

Small-Angle Neutron Scattering of P(NDI2OD-T2) Solutions: Importance of Network Structure for Data Interpretation and Film Morphology

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molecular weight samples. In this way, the scattering patterns of P(NDI2OD-T2) solutions with different molecular weights, different solvents, and at different temperatures can all be adequately modeled and parametrized in terms of varying cylinder length, cylinder width, and mass fractal dimension. To connect the SANS results to thin film microstructure and charge transport, thin films are prepared and studied with atomic force microscopy and organic field effect transistor (OFET) measurements. Significantly, excess network formation in solution is associated with a decrease in the in-plane alignment of polymer chains and decrease in OFET mobility. Thus, while increased aggregation can enhance chain ordering and charge transport in thin films, excess aggregation in the form of a compact entangled network of these aggregates can be detrimental to the formation of ordered structures during solution deposition.

■ INTRODUCTION

Semiconducting polymers are being actively researched with potential applications in polymer solar cells, organic field-effect transistors, and organic electrochemical transistors.¹⁻³ The performance of organic electronics strongly depends on the multiscale morphology of polymer thin films.^{4,5} As such, significant effort has been devoted to optimizing film morphology, including controlling the conformation of polymers in solution prior to deposition into thin films.^{6–8} However, many studies are empirical, focusing on the correlation of the change in experimental parameters such as solvent quality and temperature of the polymer solutions with the morphology of the solid films with little focus in such studies paid to establishing the actual conformational behavior of polymers in solution. The solution-phase behavior of semiconducting polymers has mostly been characterized using optical spectroscopy techniques yielding structural information such as the degree of disorder or aggregation of the polymer chains.^{9,10} While optical spectroscopy is a convenient lab-based technique, the information provided by optical techniques has limited correlation with the solid-state film morphology due to the multilength scale nature of thin film morphology. In general, optical techniques provide structural information on

the molecular scale as they are largely sensitive to short-range interactions between chromophores as well as the local planarity of the backbone.^{9,10} Meanwhile, the morphology of solid-state thin films includes properties such as chain alignment and the length of polymer fibers, which can be on the length scale of hundreds of nanometers to micrometers.⁵ Even in solution, it can be hard for optical spectroscopy to differentiate between different types of aggregates, and thus it provides an incomplete picture of the conformation of polymer particles. A fundamental understanding of the actual conformation of conjugated polymers in solution at larger length scales commensurate with solid-state film morphology is still lacking.

Small-angle scattering techniques based on light, X-ray, and neutron sources are well-suited for characterizing the

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conformation of polymer chains in solution. These techniques are able to characterize the size and shape of objects in solution, enabling the nature and extent of aggregation to be characterized on length scales up to hundreds of nanometers (or even larger). 11,12 Among these techniques, small-angle neutron scattering (SANS) has been used widely in the field of polymer science due to the ability to enhance scattering contrast through deuteration and contrast matching and has recently been applied to study semiconducting polymers.¹¹⁻¹ SANS also circumvents sample beam damage issues frequently faced in small-angle X-ray scattering (SAXS) due to the lower energy of neutrons and lower flux of neutron sources. The neutron absorption cross-section of commonly used chlorinated solvents is also much lower than that of X-rays.^{12,15} SANS also probes several orders of magnitude of length scale ranging from the nanoscale to the mesoscale, which is well suited for semiconducting polymers that self-assemble in solution forming hierarchical structures within these length scales. Qualitative and quantitative structural information at each level of hierarchical structure can be extracted using SANS. For instance, the hierarchical structure of poly(3hexylthiophene) (P3HT) in solutions is reported to comprise molecularly dissolved chains that adopt fully flexible conformations at the smallest length scale, which then aggregate into parallelepipeds and finally form a network structure at the largest length scale.^{13,16,17} The structural parameters of the hierarchical structure, such as the fraction of dissolved P3HT, the cross-sectional dimensions of parallelepiped-shaped P3HT aggregates, and the compactness and mesh size of the network were extracted and found to depend on various factors such as the processing solvent and temperature.^{13,16,17}

While a wealth of structural information is offered through SANS, analysis of SANS data of semiconducting polymers can be complicated and requires careful interpretation because of the complex aggregation behavior of chains. Indeed, semiconducting polymer chains can exhibit multiple different conformations, such as single chains and multichain aggregates, that coexist in the solution, all of which contribute to the scattering patterns.^{13,15} Semiconducting polymers can also form a hierarchical structure, with each level of the structure contributing to the scattering profile.^{13,18–21} Interpreting such scattering data involves several challenges, such as the identification of scattering corresponding to different conformations or structures and the selection of appropriate fitting models. A detailed discussion of the general approach and challenges in analyzing SANS data of semiconducting polymers is provided in the Theory section. These challenges have restricted previous studies, preventing a complete picture of the structure of semiconducting polymers in solution. For instance, SANS data have often been interpreted solely based on the slope, that is, the exponent of the power-law decay of the scattering intensity, typically due to having scattering data with an insufficient q range (e.g., missing out Guinier and Porod regions), rendering the data interpretation ambiguous.^{22,23} Scattering models are also often adopted without full justification or without consideration of the potential appropriateness of other models.^{22,24} Reported fitting results have been found to be inconsistent with the experimental scattering data, such as the absence of Guinier and Porod regions when the contour length and radius of flexible cylinders are reported.^{22,25} Other studies have disregarded the steep scattering feature at low q in data analysis, which is a

strong indication of the formation of large length scale structures such as networks.²⁶ Nevertheless, there have been endeavors toward the proper and careful interpretation of small-angle scattering data which have led to an improved understanding of the solution-phase behavior of semiconducting polymers such as the studies reported by the groups of Segalman,^{14,19} Pozzo,^{13,16,17,21} Gu,^{27,28} and Diao.^{15,29-31} Several studies have further established the correlation of solution-phase chain conformation with solid-state film morphology and electronic properties of the polymers. For instance, Kwok et al. developed models to describe the conformation of donor-acceptor copolymers as coexisting dispersed polymer chains and fibrillar aggregates, both modeled as semiflexible cylinders, along with lamellar stacking order within the aggregates giving rise to the broad high-q structure factor peak commonly observed in small-angle scattering patterns.¹⁵ Using SANS, Liu et al. revealed the multiscale assembly process of poly[2,5-(2-octyldodecyl)-3,6diketopyrrolopyrrole-*alt*-5,5-(2,5-di(thien-2-yl))thieno[3,2*b*]thiophene] (DPPDTT) polymer chains from rod-like chains to parallelepiped-shaped aggregates, with the self-assembly behavior depending on solution temperature and concentration.²⁰ Xu et al. found that the aggregate structure of the isoindigo-bithiophene-based polymer PII-2T could be modulated through the choice of solvent, with the formation of amorphous solution aggregates resulting in significantly improved chain alignment and reduced paracrystalline disorder in solid-state thin films, and ultimately leading to enhanced charge-carrier mobility.²

Poly[N,N'-bis(2-octyldodecyl)naphthalene-1,4,5,8-bis-(dicarboximide)-2,6-diyl]-*alt*-5,5'-(2,2'-bithiophene)] [P(NDI2OD-T2)], also known as N2200, is a high-mobility donor-acceptor copolymer that has been reported to exhibit varying degrees of aggregation in solution depending on many parameters such as the molecular weight, temperature, and processing solvent as probed using optical spectroscopy.^{10,32-36} Aggregates of P(NDI2OD-T2) have been categorized into two forms based on their spectroscopic features, namely aggregate I and II, which are differentiated by their modes of aggregation.¹⁰ Formation of a polymer network in solution is also evident, supported by an abrupt increase in specific viscosity with increasing molecular mass.^{32,37} The solution-phase behavior of P(NDI2OD-T2) has been correlated with solid-state morphology and electronic properties in the literature. For instance, our group reported that the degree of in-plane chain alignment in the film can be improved by promoting aggregate formation through reducing solvent quality³³ or by suppressing aggregate formation in tolerably good solvents through reducing molecular weight,³⁴ which led to improved charge-carrier mobility. Han's group reported the role of the formation of a network structure through multichain aggregation and chain entanglement upon increasing molecular weight in improving charge carrier mobility in transistors and the photovoltaic performance of J51:P-(NDI2OD-T2) blends.^{32,37} Preaggregation of P(NDI2OD-T2) in solution has also been reported as one of the key factors for enabling scalable deposition of aligned films with high charge mobility of up to 6.4 cm² V⁻¹ s^{-1.38} Despite the importance of the solution-phase behavior of P(NDI2OD-T2), there is surprisingly little progress in understanding the exact conformation of P(NDI2OD-T2) in solution. Using SAXS, our group presented evidence that P(NDI2OD-T2) forms extended rod-like aggregates in poor solvents and adopts a



