## Aggregation and Solubility of a Model Conjugated Donor-Acceptor Polymer

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#### Abstract

In conjugated polymers, solution-phase structure and aggregation exert a strong influence on device morphology and performance, making understanding solubility crucial for rational design. Using atomistic molecular dynamics (MD) and free energy sampling algorithms, we examine the aggregation and solubility of the polymer PTB7, studying how side-chain structure can be modified to control aggregation. We demonstrate that free energy sampling can be used to effectively screen polymer solubility in a variety of solvents, but that solubility parameters derived from MD are not predictive. We then study the aggregation of variants of PTB7 including those with linear (octyl), branched (2-ethylhexyl), and cleaved (methyl) side-chains, in a selection of explicit solvents and additives. Energetic analysis demonstrates that while side-chains do disrupt polymer backbone stacking, solvent exclusion is a critical factor controlling polymer solubility.



In thin-film organic semiconductors, specifically bulk-heterojunction organic photovoltaic (OPV) cells,<sup>1,2</sup> the film morphology is exceedingly complex.<sup>3</sup> The inability to control morphologies of organic semiconductors (OSC) is perceived as a limiting step in the successful commercialization of these materials.<sup>4</sup> While some OSC exhibit glass transition temperatures ( $T_g$ ) below room temperature,<sup>5</sup> many have  $T_g$ 's significantly above 298 K<sup>6–8</sup> and exist in kinetically trapped, glassy morphologies. As solution-deposition is the most common processing route for many OSC, solution-phase conformations may be kinetically trapped into the deposited film morphology.

Evidence has emerged indicating that solution-phase polymer conformations influence the morphologies of thin-films, <sup>9–19</sup> with increases in OSC performance obtained via solutiondeposition at high temperatures<sup>20</sup> or in poor solvents.<sup>21–23</sup> These results are supported by fundamental studies demonstrating solution-phase aggregation of conjugated polymers even in solvents considered "good" in the traditional Flory definition.<sup>24</sup> Indeed, even for short oligomeric chains, optical studies have revealed the occurrence of single-chain folding in oligomers above a critical molecular mass;<sup>25,26</sup> in test systems, the enthalpic contributions to similar processes have been quantified.<sup>27</sup> Side-chain engineering has proven a powerful avenue for manipulating solubilities of conjugated polymers, with branched alkylic side-chains often improving solubility relative to that of chemically equivalent linear side-chains.<sup>28</sup>

Molecular modeling is used here to shed light on the solution-phase conformations of conjugated polymers. While experimental methods can be applied to assess general aggregation trends,<sup>29–31</sup> molecular simulations can reveal the atomistic structure of aggregates that give rise to complex optoelectronic phenomena. We emphasize that in recent studies, atomistic<sup>32–37</sup> and coarse-grained<sup>38–40</sup> simulations have broached the topic of solution-phase conformations of conjugated polymers. However, an understanding of the thermodynamic contributions to conjugated polymer solubility is still lacking.

In this letter we examine the conformations and solubilities of the polymer PTB7 in explicit solvents, and determine the mechanisms by which side-chain structure influences thermodynamics. To assess solubility, we determine the free energy change upon aggregation of pairs of PTB7 oligomers. We validate this approach by comparing free energies to experimental solubilities and find qualitative agreement for a series of common solvents. Model results are also validated against experimental persistence lengths and simulations of 10 repeat unit oligomers. We then study the solubility of three side-chain variants of PTB7: branched (2-ethylhexyl), linear (octyl), and cleaved (methyl), finding that side-chains disrupt the stacking of conjugated polymer backbones, and in the case of branched side-chains, enhance solubility. However, the enhanced solubility is not directly related to the disrupted backbone structure, but rather the destabilization of the solvent associated with the more disordered, bulky structure, similar to mechanisms found previously.<sup>41</sup> These results provide both an experimentally-validated framework for screening conjugated polymer solubility and a means of understanding the structural origin of solubility in conjugated materials.

