalpy of fusion of a perfect P3HT crystal (ΔH_u) is 49 J/g. [6]

Based on the molecular structure of P3HT, it is surmised that the critical distance d_c for tie chain formation in P3HT to be between l_a and $2l_c + l_a$. In this work we used ($l_c + l_a$) as the critical distance d_c to calculate $P(M)$, which is consistent with that reported by Gu et al.[4]

$P(M)$ shown as Equation 1 is based on a monodisperse system. [1] In our work, P3HTs are polydisperse polymers, we must take into account the distribution of molar mass for P3HT. For P3HT having a finite distribution of molar mass, $f(M)$, where $f(M)\mathrm{d}M$ is the mole fraction of polymer with molar masses between M and $M + \mathrm{d}M$. $f(M)$ is given by

$$f(M) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(M-M_0)^2}{2\sigma^2}\right] \qquad (5)$$

where σ is a parameter characterizing the weight distribution width of molecular weight, M_0 is the molecular weight corresponding to the peak of the mass differential distribution curve.

In order to more precisely capture the electrical connectivity across the crystallites in the charge transport direction, following Huang and Brown, the factor 1/3 was introduced because the fraction of tie chains along the charge-transport direction can be approximated by multiplying the overall probability by 1/3.[2,4] The overall probability of tie-chain formation can be given by [4]

$$f_{\mathrm{TC}} \cong 1/3 \int_0^{\infty} f(M)P(M)\,\mathrm{d}M \qquad (6)$$

References:

1. Y.-L. Huang and N. Brown, *J. Mater.Sci.*,1988, **23**, 3648−3655.

2. Y. L. Huang and N. Brown, *J. Polym. Sci. Part B: Polym. Phys.* 1991, **29**, 129-137.
3. E. W. Fischer, *Pure Appl.Chem*, 1978, **50**, 1319−1341.
4. K. Gu, C. R. Snyder, J. Onorato, C. K. Luscombe, A. W. Bosse and Y.-L. Loo, *ACS Macro Letters*, 2018, **7**, 1333–1338.
5. B. Mcculloch, V. Ho, M. Hoarfrost, C. Stanley, C. Do, W. T. Heller and R. A. Segalman, *Macromolecules*, 2013, **46**, 1899−1907.
6. M. G. Broadhurst, *J. Chem.Phys*. 1962, **36**, 2578−2582.
7. C. R. Snyder, R. C. Nieuwendall, D. M. DeLongchamp, C. K. Luscombe, P. Sista and S. D. Boyd, Macromolecules, 2004, 47, 3942-3950.
8. M. Brinkmann and J.-C. Wittmann, *Adv. Mater,* 2006, **18**, 860−863.
9. P. J. DesLauriers and D. C. Rohlfing, *Macromol. Symp*, 2009, **282**, 136−149.
10. C. S. Lee and M. D. Dadmun, *Polymer,* 2014, **55**, 4−7.