Figure 1. Summary of simulated small-angle scattering patterns of various conformations of polymers that have been reported in the literature, including (a) distinct shapes, (b) flexible polymers, (c) semiflexible polymers, and (d) mass fractals on larger length scale (lower q scale) such as networks and clusters. The bottom panel summarizes the values of the scattering slope associated with each region in a scattering pattern: Guinier, intermediate, and Porod regions. The possible conformations of polymers associated with the value of intermediate-q scattering slope are also summarized. SasView was used to simulate scattering patterns with the following models: polymer excluded volume model for flexible polymers in (b); flexible cylinder model for semiflexible polymers in (c); Guinier–Porod model for a low-q mass fractal in (d). In (d), the scattering profile sum has been offset on the y-scale to visualize the underlying contribution from the scattering profiles of the mass fractal and Gaussian chain.

coil-like conformation in better to good solvents.³³ The formation of extended aggregates in poor solvents was validated in recent modeling work and was rationalized by the formation of multichain aggregates occurring faster than single-chain folding.³⁹ Recent SANS characterizations have reported P(NDI2OD-T2) to be semiflexible, exhibiting worm-like chain behavior in a tolerably good solvent (i.e., *o*-dichlorobenzene).^{40,41}

In this work, we aim to establish a generalized understanding of the structural behavior of P(NDI2OD-T2) polymer in solution. We approach this endeavor by unravelling the solution-phase conformation of polymer chains under the influence of a wide range of processing parameters known to modulate the degree of aggregation as inferred through absorption spectroscopy, namely molecular mass, temperature, and solvent. The solution-phase conformation of the polymer is characterized using SANS complemented by findings from dynamic light scattering (DLS), with critical analysis of SANS data providing unambiguous data interpretation. Using SANS, we provide evidence for the formation of a rod network of P(NDI2OD-T2) in solution that forms for samples with higher molar mass, and extract structural parameters of the hierarchical structure of the network, which exhibits a strong dependence on the solution processing parameters. Compared to previous SANS studies, we find that P(NDI2OD-T2) chains in solution are best described as rigid cylinders rather than semiflexible chains. Furthermore, the low-q scattering data provides direct evidence for the formation of a network of entangled, rigid aggregates, requiring a hybrid model consisting of a Guinier-Porod model to explain network scattering at low q and a cylinder model to explain scattering from individual aggregates at high q. The hybrid model proposed thus enables a global description of the behavior of P(NDI2OD-T2) chains covering variations in molecular weight, solvent quality, and temperature. We also highlight that the information provided by SANS is distinct from that provided by absorption spectroscopy, with SANS providing more complete structural information on polymer aggregates in solution. The conformation of polymer networks in solution is further correlated with solid-state film morphology, which ultimately determines

the performance of transistor devices. Importantly, we find that excessive network formation in solution at high molecular weight impedes the long-range alignment of polymer chains in films, resulting in a decrease in the organic field-effect transistor (OFET) mobility.

THEORY

Analysis and interpretation of small-angle scattering data require an understanding of the expected scattering patterns of an object. For isolated and noninteracting objects, typical scattering patterns exhibit different regions with distinct power-law dependences of intensity decay, starting from (i) a plateau ($I \propto q^0$) in the low-q Guinier region, followed by (ii) an intermediate-q region in which the intensity decay ranges from $I \propto q^{-1}$ to $I \propto q^{-3}$, and (iii) a very steep ($I \propto q^{-4}$) high-q Porod region as shown in Figure 1a.^{11,12}

The Guinier region corresponds to the probed length scale being larger than the largest dimension of the scattering object, whereas the Porod region corresponds to the probed length scale being smaller than the smallest dimension of the scattering object. Accordingly, the crossovers of scattering slope from the intermediate-q region to the low-q Guinier and high-q Porod regions are associated with the largest (e.g., length of a cylinder) and smallest (e.g., radius of a cylinder) dimensions of the object, respectively.

The power-law dependence of scattering in the intermediate-q region provides important information regarding the structure of the object or, in the context of semiconducting polymers, the conformation of polymers at the length scale being probed.¹² For instance, the intermediate region scales according to $I \propto q^{-1}$ for a cylinder (e.g., stiff polymers) and $I \propto q^{-2}$ for lamellae (e.g., sheet-like polymer aggregates), see Figure 1a. For flexible polymers, the power-law dependence ranges from $I \propto q^{-5/3}$ to $I \propto q^{-3}$ depending on the excluded volume parameter, see Figure 1b.¹¹ The high-q Porod region is absent in these SANS patterns as the scattering model (flexible chains with the excluded volume effect) is not derived to fit the high-q Porod region.¹⁹ In the case of semiflexible polymers following worm-like chain behavior (Figure 1c), the scaling in the intermediate-q region ranges from $I \propto q^{-1}$ to $I \propto q^{-2}$ at lower q_i corresponding to length scales larger than the persistence length (L_p) , and then transitions into $I \propto q^{-1}$ at higher q as the chain behaves rod-like on length scales smaller than the persistence length.^{19,42}

The aforementioned values of the power-law exponent of the intermediate-q region are associated with conformations of the polymer at smaller length scales (i.e., higher q) where the polymers exist as single chains or multichain aggregates. Polymer chains/aggregates may entangle to form a network or cluster at a larger length scale, exhibiting mass-fractal-like scattering behavior at lower q (see Figure 1d). The scaling in the intermediate-q region of such mass fractal scattering ranges from $I \propto q^{-1.5}$ to $I \propto q^{-3}$ depending on the compactness of the mass fractal.^{43,44} The values of the power-law scattering slope expected for each scattering region in the SANS pattern for possible conformations of polymer chains at different length scales have been summarized in Figure 1e. Note that the high-q Porod region can have power-law dependence with the slope varying from 3 to 4 depending on the smoothness of the surface of the object (the so-called surface fractals); $I \propto q^{-4}$ corresponds to a smooth surface whereas $I \propto q^{-3}$ corresponds to a rough surface.¹¹ It is important to highlight that all SANS patterns shown in Figure 1 correspond to scattering objects

which are noninteracting. Strongly interacting samples produce a peak in the SANS pattern, which is also referred to as a structure factor peak, with the position of the peak associated with the characteristic distance between the interacting objects following Bragg's law.¹⁵