Three common solvents/additives are studied: chlorobenzene (CB), chloronapthalene (CN), and diiodooctane (DIO). The details of our simulation procedure are described in the Methods and Supporting Information. To summarize: Pairs of PTB7 aggregated oligomers are solvated. Dimers of PTB7 are used for branched and linear side-chains, and tetramers for cleaved side-chains; these degrees of polymerization ensure that the aggregate shows an aligned and stacked structure, as would be seen in a larger polymer. Steered molecular dynamics (MD) is performed to generate initial configurations for free energy sampling, which is performed using replica exchange umbrella sampling, measuring the free energy with respect to the center-of-mass (COM) separation of the two conjugated PTB7 backbones.

Calculated free energies of aggregation ( $\Delta A$ ) are shown in Figure 1, where r is the COM separation, n is the degree of polymerization, and  $L_c$  is the PTB7 oligomer contour length. Free-energies are normalized by the degree of polymerization (n). PTB7 in CB and CN shows a shallow free energy basin with a minimum of  $\approx -8.4$  kJ/mol-n, whereas in DIO it exhibits a deeper basin of  $\approx -25.1$  kJ/mol-n. The deeper free energy basin in DIO indicates that DIO is a worse solvent than both CB and CN. Note that experimentally DIO is never used alone as a solvent, but in our simulations we do so to magnify its effect on PTB7's solubility and avoid complications in the analysis that might arise from a ternary system (e.g. PTB7/CB/DIO) system at small box sizes. Experimentally determined solubilities for PTB7 in CB, CN, and DIO are (>75, >75 and <0.1) mg/mL, respectively. It was not feasible to determine exact solubilities, and solutions with high concentrations of PTB7 were opaque and gel-like. Despite this, experiments clearly differentiate between good and poor solvents, and simulations are in agreement. The two free-energy minima of Figure 1 present at  $r/L_c \approx 0.5$  and  $r/L_c \approx 0.05$  correspond to the dimers having one or both, respectively, of their monomers stacked with the other dimer. This suggests that PTB7 (dis)aggregates via a sliding process, rather than a rotationally isotropic approach. Visual examination of trajectories as shown in Supporting Information supports this hypothesis.

To validate that the previous dimer aggregation simulations capture simulated polymer solubilities more broadly, we also perform MD simulations of single PTB7 10-mers in CB, CN, and DIO. Single PTB7 10-mer chains are initialized in a self-aggregated (folded) state and are run for 100 ns at 300 K to observe the stability of the self-aggregated state. Three replicates are run for each solvent. All 10-mer aggregation results are presented in the Supporting Information. 10-mers disaggregate in good solvents and remain self-aggregated in poor solvents. The 10-mers in CB disaggregate at 4 ns, 10 ns, and 53 ns. Two of three 10-mers in CN disaggregated at 13 ns and 40 ns, while the third remains self-aggregated. All 10-mers in DIO remain self-aggregated. These results are consistent with solubility trends from dimer simulations. From configurations which disaggregate, persistence lengths of PTB7 are calculated to be 4.3 nm and 4.1 nm in CB and CN, respectively, which are in good agreement with previous computational results.<sup>33</sup> Persistence lengths were estimated using the computed bond-bond correlation function and a simple worm-like chain model<sup>42</sup> defined by

$$\langle t_i \cdot t_{i+s} \rangle = e^{-\frac{s*t}{L_p}} \tag{1}$$

where  $t_i$  is the bond vector for PTB7 monomer i, l is the length of a PTB7 monomer, and  $L_p$  is the persistence length. To further validate the computational model, small angle neutron scattering measurements were performed on low molar mass PTB7 ( $\approx 35 \text{ kg/mol}$ ) in d<sup>5</sup>-CB. From these measurements, the persistence length was determined via a flexible cylinder model to be (5 ± 1) nm at 298 K, which is in agreement with our calculated value, particularly since the persistence length is expected to be larger for higher molar masses (see Supporting Information for details on the measurements and fit). These results suggest that dimers capture the relevant polymer behavior to predict solubilities.

Solubility parameters derived from MD simulations are also determined, as explained in the Supporting Information; however, they fail to capture experimental solubility trends.



Figure 1: Free-energy vs COM separation of two PTB7 oligomers with 2-ethylhexyl sidechains in CB, CN, and DIO. Free-energy is normalized by the degree of polymerization (n) and the COM separation (r) by oligomer contour length  $(L_c)$ . Poor solvents yield more stable aggregated states, corresponding to low values of  $\Delta A$  at  $r/L_c \approx 0$ . 95 % confidence intervals are shown.

