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Important thermodynamic characteristics of poly(3-hexyl thiophene)

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ABSTRACT

Poly(3-hexyl thiophene) (P3HT) is widely studied as a model material in many electrical and photovoltaic applications, and has become the benchmark polymer when studying the physics of these devices. Despite its extensive use, its precise crystalline structure and thermodynamic characteristics, such as its enthalpy of melting of an ideal crystal, crystalline density, and amorphous density, are not well characterized. This work seeks to provide more certainty in defining these thermodynamic characteristics for regioregular P3HT. This is accomplished by determining the density of rr-P3HT with various thermal histories, and thus percent crystallinity. These densities are correlated to their melting enthalpy melting (ΔH_m) via DSC. This relationship estimates that ΔH_0 for P3HT is between 37 and 50 J/g, that the density of the amorphous portion of semicrystalline rr-P3HT is 1.094 g/cc, and that the density of crystalline P3HT is 1.12−1.14 g/cc. Interestingly, the density of the amorphous portion of rr-P3HT differs significantly from that of regio-random P3HT. This result indicates that the local packing of the segments differs in regio-random P3HT from that in the amorphous portions of rr-P3HT and that care must be expended when equating the behavior of these two phases.

Poly(3-alkylthiophenes) are of significant interest due to their excellent electrical conductivity, electroluminescence and nonlinear optical properties, resulting in their potential use in applications such as light emitting diodes (LEDs), organic field-effect transistors (OFETs), and organic photovoltaic (OPV) devices. The electrical properties of the polymer depend strongly on stereoregularity, *i.e.* head-to-tail regio-regularity [1], processing solvent [2–4] processing procedure, crystallization conditions [5–7], and molecular weight of the sample [8,9]. Poly(3-alkylthiophenes) are highly anisotropic semi-crystalline materials [10], where charge conduction occurs via intrachain and interchain charge transport in the crystalline portion, while the amorphous portion conducts through hopping or tunneling processes [11,12]. Regio-regular poly(3-hexylthiophene) (rr-P3HT) has emerged as a specific archetype for the evolving field of organic electronics utilizing these materials. Unfortunately, important thermodynamic characteristics of rr-P3HT are still not accurately defined, such as the density of the crystalline phase, the density of the amorphous phase, and the enthalpy of melting an ideal crystal (ΔH_0). The absence of this crucial information hinders the quantitative characterization of the structure of P3HT samples that are used in optoelectronic applications, inhibiting the correlation of performance to structure. For instance, the absence of

an accurate value for ΔH_0 constrains the use of one common analytical technique (differential scanning calorimetry) to determine the percent crystallinity of a P3HT sample. Similarly, imprecise values of the density impede the quantitative analysis of scattering data, where scattering power of each phase is dependent on its density.

There are a number of studies that have attempted to determine the structural and thermodynamic characteristics of P3HT. For instance, Fig. 1 illustrates a model for the P3HT crystal structure, which displays the characteristic distance in the *a-direction* as the segregation between adjacent chains and the $\pi-\pi$ stacking of the planar thiophene backbone in the *b-direction* [13,14]. The *c-direction* describes layer periodicity of the larger lamellar structure. The unit cell is commonly described as orthorhombic, although some investigations show deviations that result in a monoclinic structure [15]. Experiments including x-ray diffraction, density functional theory, and selected-area electron diffraction have all been used to define unit cell parameters [9,15−20] (See Table 1). Contrary to most polyolefins, it is difficult to grow extended lamellar single crystals of P3HT [21], limiting the ability of x-ray diffraction to quantify the absolute crystallinity of a sample. Additionally, it's been reported that the main chain and side chains can display different degrees of order, such as interdigitation [22] and tilting [23] of the alkyl side chains, which contributes to a variation in layer periodicities. Because of this, the structure is described as polymorphic [11,16,23].

This uncertainty in crystal structure leads to ambiguity in the density of the P3HT crystalline phase, and similarly the density of

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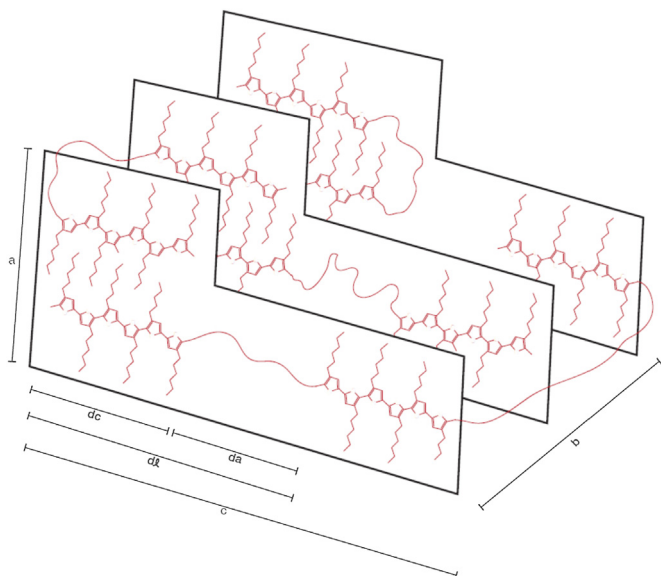E-mail address: Dad@utk.edu (M.D. Dadmun).

Fig. 1. Representation of the packing of P3HT chains into the crystal unit cell.

the amorphous portion of the semi-crystalline polymer. As mentioned above, this uncertainty obscures the accurate analysis of neutron and x-ray scattering curves of P3HT and its mixture with [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) in organic photovoltaics, where an accurate value for the density of the phases is required to quantitatively extract phase composition by modeling the scattering curve [24,25].