Due to the complex aggregation behavior of semiconducting polymers in solution, experimental SANS patterns often comprise scattering from more than one scattering object, such as coexisting multichain aggregates and freely dispersed single chains (see Figure 1d), or hierarchical structures (e.g., network- and chain-like scattering from a polymer network). Interpreting such scattering data involves several key challenges including the identification of scattering contributions from different structures and the selection of appropriate fitting models. Identification of scattering is straightforward for structures with a significant difference in length scales because the corresponding scattering features are well-separated on the q scale, such as the example shown in Figure 1d.^{20,21,43} However, it is challenging when different structures have similar length scales as the scattering features overlap on the qscale. Such a case is frequently observed for semiconducting polymers. For instance, when polymer chains aggregate through $\pi - \pi$ interactions into a sheet-like structure, scattering from the aggregate and single polymer chain overlap in the high-q region because of the similar thickness of the sheet-like aggregate and the radius of the single polymer chain.⁴⁵ In this instance, access to clean, reference solutions in which only one form of structure is present, i.e., either aggregate or single chain in this case, to provide reference scattering patterns for deconvolution is highly beneficial.^{15,19} The scattering from each structure then needs to be identified for the different scattering regions of the pattern (i.e., Guinier, intermediate and Porod regions) based on characteristic power-law dependences. A plateau $(I \propto q^0)$ corresponds to a Guinier region, a slope ranging from 1 to 3 suggests an intermediate-q region, whereas a steep slope ranges from 3 to 4 suggests a Porod region. The incoherent scattering background at high q needs to be fitted when determining the scattering slope to obtain a reliable estimate of the value of the slope. Being able to identify the intermediate-q region plays a key role in identifying the possible conformations of polymer chains, as summarized in Figure 1. An appropriate scattering model is then selected based on the intermediate-q slope, which needs to be done cautiously as one value of the slope can be associated with more than one conformation. For instance, $I \propto q^{-2}$ scaling may be associated with a Gaussian chain, sheet-like aggregate or a network-like mass fractal. In such cases, additional information is needed to discern the most plausible conformation, such as the trend of the intermediate-q slope with experimental parameters (e.g., temperature) or prior knowledge of the solution-phase structure acquired from other methods (e.g., structure, flexibility or aggregation tendency of the chains characterized using TEM or atomic force microscopy (AFM) of freeze-dried samples). The scaling of the intermediate-q scattering behavior also helps to discern the most appropriate model. For instance, $I \propto q^{-2}$ scaling at a low-q scale is more likely to be associated with a network-like mass fractal than a Gaussian chain, as the corresponding length scale is too large to be associated with the dimensions of the single polymer chain.

RESULTS AND DISCUSSION

P(NDI2OD-T2) polymer solutions were prepared from four batches of number-average relative molecular masses ($M_n = 13$, 28, 45 and 67 kDa, see Table S1 in the Supporting Information for the properties of these polymers) using three processing solvents (toluene (Tol), chlorobenzene (CB), and *o*-dichlorobenzene (DCB)) and three solution temperatures (25, 80, and 110 °C), totaling 36 solution samples for the investigation of the behavior of P(NDI2OD-T2) polymers in solution. Note that the boiling point of toluene is reported to be 110.8 ± 0.2 °C.⁴⁶

UV-vis absorption measurements were performed for polymer solutions for all molecular weights, solvents, and temperatures, with a solution concentration of 0.02 g/L unless stated otherwise. The resulting absorption spectra are shown in Figure S1, with representative spectra presented in Figure 2a



Figure 2. Characterization of aggregate information using absorption spectroscopy. (a) Example UV-vis absorption spectra of P(NDI2OD-T2) solutions of disordered and aggregated chains, as observed for the 13 kDa polymer in CB at 80 °C and the 67 kDa polymer in Tol at 25 °C, respectively. Structure of P(NDI2OD-T2) is shown in inset. (b) Fraction of chromophore aggregation inferred from the absorption spectra. Note that all polymers are completely disaggregated in CB at 110 °C, and in DCB at 80 and 110 °C, having a fraction of aggregate = 0 [the star at the lower right-hand corner in (b)].

showing the features characteristic to P(NDI2OD-T2), which comprise a high-energy $\pi - \pi^*$ transition band centered around 390 nm and a low-energy charge-transfer (CT) transition band between 450 and 900 nm.¹⁰ The nature of the CT peak depends on the conformation of polymer chains in solution. Having a broad featureless peak centered around 600 nm (e.g., 13 kDa polymer in CB at 80 °C) is associated with a molecularly dissolved chains with a disordered backbone conformation—the polymer chain is completely disordered or disaggregated. On the other hand, having well-structured vibronic peaks around 710 and 815 nm, resembling the absorption of P(NDI2OD-T2) in solid-state thin films (e.g., 67 kDa polymer in Tol at 25 °C), is associated with aggregation.¹⁰ The extent of chain aggregation can be inferred from the relative absorption strength of peaks associated with disordered and aggregated chains through absorption spectra deconvolution, as shown in Figure S2, with the calculated fractions of aggregate summarized in Figure 2b.^{10,47} Overall, these measurements show that the extent of chain aggregation is tuned by the parameters investigated in this work; that is, chain aggregation increases with increasing molecular weight, decreasing solvent quality (the quality of solvent decreases in the following order: DCB to CB to Tol) and decreasing temperature.

Absorption spectroscopy, however, provides an incomplete picture of the conformation of the polymer chain as aggregate information inferred from this technique is limited to small length scales similar to the chromophore size. For example, such information does not distinguish whether the aggregation is an intra- or interchain (multichain) phenomenon. Chromophore aggregate information on such a small length scale also may not be correlated directly with the chain conformation on a much larger nanoscopic or microscopic length scale, which is more relevant to the solid-state film morphology and electronic properties. For instance, a comparison of concentration-dependent absorption spectra of 67 kDa polymer solutions (Figure S3) suggests that the degree of aggregation remains similar going from a solution concentration of 0.02 to 2 g/L. In reality, a pronounced change in viscosity is evidenced by the fact that the 67 kDa solutions form a gel at 2 g/L, indicating that chain conformation on a much larger length scale such as chain entanglement and network formation is not captured by absorption spectroscopy.

Characterization of Solution-Phase Aggregation. To reveal the conformation of P(NDI2OD-T2) chains in solution on the length scale of the size of the chains, SANS was performed on P(NDI2OD-T2) with different molecular weights, in different solvents and at different temperatures. Deuterated solvents were used to improve the contrast for coherent scattering and to suppress the incoherent scattering originating from the hydrogen atoms in the solvent. Polymer solutions of 2 g/L concentration were used to improve the signal-to-noise ratio of the scattering patterns while still keeping the probability of multiple scattering events low.

Figure S4a shows typical raw SANS patterns for P(NDI2OD-T2) in solution, characterized by a decaying intensity with increasing q (for $q < 0.2 \text{ Å}^{-1}$), which is the qdependent coherent scattering originating from the conformation of the polymer chain in solution, and a mostly flat scattering background for q > 0.2 Å⁻¹ which is dominated by the *q*-independent incoherent scattering from the solvent. The presence of such a strong background in the scattering pattern results in a lower effective slope in the intermediate q region, as elucidated in Figure S4b. Accurate determination of the slope of the intermediate-q regime is highly critical for identifying possible conformations of polymer particles at different length scales (Figure 1); see the detailed discussion in the Theory section. Slope values for the intermediate-q region estimated from the raw SANS data were found to range from 0.4 to 0.8, which is lower than the theoretical lower limit of 1, indicating a strong contribution of background scattering in the raw data. A

strong background could also overshadow scattering signals in the Porod region, as shown in Figure S4b, which complicates preliminary analysis on the smallest dimensions such as the rod diameter. Therefore, the raw SANS patterns were corrected for the scattering background through subtraction of a constant over the entire q range to enable a more accurate qualitative interpretation of the scattering patterns (see further details in Figure S4). We note that the choice of the incoherent background in this data correction step is arbitrary; subsequent quantitative structural information was extracted by fitting the background-corrected data using an appropriate structural model with a background term included to account for the actual incoherent background. This data correction step, however, greatly facilitates preliminary analysis of scattering patterns through visualizing the key features of SANS patterns such as scattering regions (e.g., Porod region), slope crossovers, and scattering slopes in the intermediate q region, as shown in Figure S4c. In this manuscript, the SANS patterns being presented are the background-corrected patterns.

Overview of Scattering Features of P(NDI2OD-T2) in Solution. Figure 3 shows typical scattering patterns of



Figure 3. Overview of the SANS data of P(NDI2OD-T2) polymer in solutions as a function of molecular weight, using Tol and 25 °C temperature as an example. With increasing molecular weight, the high-q region displays similar scattering behavior while the low-q region displays an intensity upturn. A similar trend is observed for polymer solutions in other solvents and temperature as shown in Figure S5, indicating generalized conformational behavior of P(NDI2OD-T2) in solution.