Having established the accuracy of our free energy calculations, we examine the mechanisms by which PTB7 side-chains influence solubility and aggregation. Simulations of PTB7 are



Figure 2: Representative configurations of PTB7 aggregates with (a) branched (2ethylhexyl), (b) linear (octyl), and (c) cleaved (methyl) side-chains. The aggregate with branched side-chains is poorly stacked while that with linear or cleaved side-chains is wellstacked. These behaviors are quantified through average backbone stacking energies of  $\Delta U =$ (-58, -71, and -88) kJ/mol-n for a), b), and c), respectively.

performed in explicit CB solvent with three different types of side-chains: branched, linear, and cleaved. The branched and linear variants are chosen to conserve carbon atoms (2ethylhexyl/octyl). Representative snapshots of the polymer architectures are shown in Figure 2.

The free energies of aggregation for the PTB7 side-chain variants are shown in Figure 3 a). The free energy minima suggest that PTB7 with linear and cleaved side-chains also aggregate via a sliding mechanism. Branched side-chain PTB7 is more soluble than linear side-chain PTB7, as demonstrated by the 8.4 kJ/mol-n difference in the depth of the free energy basin. This solubility trend is commonly observed in experiments,<sup>28</sup> accounting for the proliferation of polymer architectures with branched side-chains. Curiously, cleaved side-chain PTB7 shows a free energy basin very similar to that of the linear side-chain variant.



Figure 3: a) Free energy b) potential energy and c) entropy vs scaled COM separation  $r/L_c$  of two PTB7 oligomers with three variants of side-chains in explicit CB solvent. All energies are normalized by the degree of polymerization (n). 95 % confidence intervals are shown.

This goes against the intuition that the addition of side-chains reliably increases solubility.

To quantify how side-chain architecture influences solubility, the free energies of aggregation are decomposed into enthalpic and entropic contributions in Figure 3 b) and c), respectively. The linear side-chain variant is the most enthalpically stable, and also exhibits the lowest entropy, suggesting an ordered aggregate, which is corroborated by Figure 2 b). The branched side-chain variant differs, showing the highest enthalpy and the second lowest entropy. The cleaved side-chain variant, on the other hand, shows the highest entropy. This is likely due to the side-chain degrees of freedom being constrained upon aggregation, which does not occur in the cleaved side-chain case. The backbone stacking energy for the three side-chain variants suggests that this entropic difference is not due to backbone stacking disorder ( $\Delta U = -88$  kJ/mol-n vs (-58 and -71) kJ/mol-n for branched and linear, respectively).

Entropic contributions can be attributed to backbone and side-chain disorder, however enthalpic contributions require more study. Figure 4 a) partitions  $\Delta U$  into polymer-polymer interactions shown in solid lines and solvent interactions shown in dashed lines. The negative of the solvent interaction energy is shown. The variant without side-chains shows the smallest  $\Delta U$  for both types of interactions, as it has the fewest atoms. Interestingly,  $\Delta U$  of polymerpolymer interactions is strongest for branched side-chain PTB7, despite showing the highest system  $\Delta U$ . Two features must be explored: first, why does PTB7 with branched side-chains exhibit the strongest enthalpic interactions, and second, how do these stable branched sidechain aggregates lead to a less stable system overall?

The favorable polymer-polymer interactions are not explained by enhanced backbone stacking interactions. Backbone-backbone stacking interactions are calculated as the pairwise interactions between atoms in the thienothiophene and benzodithiophene units. Figure



Figure 4: Potential energy  $(\Delta U)$  contributions of the three PTB7 variants. For all panels, blue, green and red data sets refer to branched, linear, and cleaved side-chain structures. a)  $\Delta U$  of polymer-polymer interactions (solid lines) and the *negative* sum of solvent-polymer and solvent-solvent interactions (dashed lines). The difference between these two is the total  $\Delta U$  of the system. b)  $\Delta U$  of interactions between PTB7 backbones. Results indicate that side-chains disrupt backbone stacking. c)  $\Delta U$  of side-chain-backbone (solid lines) and side-chain-side-chain (dashed lines) interactions. d)  $\Delta U$  of polymer-solvent (solid lines) and solvent-solvent (dashed lines) interactions. 95 % confidence intervals are shown.

