Effect of Regioregularity on the Semicrystalline Structure of Poly(3-hexylthiophene)

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Supporting Information

**INTRODUCTION**

Poly(3-hexylthiophene-2,5-diyl) (P3HT) is a widely studied polymer because of its potential use in printable electronics and photovoltaic devices. Initially, P3HT was available only in low-regioregularity forms made by oxidative polymerization that rarely exhibited high charge mobility. In the 1990s, new synthetic techniques enabled the production of controlled, high-regioregularity materials that exhibited significantly increased charge mobility. Although improved control over regioregularity was an important innovation, there has not been a systematic evaluation of the quantifiable impact of P3HT’s regiodefects on crystal lamellar thickness, crystallinity, and crystallization kinetics. As is the case for other materials such as isotactic polypropylene (iPP) or dl-polylactides, the presence of a regio or stereo defect makes it effectively a copolymer. In P3HT, the effective copolymer units are head–tail (H–T), head–head (H–H), or tail–tail (T–T) couplings. During crystallization, the defects will either be excluded from the crystal or will be subject to an enthalpic penalty if incorporated into the crystal. As pointed out by Crist,* such a material (copolymers) will behave differently from a defect-free homopolymer in that (1) the lamellar thickness (i.e., chain axis crystallographic direction) will also be determined thermodynamically by the length distribution of crystallizable defect-free segments rather than solely by kinetic nucleation barriers and that (2) the crystallization process involves an entropic term due to demixing in the melt of pure crystallizable segments from those segments possessing defects. The lamellar thickness has a critical impact on the electronic properties of P3HT because it is by definition the crystal domain size parallel to the polymer backbone, which is thought to be the fastest transport direction for charge carriers.

For P3HT, H–H defects result in a “kink” in the chain (see Figure 1). It is likely that such a kink would be rejected from the P3HT crystal, or, if incorporated, there would be a considerable effect of regioregularity on limiting ultimate crystal lamellar thickness. For simplicity, and based on the geometric perturbation induced by a H–H defect, we are limiting ourselves to a model based on complete exclusion of the defect from the crystal.

**RESULTS AND DISCUSSION**

For our purposes, the parameters of interest in the FCT are the minimum crystal (lamellar) thickness $n^*$ and the equilibrium degree of crystallinity $f_c$ as functions of temperature. $n^*$ and $f_c$ both arise from consideration of the thermodynamically defined distribution of sequences in the melt of a given length $n$ in equilibrium with a crystal of the same size (cf. definition of crystal melting) and the corresponding statistically defined distribution of sequences also of length $n$ available for crystallization in the initial material due to the presence of the noncrystallizing comonomer. To compute $f_c$ and $n^*$ for P3HT, we used the following values as inputs in the model: fold/end surface interfacial free energy $\gamma_s = 3.8 \times 10^{-2}$ J m$^{-2}$, enthalpy of fusion of the perfect crystal $\Delta H_f = 8.3$ kJ mol$^{-1}$, cross-sectional area of a chain in the crystal $A_0 = 3.9 \times 10^4$ m$^2$ mol$^{-1}$, and equilibrium melting temperature of a perfectly regioregular P3HT crystal $T_m^0 =$ 569 K (see Supporting Information).

The applicability of FCT to P3HT crystallization is best tested by comparing experimental differential scanning calorimetry (DSC) data with the change in equilibrium crystallinity with temperature $-d\Delta f_c/dT$, which is closely related to a DSC trace because larger decreases in crystallinity with increasing temperature are analogous to higher heat flows when more crystals melt at a given temperature. To this end, we compare P3HT samples of varying regioregularity ($p$) but with similar number- and mass-averaged molar masses ($\langle M_n \rangle$ and $\langle M_w \rangle$), polydispersity indices (PDI), and prepared by the same synthetic technique to minimize any other potential effects. Table 1 shows the materials studied and the molecular parameters provided by their suppliers. For additional comparison, we have also included P3HT-C, a sample of a lower molecular mass P3HT prepared by a different synthetic method.

In Figure 2, we show $-d\Delta f_c/dT$ calculated using the FCT (as described in the Supporting Information), and the corresponding DSC scans prepared by slow cooling of the samples from the melt, followed by slow heating to minimize superheating effects and to maximize the approach to equilibrium...
conditions.\textsuperscript{14} Before comparing the experimental DSC traces with the theoretical predictions, we corrected the measured heat flow by a factor of $T_m^c / T_m$, where $T_m^c$ is the equilibrium melting temperature for a given copolymer composition, i.e., regioregularity, to account for the melting of thin, imperfect crystallites.\textsuperscript{12} For copolymers, the absence of this correction may result in significant underestimates for the degree of crystallinity. The correction factor was computed using our values for $T_m^c$ and $\Delta H_f^c$ and Flory’s equation for copolymer melting point depression as a function of regioregularity ($p$):

$$\frac{1}{T_m^c} - \frac{1}{T_m} = - \left( \frac{R}{\Delta H_f^c} \right) \ln p$$

where $R$ is the ideal gas constant.