P(NDI2OD-T2) solutions as a function of molecular weight, using toluene solvent at room temperature (25 °C) as representative SANS data. In general, variations in scattering intensity of over an order of magnitude are observed, covering more than 2 orders of magnitude in q. Systematic trends in scattering patterns can be observed as a function of molecular mass. Specifically, similar scattering features are observed in the high-q region (q > 0.1 Å⁻¹) indicating that polymers with different chain lengths adopt similar structure on smaller length scales. This region is likely the Porod region as the power-law exponent is the steepest over the entire q range, indicating that the crossover of the scattering slope at $q \approx 0.1$ Å⁻¹ provides information on the smallest dimension of the scatterer. On the other hand, distinct scattering features are

observed in the low-q region (q < 0.015 Å⁻¹), indicating structural differences on larger length scales with varying chain length. The lowest molecular mass batch (i.e., 13 kDa) exhibits a plateauing of the scattering intensity corresponding to a Guinier region, whereas the higher molecular mass batches (i.e., 45 and 67 kDa) exhibit an obvious intensity upturn below $q = 0.015 \text{ Å}^{-1}$ with a fitted power-law exponent of about 2. This slope of scattering in the low-q region is steeper than that of the intermediate-q region (0.015 < q < 0.1 Å⁻¹), which ranges between 1 and 1.3. A similar trend in SANS data, that is, having an intensity upturn at low *q* for larger molecular weights and similar high-q scattering, was consistently observed for other solvents (CB and DCB) and temperatures (80 and 120 °C), as shown in Figure S5, suggesting similar conformational behavior of P(NDI2OD-T2) regardless of solvent and temperature.

The analysis of the scattering patterns was approached by first understanding the origin of the intensity upturn at low q, i.e., whether it is associated with scattering from freely dispersed, individual polymer particles or due to the presence of a hierarchical structure. In the case of the former, scattering should originate from isolated polymer particles that adopt a semiflexible conformation; the steeper slope of 1 to 2 in the low-q region (q < 0.015 Å⁻¹) and the slope of about 1 in the intermediate-q region $(0.015 < q < 0.1 \text{ Å}^{-1})$ suggests a semiflexible conformation on larger length scales with a rigid conformation on smaller length scales (Figure 1c). However, fitting the data assuming a semiflexible conformation yields an unsatisfactory residual plot as shown in Figure S6, indicating that the intensity upturn at low *q* cannot be fully explained by a semiflexible conformation. Instead, a hierarchical structure that has two levels of structure better explains the observed SANS data, with the intensity upturn at low q originating from the larger length scale feature of a hierarchical structure such as network formation through entanglement or overlapping of chains/aggregates.^{13,48-51} The formation of a network structure would also be consistent with the observation that 2 g/L solutions form gels. The possibility that this low-q feature originates from two-dimensional sheet-like aggregates⁴² is discounted as such structures should give a fixed slope of 2, but the fitted slopes in the low-q range vary between 1.7 and 2.1 (see Figures 3 and S5). Therefore, the intensity upturn at low q is attributed to the formation of a polymer network in solution, with the slope ranging from 1.5 to 3 depending on the compactness of the network (Figure 1d).^{13,16,17,48} At small enough length scales where only the substructure of the network is probed (instead of the network itself), the scattering behavior becomes similar to that of the conformation of freely dispersed polymer particles.

The SANS profiles of the 13 kDa batch consistently show no upturn at low q (see Figures 3 and S5), which is consistent with the short chains of this batch not being able to support network formation. Observing a flat Guinier scattering behavior instead of an intensity upturn at low q supports the idea that these solutions contain freely dispersed polymer particles with the global size of these particles captured in the Guinier region at low q. The slope of the intermediate-q region describes the conformation of these free polymer particles, whereas the slope crossover of the intermediate to Porod region at $q \approx 0.1$ Å⁻¹ corresponds to the smallest dimension, most likely the cross-sectional dimension of the chains/ aggregates. Importantly, the similar slope of the intermediate-qand high-q scattering features regardless of the molecular weight indicates that the conformation and cross-sectional dimension of the substructure of the network are similar to those of freely dispersed polymer particles. In the following, we use the 13 kDa data to identify an appropriate model to describe polymer particle scattering, which is dominant in the high-q region, and then extend the model to include network scattering, which is dominant in the low-q region.

Analysis of Multichain Aggregate Scattering Behavior. Analysis of the scattering behavior of freely dispersed polymer particles was based on interpretation and fitting of the 13 kDa data, as shown in Figure S7. The scattering slope in the intermediate-q region $(0.025 < q < 0.07 \text{ Å}^{-1})$ was found to range from 0.9 to 1.1. Comparison of these values to the expected slope for different conformations (Figure 1) clearly shows that an elongated cylindrical shape best describes the polymer conformation, as confirmed by the satisfactory fit of the scattering data to the cylinder model in all solvents and temperatures (Figure S7);⁵² details on the fitting of scattering data can be found in Section S1 in the Supporting Information. While the possibility of semiflexibility has been reported in the literature, 15,20,21 fitting of the SANS data assuming a semiflexible conformation returned Kuhn lengths similar to the contour length along with a large uncertainty (Figure S8b), confirming that the polymer particles are essentially rigid. The possibility of a flexible conformation was also excluded as the experimental scattering slope is too shallow as compared to the expected values (ranging from 1.67 to 3; see Figure 1). It is worth noting that fitting of the 13 kDa Tol samples in the highq Porod region can be slightly improved by using a parallelepiped model with an anisotropic cross-section (Figure S8c), which may better represent the triclinic crystal structure of P(NDI2OD-T2) in the solid state.⁵³ However, the lack of fine details in the Porod region does not allow for a robust fit of cross-sectional dimensions. The simpler cylinder shape was thus adopted to capture the cross-sectional dimension of the polymer particles with increasing temperature.

Figure 4 summarizes fitted cylinder dimensions for the 13 kDa batch for all solvents and temperatures. The suitability of the cylinder model to describe the scattering data is further confirmed by the values of the fitted cylinder dimensions, which are physically reasonable when compared with the expected dimensions of a single rigid polymer chain. Specifically, the fitted lengths fall within the reasonable range of the simulated contour length of about 17.6 nm and the fitted diameters are also larger than the smallest cross-sectional dimension of a single P(NDI2OD-T2) chain, which is the π stacking distance of about 0.4 nm. Insight into the conformation of these individual polymer particles in solution is revealed from the trend of cylinder dimensions with temperature and solvent. At 25 °C, cylinder lengths were found to be considerably longer than the simulated length of a single chain regardless of the solvent, indicating that the rodlike polymer particles that are freely dispersed in solution as observed in SANS are likely to be multichain aggregates instead of single polymer chains.³⁹ The formation of aggregates is also confirmed by the decrease in cylinder length with increasing temperature, which indicates disaggregation of these multichain aggregates. The dominant mode of aggregation, whether it is through lamellar or π -stacking, can be inferred from the trend of cylinder diameter with increasing temperature. As shown in Figure 4c, the cylinder diameter exhibits an overall decreasing trend with increasing temperature except in DCB, where it remains relatively constant. This observation is



Figure 4. Modeling scattering of freely dispersed polymer particles. (a) Representative SANS data of the 13 kDa polymer at 25 °C fitted with the cylinder model. Summary of fitted (b) length, L_{Cyl} , and (c) diameter, D_{Cyl} of the cylinder for the 13 kDa polymer in all solvents and temperatures.