4 b) shows backbone-backbone energies for the three PTB7 variants, demonstrating that cleaved, linear, and branched side-chains destabilize aggregates from least to greatest, respectively. These backbone energies do not correlate with polymer-polymer energy (Figure 4 a)), suggesting that while side-chains disrupt  $\pi$ -stacking, this disruption is not directly responsible for the change in solubility.

Figure 4 c) demonstrates that the enhanced stabilization of dimers with branched sidechains originates from increased side-chain-backbone interactions. With the backbone stacking disrupted, the branched architecture of the side-chain can associate freely with the backbone, resulting in strong polymer-polymer interactions within the dimer aggregate.

We now examine the role of solvent interaction energies in Figure 4 d). Solid lines depict the  $\Delta U$  of polymer-solvent interaction energy, and dashed lines the  $\Delta U$  of solvent-solvent interaction energy. The data show that aggregates with branched side-chains interact least favorably with the solvent, despite having the same number of atoms as the linear side-chains. This energetic contribution is largely responsible for destabilizing the system of aggregated PTB7 with branched side-chains. This result suggests that the more disordered aggregation motifs caused by the branched side-chain structures create a less favorable interaction surface for the solvent, which plays a crucial role in determining the solubility of the aggregate. In the Supporting Information it is verified that the absolute, in addition to relative, energies of oligomer-solvent interaction support this idea.

Taken together, these results unveil the intricate behavior of solubility in conjugated polymers. While dogma has held that branched side-chains increase solubility by disrupting backbone stacking, we propose a more subtle picture. While side-chains do disrupt backbone stacking, this does not directly lead to increased solubility. In fact, branched side-chain PTB7 is more stable than linear side-chain PTB7 in the absence of solvent. Rather, the sidechains' effect on solvent interactions dominate the enthalpic contribution to the free energy of aggregation. Entropic contributions can be understood through the lens of side-chaininduced disorder, however these interactions are relatively small compared to the enthalpic contributions. To design materials with higher solubility, we suggest that new designs should include side-chains that maximize polymer disorder to the extent that it disrupts solvent structure. Finally, it is important to emphasize that, even in the solution-phase, side-chain induced aggregation may be under kinetic control. While the calculations performed here shed light on the thermodynamics of this process, future work exploring the kinetics of conjugated polymer aggregation will be critical to further controlling film morphologies. Moving forward, it will be of interest to explore the approaches introduced here to investigate the role of structure or chemical modifications, such as side chains, in aggregation and ultimately the performance of materials.<sup>43,44</sup>

## Methods

Simulations utilize the opls-aa force-field for explicit solvent,<sup>45</sup> and an opls-style atomistic force-field for PTB7 recently parameterized in the literature.<sup>32</sup> This parameterization utilizes opls-aa Lennard Jones parameters that reproduce high-accuracy quantum-chemistry simulations of  $\pi$ -stacking energies to within ~ 1 kcal/mol, and has been validated on a set of experimental thermophysical properties of PTB7.<sup>33</sup> Simulations employ the graphics processing unit (GPU) code DASH.<sup>46</sup> A Lennard Jones interaction cutoff of 1 nm was used for all simulations. Coulombic interactions in the solubility parameter simulations used the damped shifted force with a cutoff of 1.2 nm. Coulombic interactions in the free-energy simulations used a short-range cutoff of 1.2 nm and the particle-particle-mesh formalism for long-range interactions. The Nose-Hoover thermostat was used, with a time constant of 200 fs. Details of the free energy sampling are given in Supplementary Information.

#### **Experimental Solubilities**

Saturated solutions were prepared by mixing an excess of PTB7 with a small volume of each test solvent, (200 to 300)  $\mu$ L, and stirring for 24 h at room temperature. The saturate was

filtered from the solution using a 0.45  $\mu$ m PTFE filter and diluted in ortho-dichlorobenzene (oDCB) to achieve an optical density suitable for ultraviolet-visible (UV-Vis) absorption measurement. Measurements were performed at room temperature using a PerkinElmer Lambda 950 UV/Vis spectrometer.<sup>47</sup> Absorbance was compared to a set of standard curves with known concentrations of PTB7 in oDCB.