Because of the uncertainties in reported crystal structures, the shortcomings of scattering data, and other factors related to the anisotropy of poly(3-alkylthiophenes), it is difficult to define the structural and thermodynamic properties of ideal crystals of this class of polymers, and specifically the highly studied P3HT. For instance, the enthalpy of fusion of an ideal crystal, ΔH_0, of rr-P3HT has been reported to range from 37 to 99 J/g [10,14,26,27] using various experimental techniques. Malik and Nandi used melting point depression in a polymer-diluent system [28] to estimate that $\Delta H_0 = 99$ J/g[14], a commonly cited value in the literature. Pascui and co-workers used 1D and 2D ^{13}C NMR experiments to determine the ordering of the P3HT side chains, establishing a direct method to determine crystallinity. Correlation of these results to DSC estimates that $\Delta H_0 = 37$ J/g[10]. Finally, Snyder and coworkers determined the enthalpy of fusion of a high molar mass 98% regioregular P3HT using a combination of both T1xz and T1r ^{13}C NMR measurements on the backbone. Correlation of these results to DSC measurements provides a value of (50 ± 4) J/g for ΔH_0 [27].

Thus, there is a clear need to more carefully define the densities of the crystalline and amorphous phases as well as the enthalpy of fusion of poly(3-hexyl thiophenes). With this in mind, we have monitored and correlated the density and enthalpy of melting of

P3HT samples that have varying crystallinities. In these experiments, the density is measured by gas pycnometry, using a Micromeretics Accupyc II 1340 and helium as the purging gas. Density is not directly measured, as it is simply the ratio of mass to volume. The instrument measures the three-dimensional volume of space not accessible to the helium. Helium is used not only because of its small atomic radius, which can measure surface roughness with acute sensitivity, but also because it is known to demonstrate permeability through polymers and other low density materials, enabling contributive measurements of closed pores and voids to the overall volume [29]. DSC melting curves were obtained using a Mettler-Toledo DSC821e with a single temperature ramp from 25 to 260 °C at a rate of 20 °C min^{-1}. The analysis of this curve determines the enthalpy of melting, and the extent of crystallinity is varied by thermal history. The DSC curves analyzed in this research program are provided in the Supplementary Information. The correlation between the polymer density and enthalpy of melting allows the critical evaluation of the previously reported crystalline densities, provides a measure of the density of the amorphous phase of rr-P3HT, and more narrowly defines the ΔH_0 of P3HT.

In the analysis of this data, the experimentally measured density of the P3HT is related to the density of the amorphous phase and the density of the crystalline phase by

$$\rho_{\text{meas}} = \phi_{\text{amorph}} \, \rho_{\text{amorph}} + \phi_{\text{cryst}} \, \rho_{\text{cryst}} \tag{1}$$

where ϕ_i represents the mass fraction of phase i, and ρ_i is the mass density of phase i. The melting peak integral in differential scanning calorimetry (DSC) is related to the ρ_{cryst} as $\Delta H_{\text{m}} = \rho_{\text{cryst}} \Delta H_0$. With this relationship, Equation (1) becomes Equation (2), which correlates the measured density of the sample to the DSC determined enthalpy of melting (ΔH_{m}), the densities of the crystalline and amorphous phases, and ΔH_0.

$$\rho_{\text{meas}} = \frac{\Delta H_{\text{m}}}{\Delta H_0} \rho_{\text{cryst}} + \left(1 - \frac{\Delta H_{\text{m}}}{\Delta H_0}\right) \rho_{\text{amor}} \tag{2}$$

This analysis assumes that the crystalline and amorphous phases are separate entities. While this is a reasonable assumption, the amorphous region may influence the crystal-packing in semicrystalline materials. For instance, Wunderlich, et al. have studied semicrystalline poly(trimethylene terephthalate) (PTT) over a wide temperature range [30]. Their results indicate that there are contributions of both rigid and mobile amorphous phase as well as the crystalline phase to the heat capacity. To arrive on these results, they estimate the enthalpy of melting, ΔH_0, near the equilibrium melting temperature and compare that to the heat capacity of a 100% amorphous polymer calculated using the ATHAS addition scheme and by experimental results of the polymer in the melt. Their results mark the change in heat capacity due to the contribution of the rigid amorphous component, which increases as additive contributions from the functional groups move into the amorphous phase, and additionally the additive contributions due to defects. Their results show a lower ΔH_0 of samples containing larger relative amounts of

Table 1
Unit cell parameters of regio-regular P3HT reported in the literature, with the corresponding densities calculated from the unit cell geometry. Taken from Refs. [9,15–20].

Investigator	Method	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Density (g/cc) calculated
Mardalen, 1992	XRD	16.9	4.85	7.84	51.1	90	90	1.11
Prosa, 1992	XRD	16.8	7.66	7.7	90	90	90	1.12
Tashiro, 1997	XRD, computer simulation	16.63	7.75	7.77	90	90	90	1.10
Brinkmann, 2007	SAED	16	7.8	7.8	90	90	93.5	1.13
Maillard, 2009	density-functional theory	15.82	6.84	7.83	90	90	90	1.13
Brinkmann, 2009	electron diffraction	16	7.8	7.8	90	90	86.5	1.14
Colle, 2011	density-functional theory	16.7	7.5	7.9	90.1	89.9	90.2	1.10