further evidence for the formation of multichain aggregates as one may expect an increase in diameter for single chains due to expanding side chains with increasing temperature.⁵⁴ We were unable to associate the cylinder diameter with the exact crosssectional dimensions of P(NDI2OD-T2), whether it is the dimension along lamellar and π -stacking directions; or the fitted cylinder diameter represented the value averaged from these two cross-sectional dimensions. However, from simulations of the aggregation behavior of P(NDI2OD-T2) chains in solution, aggregation predominantly occurs via π -stacking interactions of the naphthalene diimide groups.³⁹ The decrease in the cylinder diameter with increase temperature for Tol and CB can be understood in terms of disaggregation along the π stacking direction, consistent with the small decrease in the cylinder diameter of up to 0.9 nm; disaggregation along the lamellar stacking direction would have resulted in a larger reduction in diameter of at least 1.1 nm (see further explanation in Figure S9). For the case of DCB, the situation is potentially more complicated. We posit that the overall larger diameter in DCB compared with CB and Tol is due to the more swollen nature of the aliphatic side chains in DCB,



Figure 5. Modeling rod networks of P(NDI2OD-T2) in solution. (a) Representative SANS data fitted with the rod network model; scattering data for 67 kDa has been offset in *y*-scale for clarity. Schematic illustrations of the conformation of P(NDI2OD-T2) in solution (b) without and (c) with network formation. Without network formation, the multichain aggregates are freely dispersed [e.g., 13 kDa in Tol at 25 °C in (a)] and the fitted L_{Cyl} corresponds to the finite length of aggregates. With network formation [e.g., 67 kDa batch in Tol at 25 °C in (a)], the fitted L_{Cyl} corresponds to the maximum length of the polymer aggregates being observed as rigid rods before overlapping or entangling to form the network. At a larger length scale (orange circle), network scattering behavior becomes dominant, with the fitted D_m corresponding to the compactness of the network. Fitted structural parameters of the rod network are summarized for (d) D_{Cyb} (e) L_{Cyb} and (f) D_m for polymer solutions at 25 °C.

with contrast in SANS especially sensitive to scattering from the hydrogen-rich side chains. Further solvation of the side chains with increasing temperature in DCB solvent then balances out the decrease in diameter caused by disaggregation along the π -stacking direction. From the above-mentioned analysis, an important insight into the conformation of P(NDI2OD-T2) in solution is revealed, that is the freely dispersed rod-like polymer particles correspond to multichain aggregates instead of single polymer chains. These aggregates are formed via π - π stacking, with the number of π -stacks within the aggregate being highest in toluene, followed by CB and is lowest in DCB. This difference in solution-phase polymer conformation has an important implication for the solid-state microstructure, as will be discussed in subsequent paragraphs.

Analysis of Rod Network Scattering Behavior. Having modeled the scattering of multichain aggregates at high-q as rigid rods, we proceed to identify an appropriate model to describe network scattering, which dominates scattering at low q. Network scattering has been described as mass fractal scattering following a simple power-law behavior. The fitted power-law slope is termed the mass fractal dimension, $D_{\rm m}$ which corresponds to the compactness of the mass fractal (i.e., polymer network in the current work). D_m takes values ranging from 1.5 to 3, with a higher value indicating a more compact polymer network and vice versa.^{13,18,48,49} The suitability of the power law to describe network scattering was validated by fitting the data with strong network scattering character (e.g., the 67 kDa batch in CB at 25 °C) using the power law combined with the cylinder model, as shown in Figure S10a(ii). The fit result shows satisfactory quality, confirming that the intensity upturn can indeed be rationalized by a power law. However, a less satisfactory fit is observed when fitting the data with weaker network scattering contributions such as in the 67 kDa batch in CB at 120 °C, as shown in Figure S10c(ii).

Specifically, the downward trend in the residual plot observed at low q below 0.01 $Å^{-1}$ means that the slope of network scattering does not persist down to the lowest q value but becomes shallower. The reduced slope of network scattering at low q can be accounted for by introducing a flat Guinier term before the power law term in the form of a Guinier-Porod plot⁵⁵ and the fit result can be interpreted according to the mass fractal scattering concept introduced by Teixeira.44 Briefly, the Guinier-Porod plot comprises a generalized Guinier term at low q and a power-law type Porod term at high q, as shown in Figure S11. The Guinier plateau $(I \propto q^0)$ relationship) is achieved by fixing the dimension variable, *s*, in the Guinier term as 0. The fitted Porod exponent, $D_{\rm m}$, is the mass fractal dimension of the polymer network. A detailed discussion on the use of this plot to model network scattering and the associated subtleties in modeling is presented in Section S1 in the Supporting Information. Figure S10 shows that the use of the Guinier-Porod plot instead of the simpler power law to describe polymer network scattering significantly improves the fit quality for many data sets, which enabled more reliable extraction of critical network parameters such as the length of the cylinder, L_{cyl} , and the mass fractal dimension, D_{m} .

Having the Guinier–Porod model to describe network scattering and the cylinder model to describe scattering of rodlike multichain aggregates, a complete picture of the conformation of P(NDI2OD-T2) in solution is established; that is, P(NDI2OD-T2) forms a network of rods in solution. All SANS data have been fitted with a hybrid model combining the Guinier–Porod and cylinder models, hereafter referred to as the rod network model. A similar hybrid model has been reported in the literature to model a branched system of worm-like chains.⁵⁶ Note that the "additive" nature of this model does not imply a physical mixture of two species. The "additive" relationship used in the model applied here rather reflects the fact that scattering is dominated by the shape of the



Figure 6. Summary of results of fitting of SANS data to the rod network model for all polymer solutions, showing the trend of $D_{cyb} L_{cyb}$ and D_m as a function of molecular weight, processing solvent and temperature.

polymers a short length scales (high-q) and by the density fluctuation from their resultant network at low-q, see Figure 5c. Polymer networks with structural inhomogeneity have been well-studied with scattering methods by the traditional polymer research community with real-space images also reported.^{18,57,58} Full expressions of the rod network model and its physical interpretation can be found in Section S1 in the Supporting Information. Parameters being fitted include the length, L_{cyl} , and diameter, D_{cyl} , of rod-like multichain aggregates, and the mass fractal dimension, D_m , and characteristic distance, ξ , of network scattering. Details on the fitting of scattering data can be found in Section S1 in the Supporting Information.

Representative fits of scattering data with the rod network model are presented in Figure 5a. SANS data for polymers that do not form a network but are freely dispersed in solution (e.g., the 13 kDa batch in Tol at 25 °C) were fitted only with the cylinder model without a contribution from network scattering (setting the scale factor of network scattering, k_2 , to 0). The fitted L_{cyl} corresponds to the length of dispersed rod-like multichain aggregates (see Figure 5b). When the data is fitted with the rod network model (e.g., for the 67 kDa batch in Tol at 25 °C), the fitted L_{cyl} corresponds to the maximum length of aggregates being observed as rigid rods before overlapping or entangling to form the network (see Figure 5c).

A summary of the fit results is shown for the samples at 25 °C in Figure 5d–f and Table S5. As expected, the compactness

of the rod network indicated by the mass fractal dimension, $D_{\rm m}$, increases with chain length due to the increased likelihood of overlapping or entanglement of multichain aggregates. Note that $D_{\rm m}$ for the 67 kDa batch in DCB at 25 °C exceeds 3, the higher limit of a mass fractal dimension, indicating that low qscattering for this sample may originate from surface fractal scattering (slope ranges from 3 to 4 as shown in Figure 1e) of large network aggregates such that only the Porod scattering of the network is captured. On the other hand, network scattering is absent for batches with shorter lengths, meaning that the aggregates become isolated and freely dispersed such as in the case of the 13 kDa batch. Multichain aggregates in DCB are observed to remain isolated up to a length of 45 repeat units. This observation is consistent with DCB being the best of the three solvents, that is having the most favorable polymersolvent interaction and the least favorable polymer-polymer interactions. Therefore, the aggregates in DCB are least likely to interact to form a network. The cylinder diameter is observed to be similar, with no systematic trend across all solvents and molecular weights, ranging from 2.4 to 3.4 nm, which is consistent with the previously reported diameter for P(NDI2OD-T2).^{40,41} The length of the cylinder, L_{cyl} , however, exhibits an interesting trend as a function of chain length. L_{cyl} is initially proportional to the chain length for all solvents up to 28 repeat units. Divergence among the different solvents is then observed upon a further increase in molecular weight. Specifically, L_{cvl} continues to increase linearly for DCB,

consistent with aggregates remaining dispersed as rigid rods. On the other hand, L_{cyl} becomes shorter in Tol and CB, which can be attributed to network formation due to interactions between the multichain aggregates such as chain folding, entanglement, or overlapping. Further network formation at 67 kDa results in a more compact network (high D_m) and lower L_{cyl} for all solvents, with a similar L_{cyl} observed for both Tol and CB. A systematic trend can be observed whereby L_{cyl} of aggregates is consistently longer in Tol than in CB, suggesting that the aggregates are stiffer in Tol and less likely to fold during network formation. In general, D_{cyl} shows a lack of correlation with the network parameters (i.e., D_m) upon network formation while L_{cyl} is found to correlate strongly with D_m where a more compact network (higher D_m) results in shorter L_{cyl} .