#### Measurement of Persistence Length

Small angle neutron scattering (SANS) measurements were performed at the National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR) on the NG7 SANS instrument, and data were reduced and fit to a flexible cylinder model using software described elsewhere.<sup>48,49</sup> Detailed information is provided in the Supporting Information.

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# Supporting Information for Aggregation and Solubility of a Model Conjugated Donor-Acceptor Polymer

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## Supporting Information Available

The following files are available free of charge.

#### Free Energy Sampling

Simulations of the dimer aggregate are initialized at low density and equilibrated for 10 ns at 101.325 kPa (1 atm) with dimers held in a stacked configuration (e.g. see Figure 2 of main text) by a harmonic restraint. The collective variable sampled is the distance between the conjugated backbone center of mass for each oligomer. To create configurations for free energy sampling, steered molecular dynamics (MD) is performed in SSAGES.<sup>1</sup> Steered MD is performed from 3.0 Å to 25.0 Å over 20 ns. Snapshots of initial dimer configurations at a range of separations are shown in Figure 1. Each replicate is steered starting from independent configurations to ensure that samples are independent. Free energy sampling is performed using replica exchange umbrella sampling, also with SSAGES. Umbrella sampling windows are placed from 3.0 Å to the oligomer contour length at intervals of 0.5 Å. A harmonic restraint potential of k=3 kcal/mol is used, and exchanges between neighboring replicas are proposed every 1 ps. 16 independent replicates are averaged for free-energy sampling curve, and each replica exchange window is sampled for a total of 3 ns, totaling  $1.9 \ \mu s$  of simulation time for the shortest oligomers. Standard errors are shown as computed using data from each of the 16 replicates. A weighted histogram analysis method<sup>2</sup> is used to compute the free-energy surfaces of Figures ?? and ??.



Figure 1: Initial dimer configurations at a range of separations. Configurations are prepared as shown in Panel a and steered towards that shown in Panel d.

#### Initialization of single 10-mer configurations

To initialize 10-mer configurations, a single energy-minimized 10-mer was placed in vacuum. Initial dihedral conformations between thienothiophene and benzodithiophene units are chosen to be energy minimums according to the relevant dihedral potential. NVT molecular dynamics was run for 1 ns to allow the 10-mer to self-fold. From there, the 10-mer was solvated and equilibrated at 1 atm for 10 ns. At this point, NVT simulations were run as described in the main text to allow for 10-mers to unfold if energetically favorable. A representative snapshot of a self-aggregated (folded) 10-mer is shown in Figure 2.



Figure 2: Representative snapshot of a self-aggregated (folded) 10-mer. The two ends of the 10-mer are associated on the right side of the figure, while the 10-mer forms a kink on the left side of the figure.

#### 10-mer unfolding behavior

Initially, all 10-mers are self-folded as in Figure 2. To determine unfolding times of 10-mers, pairwise self-interaction potential energies between atoms in single 10-mers are recorded. The results are shown in Figure 3. Each data set represents one independent 10-mer in a bath of solvent. 10-mers are initialized in a self-folded state, corresponding to roughly -500 kJ/mol. Upon unfolding, pairwise energies increase to nearly 0 kJ/mol, demonstrating that the 10-mer no longer interacts significantly with itself.

#### Contour lengths

As described in the main text, contour lengths are calculated based on a worm-like chain (WLC) model. Figures 4 and 5 show the bond-bond correlation function decay and WLC fit for CB and CN. For DIO, the 10-mers did not unfold, so a WLC fit would be in inappropriate. For CN, the WLC fit was done for only replicates 0 and 1, which did unfold. Data is time-



Figure 3: Potential energy of 10-mer self-interaction energies in CB, CN, and DIO. 10-mers are initialized in the folded state and allowed to move freely. Three replicates are run for each solvent. Large changes in the potential energy ( $\sim 500 \text{ kj/mol}$ ) indicate folding/unfolding events.

averaged over 50 ns of simulation time.



Figure 4: Bond-bond correlation function for three independent PTB7 10-mers solvated in CB with WLC fit. Here, all three 10-mers unfold, and all data in included in the WLC fit.