While it is not expected that the DSC traces from the theory ($-df_i/dT$) will exactly match experimental results because we have not reached an equilibrium state, the overall trend in the data is consistent with the theory. With decreasing regioregularity (increasing defect content) the peak of the melting endotherm shifts to lower temperatures, its magnitude decreases, and its breadth increases, as was observed in ethylene–butene copolymers.\textsuperscript{12} The disagreement between the experimental data and the FCT predictions at the highest regioregularity is expected because the normal kinetic barriers to formation of large crystals become increasingly important, thereby effectively “truncating” the full distribution of crystal lamellar thicknesses. We note also for the three lowest regioregularities, P3HT-C, P3HT-94, and P3HT-96, that when the magnitude of $-df_i/dT$ was scaled such that the peak height for $p = 0.937$ matched the DSC heat flow for P3HT-94, the other two P3HT-C and P3HT-96 were similar in magnitude to their respective predictions from the equilibrium theory.

With the applicability of the theory having been demonstrated, its importance to organic thin film transistor (OTFT) or organic photovoltaic (OPV) devices can be shown. In copolymers, crystallites of a given size can form only when sequences of sufficient lengths exist between the noncrystallizing units. Copolymers are different from homopolymers where the equilibrium
lamellar thickness is predicted to be of infinite extent because of a lack of defects. A plot of the equilibrium distribution of crystallite lamellar thicknesses ($n^*$ and $n^*$ times the $c$-axis spacing) for varying levels of regioregularity $p$.

Figure 3. Equilibrium distribution (probability density function) of crystallite lamellar thicknesses ($n^*$ and $n^*$ times the $c$-axis spacing) for varying levels of regioregularity $p$.

are applicable to solution crystallization with the primary difference being the replacement of $T_m^C$ with the equilibrium dissolution temperature of the specific solvent used. For example, the trends and agreement with theory were demonstrated thoroughly for polylactide solution crystallization as a function of noncrystallizing unit. With respect to P3HT, Ihn and co-workers performed solution crystallization studies on P3HT synthesized from FeCl$_3$ via slow cooling from 50 to 25 °C and measured a crystal lamellar thickness of 15 nm. P3HT synthesized in this manner typically has a regioregularity of ≈80%, which corresponds to an equilibrium final melting temperature $T_m$ (see Supporting Information for definition) and $T_m$ computed via FCT of 192 and 232 °C. If it is assumed that the dissolution temperature of 50 °C is somewhere between the equilibrium final dissolution temperature and equilibrium copolymer dissolution temperature, then the lamellar thicknesses predicted by the FCT for a 25 °C undercooling for $T_m$ and $T_m^C$ are 11 and 25 nm, respectively, consistent with the value measured by Ihn and co-workers.

The correlation between the crystal lamellar thickness and regioregularity underscores the importance of reporting the degree of regioregularity in publications on any imperfectly regioregular semiconducting polymer. On the basis of our calculations and observations here, it is one of the most critical material properties because it can produce differences in morphology that may be responsible for variations in device performance among nominally similar P3HTs from different sources.

Ongoing studies in our laboratory are focused on determining accurate values for the thermodynamic and kinetic parameters for P3HT as a function of head–head and tail–tail regiodefects and examining the possibility of these defects being included into the crystal. We will subsequently examine the impact of regioregularity on maximum lamellar thicknesses.

**ASSOCIATED CONTENT**

Supporting Information. Additional details regarding calculations and input parameters and detailed experimental methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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**REFERENCES**

(14) The P3HT-C sample was $T_m^o/T$ corrected using $T_m^o$ of a 91.5% regioregular polymer. The corresponding differential equilibrium crystallinity was computed by assuming a Gaussian distribution $f(x) = (2\pi\sigma^2)^{-1/2} \exp\left[-(x - \langle x \rangle)^2/(2\sigma^2)\right]$ of the regioregularity with a mean $\langle x \rangle$ of 91.5% and a $\sigma$ of 0.75% to give a 2$\sigma$ = 1.5% and summing the discrete values of $f(x)(-df/dT)$ at 90%, 91%, 92%, and 93% regioregularity and then normalizing by dividing by the sum of the $f(x)$.