In addition to the molecular-weight dependence of the conformation of the rod network at 25 °C, the temperature dependence of the network conformation was also studied, as shown in Figure 6. As expected, higher temperatures reduce the compactness of the network, as reflected by the lower values of $D_{\rm m}$ and the lower likelihood of network formation, as in the case of the 28 kDa polymer in Tol. $L_{\rm cyl}$ exhibits an overall decreasing trend with increasing temperature, which can be associated with the disaggregation of multichain aggregates. Multichain aggregates in DCB are revealed to remain dispersed up to 45 kDa. Additionally, the aggregates are found to be stiff in DCB as the SANS data can only be fitted with a stiff cylinder model, not a flexible cylinder model.

Comparison of the solution-phase behavior of P(NDI2OD-T2) extracted from SANS with that from absorption spectroscopy reveals discrepancies in the information provided by these two techniques. For instance, $L_{\rm cyl}$ of the rod networks at 25 °C exhibits a complex relationship with molecular weight and solvent (Figure 5), whereas absorption spectroscopy infers a simple relationship, that is, an increasing degree of chromophore aggregation with increasing molecular weight regardless of the solvent (Figure 2). In another example, absorption spectroscopy infers that the chains are already completely disaggregated for the 13 kDa polymer in CB and DCB at 80 °C (Figure 2), but SANS suggests that further disaggregation occurs upon heating above 80 °C up to 110 °C, as indicated by a further decrease in diameter and length of multichain aggregates (Figure 4). Fitted cylinder dimensions at 110 °C are larger than that of a single chain indicating that the chains are still aggregated. These findings show that being "dissolved" as inferred from absorption spectroscopy does not mean the chains are fully dissolved in solution. There may, however, be a small fraction of molecularly dissolved polymers that lies below the detection limit of SANS. However, the presence of these dissolved polymers is unlikely to affect the SANS findings in this work as the SANS data is sensitive to the majority fraction of polymers that are aggregated. With the comparisons presented, it becomes apparent that absorption spectroscopy is not an accurate representation of the actual conformation (i.e., molecularly dissolved or aggregated) of the majority of polymer chains. Compared to absorption spectroscopy, the structural information provided by SANS represents a more complete picture of the solution-phase behavior of P(NDI2OD-T2) polymers that better correlates with the microstructure and OFET performance of spin-coated films, as discussed below.

Dynamic Light Scattering. To support SANS results, dynamic light scattering (DLS) experiments were performed as

an independent probe of solution-state chain conformation, specifically the size of polymer particles in solution. Due to the absorption and fluorescence of visible light by semiconducting polymers, which complicates light scattering experiments, the experimental setup was optimized for semiconducting polymers, as detailed in the Experimental Section. Only polymer solutions at 25 °C were characterized due to the limited heating capability of the instrument. Dilute polymer solutions of less than 0.12 g/L were used in the DLS experiment, which is an order of magnitude lower than that in SANS measurements (i.e., 2 g/L). Therefore, polymer multichain aggregates were likely to be freely dispersed in solution instead of forming a network in the DLS experiments, meaning that the extracted structural information is likely to correspond to that of freely dispersed aggregates.

Among all polymer solutions at 25 °C, only the 67 kDa batch in Tol and CB produced sufficient scattering signal (see Figure S12) to yield autocorrelation functions for reliable DLS analysis, as shown in Figure 7. Unlike the absorbance of the polymer at the wavelength of incident light (632.8 nm), which is similar regardless of molecular mass and solvent (Figure S1), the scattered intensity detected in a DLS experiment is a function of the size of the polymer. Accordingly, reliable data could only be measured for the highest molecular weight batch in Tol and CB. No reliable data could be measured in DCB, which is consistent with the less aggregated nature of P(NDI2OD-T2) in this solvent. The electric-field autocorrelation function (EACF) was observed to be similar for the 67 kDa batch in both Tol and CB, for a range of concentrations, as shown in Figure 7, indicating that the solution-phase polymer conformation is similar within the concentration range studied and also confirming the reproducibility and reliability of the DLS results. Analysis was conducted by fitting a single exponential function to calculate the hydrodynamic radius, $R_{\rm h}$, of the freely dispersed aggregates in solution. Using a biexponential decay function did not improve the fit quality significantly, as shown in Figure S13. The calculated $R_{\rm h}$ values shown in Figure 7c are less than 35 nm, which confirms that the polymers exist as freely dispersed aggregates instead of forming a network. (The radius of gyration of a single 67 kDa polymer chain assuming a rigid rod-like conformation is calculated to be 26 nm; see Section S2 in the Supporting Information for further detail). Accordingly, a larger $R_{\rm h}$ in Tol could be associated with a longer contour length or Kuhn length, which in both cases correspond to stronger $\pi - \pi$ interactions resulting in stiffer chains. Overall, the DLS results are consistent with the SANS results, providing independent evidence that P(NDI2OD-T2) polymers are stiffer in Tol compared to CB.

Correlation of Solution-Phase Aggregation with Solid-State Morphology and Electronic Properties. To correlate the role of the conformation of polymer chains in solution with the solid-state microstructure, thin films were fabricated by spin-coating 2 g/L solutions at 25 °C, matching the conditions of SANS characterization. The morphology of the films was characterized using AFM as shown in Figure S14. Despite being deposited via the spin-coating method, evidence was found for extended in-plane orientational alignment of fibrils. Importantly, the degree of in-plane chain alignment exhibits a strong dependence on solvent and molecular weight. For instance, the degree of in-plane chain alignment is the highest for Tol 43 kDa and CB 13 kDa samples. Figure S15 shows that the chain alignment persists up to a larger area of



Figure 7. DLS characterization of solution-phase conformation of P(NDI2OD-T2). EACF of the 67 kDa batch in (a) Tol and (b) CB for a series of concentrations plotted for independent measurements at each concentration. Almost completely overlapping DLS signals confirm the reproducibility and reliability of the data, despite the noise. (c) Hydrodynamic radius, $R_{\rm h}$, of polymer aggregates extracted from DLS data following single exponential fit to the decay of EACF in (a,b).

10 × 10 μ m², confirming that the film morphology observed for a smaller area of 2.5 × 2.5 μ m² is representative of the degree of in-plane chain alignment. The direction of aligned chains was observed to differ within a substrate (1 × 1 cm² in our case), as shown in Figure S15, which is expected for a spincoated film as the different parts of the substrate experience different shear forces during coating. In our previous work, we correlated the degree of in-plane chain alignment with solvent quality and molecular mass.^{33,34} However, the systematic investigation of film morphology with a full combination of solvents and molecular weights in the current work provides new insight into the role of solution-phase chain conformation on the degree of in-plane chain alignment in thin films.