Figure 5: Bond-bond correlation function for three independent PTB7 10-mers solvated in CN with WLC fit. Here, all only two of the three 10-mers unfolded and are included in the WLC fit. The third is not included in the fit.

#### Dimer dissociation by sliding

In the main text, we suggest that dimer dissociation occurs by a sliding mechanism. In Figure 6, we show representative snapshots of this process. Each configuration shows a pair of dimers at center-of-mass (COM) distances ranging  $r/L_c$  ranging from 0.13 to 1.08. In configuration a), dimers are fully associated and fairly well stacked. Moving towards panel f), dimers dissociate one conjugated subunit at a time, showing a sliding mechanism of dissociation.



Figure 6: Stages of dimers dissociation. Moving from Panel a) to f), dimers transition from fully associated and stacked to fully dissociated and unstacked. As can be seen, this occurs by a sliding mechanism.

#### **Computational Solubility Parameters**

Solubility parameters are calculated using an approach in line with previous work, <sup>3,4</sup> in which Equation 1 is directly evaluated. In the expression of Eq. 1,  $E_{x,vap}$  and  $E_{x,liq}$  are the molar potential energy contribution of x (dispersive or electrostatic potentials) in the vapor and liquid phases, respectively, and  $V_m$  is the molar volume of the pure solute.  $E_{x,vap}$  is measured by equilibrating a single molecule in vacuum and measuring the average potential energy contribution of x.  $E_{x,liq}$  is measured by equilibrating a liquid of the molecule and measuring the separate dispersive and electrostatic components. All simulations are maintained at 300 K and 1 atm (101.325 kPa), with data taken over the course of 5 ns for both liquid and vapor simulations. To measure  $V_m$  the molar volume of PTB7, a box of 80 PTB7 dimers are equilibrated at 101.325 kPa (1 atm) for 5 ns, and the appropriate potential energies are measured.

$$\delta_x = \sqrt{\frac{E_{x,vap} - E_{x,liq}}{V_m}} \tag{1}$$

$$\delta = \sqrt{\delta_d^2 + \delta_e^2} \tag{2}$$

To assess the validity of this approach, we compute the solubility parameters of PTB7, CB, DIO, CN, oDCB, and toluene, and compare them to experimental values found in the literature (Table 1). Solubility parameters are computed as described in Methods.

Computed solubility parameters accurately reproduce experimentally observed Hildebrand parameters. The prediction for DIO, on the other hand, is significantly different, possibly because the value from literature is calculated from group contribution methods rather than experiment.<sup>5</sup> To test the ability of classical force-fields to predict the solubility parameters of conjugated polymers, PTB7's solubility parameters,  $\delta_{d,sim}$  and electrostatic  $\delta_{e,sim}$ , are computed. To assess the accuracy of PTB7's solubility parameters, we have compute the solubility radius ( $R_a$ ) of PTB7 in CB, CN, oDCB, Toluene and DIO. It is clear from Table 1 that the computed solubility radii do not accuracy describe the trends in solubility Table 1: Calculated solubility parameters as compared to literature, with  $R_a$  values for PTB7 and each solvent. Literature values of the Hildebrand parameter from experiment and group theory contribution are listed in column  $\delta_{lit}$ . Value for DIO is calculated from group contribution theory while the remainder are determined experimentally, Values of the Hildebrand parameter as calculated in simulation are given in column  $\delta_{sim}$ .  $\delta_{sim}$  is decomposed into two Hansen-like solubility parameters,  $\delta_d$  and  $\delta_e$ , which represent dispersive and electrostatic cohesive energy densities.  $R_a$  is calculated as the geometric distance between PTB7 and each other solvent's solubility parameters. Absolute solubilities  $s_{PTB7}$  were determined as described in the text. Uncertainties are the best estimate of one standard deviation in the experimental uncertainty.

