

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

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S 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.¹ 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^{2–5} (iPP) or DL-poly lactides,^{6,7} 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,⁸ such a material (copolymer) 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 P3HT⁹ 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.¹⁰

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 free energy penalty. For example, only 22% of the regiodefects in iPP are included in the crystal.⁴ Strong partitioning of defects into the noncrystalline regions would underscore the importance of controlling regioregularity in P3HT. As will be demonstrated, its impact on crystallization and melting is significant enough to require properties of interest for P3HT samples or devices to be framed in terms of the degree of regioregularity. For example, 93%, 96%, and 98% regioregular P3HTs cannot be treated as identical, and the differences between them can be determined.

Here, we demonstrate that the trend in melting behavior for a series of different regioregularity P3HT polymers follow qualitatively the predictions from Flory's equilibrium copolymer theory¹¹ as modified by Crist and co-workers^{8,12,13} (FCT). Additionally, we

use this framework to demonstrate the 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 $\sigma_e = 3.8 \times 10^{-2} \text{ J m}^{-2}$, enthalpy of fusion of the perfect crystal $\Delta H_f^0 = 8.3 \text{ kJ mol}^{-1}$, cross-sectional area of a chain in the crystal $A_0 = 3.9 \times 10^5 \text{ m}^2 \text{ mol}^{-1}$, and equilibrium melting temperature of a perfectly regioregular P3HT crystal $T_m^0 = 569 \text{ K}$ (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 $-df_c/dT$, 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 $-df_c/dT$ 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

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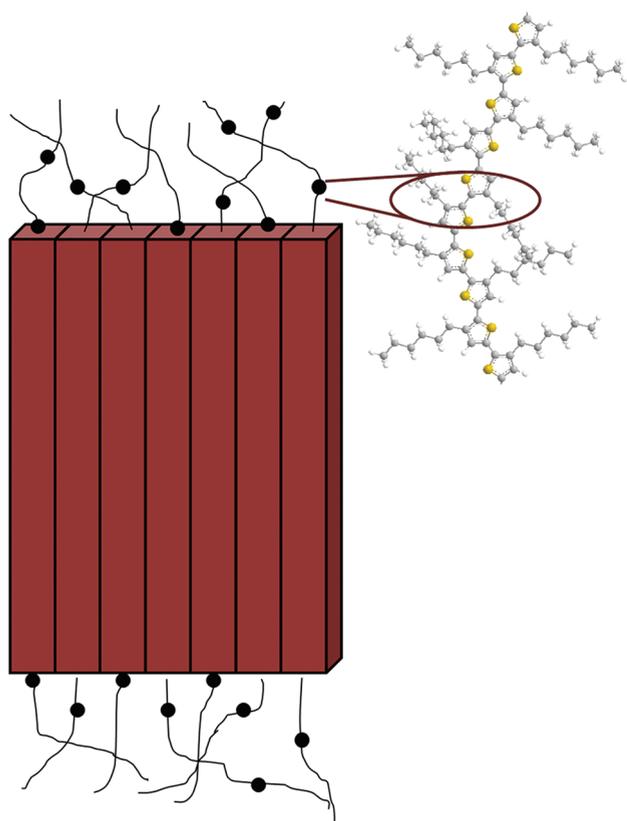


Figure 1. (left) A generalized schematic of the Flory copolymer model where the rectangle indicates a crystalline region made up of defect-free, “A”, segments. The circles indicate the locations of the noncrystallizing “B” defects; the remainder are noncrystalline “A” segments. The expanded view on the right represents a fragment of a P3HT molecule which incorporates (ellipse) a head–head defect that will function as a noncrystallizing “B” defect.

Table 1. Molecular Characteristics of P3HT Samples

sample	$\langle M_n \rangle$ (kg/mol)	$\langle M_w \rangle$ (kg/mol)	PDI	regioregularity (%)
P3HT-94	55.0	120.0	2.18	93.7
P3HT-96	51.6	138.4	2.68	95.6
P3HT-98	55.6	158.3	2.85	97.5
P3HT-C	24.4	51.3	2.1	≈90–93

conditions.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 , 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.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^0 and ΔH_f^0 and Flory’s equation for copolymer melting point depression as a function of regioregularity (p):

$$\frac{1}{T_m^c} - \frac{1}{T_m^0} = - \left(\frac{R}{\Delta H_f^0} \right) \ln p \quad (1)$$

where R is the ideal gas constant.