To enable quantitative comparison of the degree of in-plane chain alignment, AFM images were analyzed using the software GTFiber to extract the orientational order parameter, S_{full} , as shown in Figure S16; $S_{\text{full}} = 0$ and 1 correspond to completely random and perfect in-plane alignment of polymer chains, respectively.⁵⁹ The corresponding false-color orientation maps

and pole figures provide a visual representation of the orientation distribution of the chain alignment. The summarized trend of S_{full} as a function of solvent and molecular weight is shown in Figure 8 along with selected



Figure 8. Impact of solution-phase conformation of rod network of P(NDI2OD-T2) on the solid-state film morphology. Selected AFM topography images of films processed from (a,b) Tol and (d,e) CB solvents show distinct behavior in the degree of in-plane chain alignment with increasing molecular mass. (c) Summarized trend of the degree of in-plane chain alignment as represented by S_{full} extracted using GTFiber software. The dotted lines are drawn by hand as a guide to the eye on the overall trend of S_{full} .

AFM images. Interestingly the different solvents exhibit different trends. The CB-processed films exhibit a linear decrease in S_{full} with molecular weight, with S_{full} decreasing from $S_{\text{full}} = 0.83$ for the 13 kDa batch to $S_{\text{full}} = 0.09$ for the 67 kDa batch. DCB samples, on the other hand, show a very weak molecular-weight dependence of $S_{\rm full}$, with values of $S_{\rm full} \approx 0.2$ \pm 0.1. Tol-processed samples exhibit a more complicated dependence, with relatively high values of $S_{\text{full}} \approx 0.8$ for the three lower molecular-weight batches, which drops dramatically to S_{full} = 0.09 for the 67 kDa batch. For the CB and Tol samples, the observed trends can be linked to observed solution-phase behavior. For the lowest molecular-weight batch of 13 kDa, both Tol and CB show similar degrees of chain alignment ($S_{\text{full}} \sim 0.8$) as the freely dispersed rod-like aggregates with long aspect ratio in solution can align without restriction in the absence of a network structure during the film formation process. As the rod network forms with increasing chain length, the length of the network substructure, L_{cvb} is longer in Tol solvent (e.g., L_{cyl} is ~48 nm for 45 kDa) as the polymer chains are stiffer due to stronger $\pi - \pi$ interactions within the aggregates. The longer L_{cvl} within the rod network increases the tendency of polymer aggregates to be aligned along the long axis as the solvent evaporates during the film formation process, resulting in a higher degree of in-plane

chain alignment in the film. In contrast, the shorter L_{cyl} of the rod network in CB solvent at the same chain length (e.g., L_{cyl} is ~27 nm for 45 kDa) lowers the aspect ratio of polymer aggregates, leading to less aligned chains. A further increase in chain length up to 67 kDa causes excessive network formation, as indicated by a more compact network (higher D_m) but significantly shorter L_{cyl} especially for Tol solvent, which in turn leads to the random alignment of polymer chains observed for both the Tol and CB films.

On the other hand, thin films deposited from DCB generally exhibit a more random in-plane chain alignment as reflected by lower values of S_{full}. This morphology of DCB-processed films, where the directional correlation of fibrils decays within a few hundred nanometers, has previously been observed.^{60,61} While the initial aggregation behavior is generally considered to strongly influence the resulting thin film morphology, the high boiling point of DCB (180 °C compared to 132 °C for chlorobenzene and 110.8 °C for toluene) may be a factor also affecting morphology evolution. Since DCB-processed films dry much more slowly, the isolated rod-like aggregates may be afforded time to assemble into a disordered network structure during solution drying, producing similarly low values of S_{full} to the 67 kDa Tol solution, which begins with an extensive network structure. Indeed, further evolution of the solutionphase chain conformation during the film formation process has previously been reported for isoindigo-bithiophene-based polymers as being due to the significant increase in solution concentration as the solvent evaporates.²⁹ For CB and Tol solutions, the solvent dries much faster, promoting aggregate interactions that favor the extended alignment of chains.

To connect the above measurements with charge-transport behavior, OFETs with a top-gate bottom-contact configuration were fabricated. P(NDI2OD-T2) films used in these OFET devices were all coated from 2 g/L solutions at 25 °C. Details about device fabrication and characterization can be found in the Experimental Section. Figure S17a shows the resulting average saturation electron mobilities, μ_{sat} , of the transistors as a function of both the solvent and molecular weight. The corresponding output and transfer curves can be found in Figures S18-S20 in the Supporting Information. For DCBprocessed films, a low mobility of about 0.15 cm² V⁻¹ s⁻¹ was observed. A similarly low mobility was also found for all 67 kDa films. On the other hand, average mobilities of ≈ 0.3 cm² V^{-1} s⁻¹ were observed for films processed from Tol and CB at intermediate molecular masses, with mobilities above 0.4 cm² V⁻¹ s⁻¹ recorded for individual transistors. These trends in transistor mobility correlate with the degree of in-plane chain alignment, indicating a strong role of the degree of in-plane chain alignment on the OFET properties. Figure 9 plots the average saturation mobility as a function of $S_{\rm full}$. First, $\mu_{\rm sat}$ increases with increasing S_{full} —the films with higher S_{full} such as the Tol 45 kDa sample exhibit a higher average $\mu_{\rm sat}$ of above 0.3 cm² V⁻¹ s⁻¹ while films with lower $S_{\rm full}$ such as those processed from DCB and 67 kDa polymers processed from Tol and CB exhibit lower average μ_{sat} of about 0.15 cm² V⁻¹ s⁻¹. This finding is consistent with previous works reporting that charge transport is more effective in aligned films. 33, 34, 36, 62 Second, the spread of μ_{sat} exhibits a strong correlation with S_{fulb} where a larger spread in μ_{sat} is observed as S_{full} increases. This observation has been reported before and is due to the fact that for spin-coated films with strong in-plane alignment, chains will sometimes align with the transport direction of the OFET (giving a high μ_{sat}) and sometimes misalign with the transport



Figure 9. Impact of the solid-state film morphology on the performance of transistors, showing the correlation of the saturation mobility of transistors, μ_{sav} with the degree of in-plane chain alignment, S_{full} , characterized using AFM. An overall trend is apparent; that is higher S_{full} leads to higher mobility along with a larger spread of mobility values.

direction (giving a low μ_{sat}).³¹ In contrast, films with a low S_{full} have similarly isotropic in-plane chain alignment at different positions in the film, resulting in similar charge-transport efficiency, as indicated by the low spread in μ_{sat} . The performance of transistors based on the 13 kDa Tol sample falls out of the general $\mu_{\rm sat}$ vs $S_{\rm full}$ trend in Figure 9, which can be explained by the absence of tie chains to connect ordered domains.^{63,64} We exclude the role of molecular orientation of polymer crystallites as the face-on to edge-on ratio determined by grazing-incidence wide-angle scattering (GIWAXS) does not exhibit a correlation with the mobility of transistors (see Figure S21). We also exclude the role of out-of-plane alignment of polymer chains as GIWAXS measurements show no evidence for the end-on texture of polymer crystallites. We have also compared the trend of the threshold voltage of transistors, which does not correlate with the degree of in-plane chain alignment. However, the threshold voltage is observed to be consistently higher in DCB-processed films compared with those processed from Tol and CB, regardless of the molecular weight (see Figure S22). Overall, there is strong evidence for the direct correlation between OFET mobility with the degree of in-plane chain alignment. While using poor solvents (e.g., Tol) with high molecular weights can support the formation of extended in-plane chain alignment, excessive network formation can impede chain alignment, resulting in reduced OFET mobility.