	$\delta_{lit}$	$\delta_{sim}$	$\delta_{d,sim}$	$\delta_{e,sim}$	$R_a$	$s_{PTB7}(\frac{mg}{mL})$
PTB7		18.0	17.5	4.3	N/A	
CB	$19.6^{5}$	19.8	19.3	4.4	3.7	> 75
DIO	$18.8^{5}$	19.6	19.5	1.7	4.8	< 0.1
CN	$20.7^{5}$	20.9	20.4	4.3	5.8	> 75
oDCB	$20.5^{6}$	20.9	20.1	5.8	5.5	
Toluene	$18.2^{6}$	18.7	18.1	4.9	1.3	

observed experimentally. Because of this generally poor performance, we adopt a more sophisticated atomistic simulation methodology to understand the structure and aggregation of PTB7 in explicit solvents. We note that this has no impact on the utility of experimentally derived solubility parameters, which have recently been applied successfully to organic semiconducting materials.<sup>7–9</sup>

#### Small Angle Neutron Scattering (SANS) Data and Fit Results

All measurements were performed under dark conditions due to reports in the literature suggesting that the radius of gyration of a semiconducting polymer chain is reduced in the presence of illumination.<sup>10</sup> Data reduction and correction to absolute intensity was performed using the NCNR macros<sup>11</sup> in IgorPro.<sup>12</sup> Measurements were performed on a special grade of PTB7 obtained from 1-Material with a manufacturer's estimated molar mass of (25 to 50) kg/mol at a concentration of 2 mg/mL in d<sup>5</sup>-chlorobenzene. Measurements were made at 298 K and 308 K. Reduced data for the two temperatures were simultaneously fit (with the contour length and contour length polydispersity constrained to be equal for the two

samples) to a flexible cylinder model in SasView using the DiffeRential Evolution Adaptive Metropolis algorithm (DREAM) fitting engine.<sup>13</sup>SANS Data and the fits using the flexible cylinder model for PTB7 in d<sup>5</sup>-chlorobenzene (d<sup>5</sup>-CB) are shown in Figure 7. The fit results are given in Table 2 below. From the contour length, the molar mass was estimated to be  $\approx 35$  kg/mol, which falls well within the range provided by the manufacturer - further validating the fits. The persistence length ( $l_p$ ) was computed from the Kuhn length ( $l_k$ ) through the following relationship:  $l_p=l_k/2$ .



Figure 7: SANS Data for PTB7 in  $d^5$ -chlorobenzene (2 mg/mL) at a) 298 K and b) 308 K. Lines correspond to the best fit to the flexible cylinder model. Error bars correspond to one standard deviation in the experimental uncertainty.

Table 2: Parameters obtained from fits to SANS data with the flexible cylinder model. SLD is the polymer scattering length density fit parameter (not corrected by sample concentration), Radius is the cylinder radius,  $l_k$  is the Kuhn length, T is the temperature, and  $L_c$  and P.D. are the contour length and contour length polydispersities, respectively, which were forced to be equal for both fits. The scattering length density for the solvent was set to  $4.909 \times 10^{-6}$ as determined from the NCNR scattering length density calculator.

T	$L_c$	$l_k$	P.D.	Radius	SLD	Background
(K)	(nm)	(nm)	ratio	(nm)	$10^{-6}$ (Å)	$(\mathrm{cm}^{-1})$
298	$48 \pm 2$	$10 \pm 1$	$0.5 \pm 0.2$	$1.32\pm0.03$	$4.802 \pm 0.002$	$0.041109 \pm 0.00008$
308		$11 \pm 2$		$1.37\pm0.03$	$4.806 \pm 0.002$	$0.040773 \pm 0.00008$

#### Oligomer-solvent interaction energies

In the main text, polymer-solvent interaction energies are examined, and it is suggested that branched sidechains work to disrupt the ordered solvent structure around the polymer aggregate, increasing its solubility. The energies presented were set to zero at large distances, precluding comparison of overall polymer-solvent interaction strength. Figure 8 shows polymer-solvent interaction energies for polymers with branched and linear sidechains without zeroing the values at large distances. It should be noted that these two variants have the same number of carbon atoms. As can be seen, polymers with branched sidechains interact with the solvent less favorably at all distances, supporting the idea that the branched sidechains work to disrupt these interactions. The effects, however, become enhanced in the aggregate state, leading to increased solubility relative to polymer with linear sidechains.



Figure 8: Polymer-solvent interaction energies. Unlike in the main text, energies here are not set to zero at large distances.

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