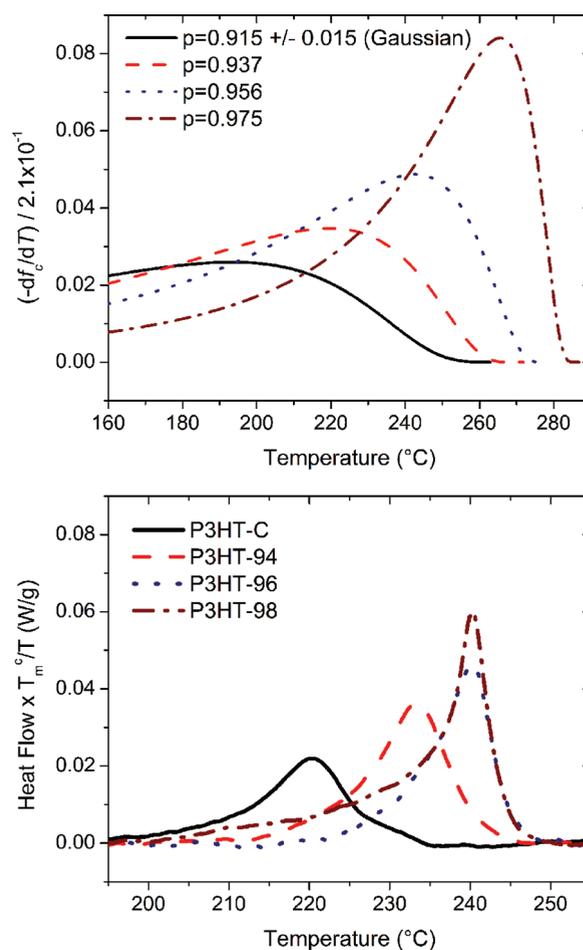


Figure 2. (top) Computed temperature derivative of equilibrium crystallinity (comparable to DSC trace) as a function of crystallizable mole fraction and (bottom) typical DSC traces (endotherm direction is up) for fractions described in Table 1 corrected by T_m^c/T .

While it is not expected that the DSC traces from the theory ($-df_c/dT$) 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.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 $-df_c/dT$ 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

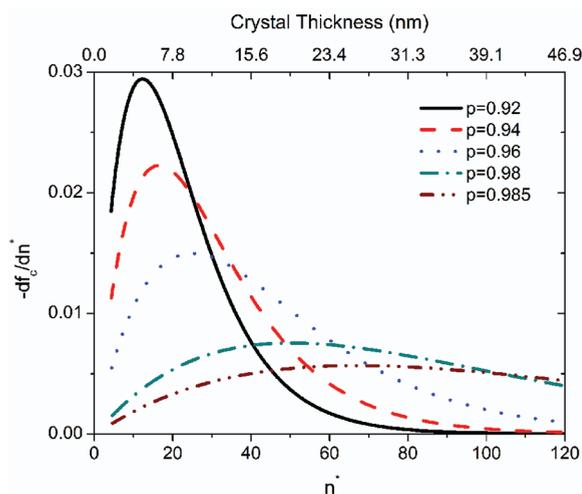


Figure 3. Equilibrium distribution (probability density function) of crystallite lamellar thicknesses (n^* and n^* times the c -axis spacing) for varying levels of regioregularity p .

lamellar thickness is predicted to be of infinite extent because of a lack of defects. A plot of the equilibrium probability distribution of crystals containing n^* repeat units computed using FCT for P3HT is given in Figure 3. As can be seen, the peak maximum, corresponding to the most probable crystal lamellar thickness decreases with increasing levels of defects, and in parallel the lamellar thickness distribution narrows as larger lamellar thicknesses become impossible. For P3HT, the most probable crystal lamellar thickness occurs around 50 repeat units for 98% regioregularity and 70 repeat units for 98.5% regioregularity. These correspond to contour lengths of ≈ 20 or ≈ 30 nm for 98% and 98.5% regioregularities, respectively. This result is intriguing because it correlates well to the typical width of P3HT nanofibrils, such as those observed in a study comparing a series of increasing molecular mass P3HTs.¹⁵ In that study, the width of the nanofibrils, associated with the chain axis dimension, increased linearly with $\langle M_w \rangle$ until an apparent plateau between 7.5 and 11.8 kg mol⁻¹ or a contour length of ≈ 17 –27 nm. The close match between these values cannot be used as a basis for determining the correctness of our choice of input parameters for the model because the regioregularity was not reported for the P3HTs in that study; the paper only stated that the regioregularity was high. However, measurements by Brinkmann and Rannou¹⁶ on an oriented P3HT film of >96% regioregularity yielded a crystal lamellar thickness of 9.1 nm, which also compares relatively well with the FCT model prediction for $p = 0.96$ of 9.9 nm.

These correlations do suggest that the self-limiting P3HT fibril width may be related to its copolymer nature, providing important insight into the control of P3HT morphology in photovoltaics. Currently, for bulk heterojunction blends the desired domain size is thought to be on the order of twice the exciton diffusion length, which is ≈ 3 –10 nm.¹⁷ Therefore, *a priori* control of the crystal lamellar domain sizes through control of the regioregularity to specific levels might enable semiquantitative tailoring of the P3HT crystal domain size as has been postulated and demonstrated qualitatively by Woo and co-workers.¹⁸

Although our conclusions have been drawn based on melt processed P3HT, they are directly applicable to solution processing of these materials because the statistics and thermodynamics

are applicable to solution crystallization with the primary difference being the replacement of T_m^0 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^{6,7} as a function of noncrystallizing unit. With respect to P3HT, Ihn and co-workers¹⁹ performed solution crystallization studies on P3HT synthesized from FeCl₃ via slow cooling from 50 to 25 °C and measured a crystal lamellar thickness of 15 nm. P3HT synthesized in this manner typically²⁰ has a regioregularity of $\approx 80\%$, which corresponds to an equilibrium final melting temperature T_m^f (see Supporting Information for definition) and T_m^c 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^f 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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