Our observations indicate that excess network formation in solution that restricts the alignment of polymer chains during film formation should be avoided. This is not to say that aggregation of polymer chains in solution in general should be avoided, as there is strong evidence that the right type of aggregation can be beneficial, with the highest mobilities achieved here for solutions that show aggregate formation, but without the further aggregation of these aggregates to form a larger three-dimensional network. We expect this finding of a "sweet spot" of aggregation to be generalizable to other polymer systems. For our study, where we vary molar mass but fix solution concentration, the "sweet spot" corresponds to an intermediate molecular weight. Fixing the molecular weight but varying solution concentration we would expect to see an optimum solution concentration instead, which indeed has been seen for recent studies of DPP-based polymers.^{65,66} Specifically, these studies observed that OFET performance was optimized using a polymer solution concentration close to the overlap concentration: up to the overlap concentration,

increased interchain interactions promoted ordering of chains in the resulting film, but above the overlap concentration chain entanglement resulted in spatial defects and charge traps.^{65,66} In the present work, in which we fixed the solution concentration, changes in molecular weight result in different overlap concentrations for each molecular mass. For a fixed solution concentration of 2 g/L, the 28 and 45 kDa solutions for CB and Tol appear to be close to the overlap concentration, with the 67 kDa batch having an overlap concentration less than 2 g/L. The optimum conditions are, therefore, a function of molecular weight, solution concentration, and solvent; for the 67 kDa batch processed in CB and Tol, improved OFET performance could be expected with lower solution concentrations.

CONCLUSIONS

We have used SANS to systematically study the solution-phase behavior of P(NDI2OD-T2) considering the influence of molecular weight, solvent quality, and temperature. This approach has enabled us to provide a global picture of solution-phase behavior spanning the conformation of individual chains and aggregates through to network formation. The main findings from our study can be summarized as follows: (i) for all solutions, P(NDI2OD-T2) chains are best described as rigid cylinders rather than semiflexible chains. (ii) A hierarchical model is required to explain the SANS profiles of all solutions which combines a cylinder model that accounts for scattering from individual rigid chains/aggregates on small length scales with a Guinier-Porod model that accounts for scattering from networks of entangled, rigid aggregates on large length scales. (iii) Excessive network formation in solution is detrimental to the long-range correlated ordering of aggregates in thin films, and hence also detrimental to charge transport in organic fieldeffect transistors. (iv) Variations in the degree of network formation on large length scales are apparent from SANS measurements but missed from optical absorption measurements of solutions. These findings are likely to be applicable to other semiconducting polymer systems, particularly the need to optimize the degree of interchain interactions in solution, which can be achieved through varying molecular weight and solvent, as done in this study, or through optimization of solvent and solution concentration.

EXPERIMENTAL SECTION

Materials. Four batches of P(NDI2OD-T2) with different molecular masses, M_n of 13, 28, 45, and 67 kDa used in this study were synthesized using the previously reported direct arylation polycondensation approach,^{36,67} Table S1 summarizes the properties of these polymers.

Thin Film and Transistor Fabrication and Characterization. Thin films were spin-coated from 2 g/L solutions at room temperature, matching the solution concentration used in SANS characterization. The spin-coating protocol was optimized for each processing solvent as tabulated in Table S2 to produce films with similar thicknesses tabulated in Table S3. To study the in-plane charge-transport properties of P(NDI2OD-T2), field-effect transistors of TGBC configuration were fabricated with fixed a channel width (designated as *U* in the equation below) of 10 mm and three channel lengths (designated as *L* in the equation below) of 5, 10, and 20 μ m. In detail, P(NDI2OD-T2) films were coated following the protocol mentioned above onto substrates patterned with Au electrodes. Prior to coating the P(NDI2OD-T2) layer, a layer of PEIE was spin-coated to enhance electron injection. Atop P(NDI2OD-T2) was a 500 nm

thick cyclic transparent optical polymer (CYTOP) layer, which served as the dielectric layer and gave rise to an areal capacitance (C_i) of 3.7 nF/cm². Finally, 40 nm Al was thermally evaporated as the gate electrode. Fabricated devices were measured using an Agilent B2902A source measurement unit together with a probe station placed in a N₂filled glovebox. Parameters of mobility (μ) and threshold voltage ($V_{\rm th}$) were extracted from saturation regime by fitting transfer curves ($I_{\rm d}$ vs $V_{\rm e}$)

$$I_{\rm d} = \frac{W}{2L} \mu C_{\rm i} (V_{\rm g} - V_{\rm th})^2$$

UV–Vis Spectroscopy. UV–vis absorption spectroscopy was performed using a Deuterium-Halogen DH-2000-CAL light source (Ocean Optics⁶⁸) and a USB4000 spectrometer (Flame-S-VIS-NIR-ES from Ocean Optics). Quartz cells with different path lengths of 10 and 0.1 mm were used for solutions with 0.02 and 2 g/L concentrations, respectively. The temperature of the cuvette was controlled with a Quantum Northwest qpod in combination with a TC1 temperature controller with an accuracy of better than ± 0.2 °C. The actual solution temperature in the cuvette may be slightly lower than the set point due to thermal loss.

Small-Angle Neutron Scattering. SANS experiments were performed on the NGB 10 m SANS instrument at the National Institutes of Standards and Technology (NIST) Centre for Neutron Research (NCNR). Standard configurations with two detector positions were used with 1D profiles stitched together to cover a q range of approximately 0.003 Å⁻¹ < q < 0.5 Å⁻¹. Sample cells of 2 mm path length were used. Quartz windows were held together by the titanium cells and sealed by Teflon-coated o-rings. Polymer solutions for SANS experiments were prepared in deuterated solvents to enhance the coherent scattering contrast of the polymers and to minimize the incoherent background. The total collection time for each sample was approximately 2 h. Reduction and correction of the SANS data to absolute scale was performed using the software package developed at the NIST Centre for Neutron Research,65 where the thickness of the cell was used for all reduction calculations. SasView software was used to fit the data to appropriate models, which is available free of charge at https://www.sasview.org/. Further details on data analysis are provided in the Supporting Information.

Dynamic Light Scattering. DLS was performed in an ALV-5022F light scattering spectrometer (ALV-GMBH, Germany) at a laser wavelength of 632.8 nm and temperature of 298 K, with a sample measurement time of 10 s and vial inner diameter of 7.3 mm. The instrument set up was optimized for semiconducting polymers due to the absorption and fluorescence of visible light by the material. Dilute concentrations of less than 0.12 g/L were used to prevent the complete absorption of scattered lights within the solution. A fixed low angle of 20° was used to maximize the intensity of scattered light to improve the signal-to-noise ratio of the resulting intensity correlation function. A laser line filter (632.8 \pm 0.6 nm) was placed in the outgoing light path to filter out most of the fluorescence signal so that predominantly scattered light is captured by the detector. Further details on experimental procedures and data analysis are provided in Section S2 in the Supporting Information.

Atomic Force Microscopy. AFM measurements were performed on a Bruker Dimension Icon AFM using ScanAsyst mode at the Melbourne Centre for Nanofabrication. Films were coated onto a Si substrate. AFM data were processed using Gwyddion and GTFiber software.⁵⁹

GIWAXS. GIWAXS characterization was performed at the SAXS/ WAXS beamline at the Australian Synchrotron.⁷⁰ A photon of 15 keV was used as the X-ray source, with the 2D GIWAXS patterns collected using a Dectris Pilatus 2M detector placed \approx 68 cm downstream from the sample. The sample-to-detector distance was calibrated using the AgBeh standard. Three scattering patterns were collected at different detector positions to cover the gap between the detector modules, with the reported 2D images being the composite of the three scattering patterns stitched using the in-house software developed at the beamline. An exposure time of 1 s was used for each scattering pattern, totaling 3 s of exposure time for each reported 2D image. The entire path of the X-ray beam was placed under a vacuum maintained at below 10^{-5} mbar to minimize diffuse background scattering from air, hence improving the signal-to-noise ratio of the scattering patterns, especially of polymer thin films less than 20 nm thick. A series of incident angles was used during the measurement with the reported 2D images collected at the critical angle, which is the incident angle that maximizes the scattering intensity, typically at about 0.1°. Data reduction and analysis were performed using a modified version of the NIKA analysis package implemented in Igor Pro.⁷¹

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.3c01435.

Additional details of the rod network model; details of DLS experiments and data analysis; further details of materials and sample preparation; and supplementary results including full the full solution UV–vis data set, full SANS data set, full set of SANS fittings, full DLS data set, full AFM data set, AFM orientation maps, OFET data, and GIWAXS results (PDF)

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Notes

The authors declare no competing financial interest.

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