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Hydrogen-Bonding-Directed Ordered Assembly of Carboxylated Poly(3-Alkylthiophenes)

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ABSTRACT: Hydrogen-bonding-induced ordered assembly of poly(3-alkylthiophene)s derivatives bearing carboxylic acid groups has been investigated from diluted and concentrated solutions to solid films using ultraviolet–visible absorption spectroscopy, polarized optical microscopy, and four-point probe conductivity measurements. In dilute solutions, the polymer undergoes a spontaneous structural transition from disordered coil-like to ordered rodlike conformations, which is evidenced by time-dependent chromism. Many factors such as alkyl-chain length, types of solvents, and temperature are studied to understand the assembly behavior. Transition kinetics of the assembly process reveals a universal second-order rate law, indicating an intermolecular origin due to hydrogen bonding. When more concentrated, hydrogen bonding drives nematic liquid-crystalline gelation above a critical concentration and the gels are thermally reversible. Under an appropriate balance of mechanical and thermal stresses, uniform liquid-crystalline monodomains are obtained through the application of a mechanical shear force. The dried films made from the sheared solutions display both optical and electrical anisotropies, with a more than 200% increase in charge transport parallel to the direction of shear as opposed to that in the perpendicular one.

INTRODUCTION

Conjugated polymers (CPs) represent a class of semiconducting materials garnering extensive applications in flexible optoelectronic devices, comprising organic photovoltaics (OPVs), organic field-effect transistors, and polymer light-emitting diodes.1–4 A complication concerning the fabrication of such high-performance CP devices is the dependence of their optical and charge-transport characteristics on nanoscale morphology and macroscopic alignment.5–8 Importantly, CPs exhibit a unique anisotropy of optoelectronic properties resulting from one-dimensional p-orbital overlaps along the backbone.9–10 When nonlinear, these backbone arrangements will broaden the electronic density of states, resulting in obstructed charge mobility through diminished electronic couplings.11 As such, the capacity to controlling macroscopic alignment in CP thin films is a key constituent to producing high-performance optoelectronic devices.12 Although established techniques, such as spin-coating, produce CP films with highly crystalline domains, the control of CP microstructures in solution has also been found to affect solid-state morphology.13 Furthermore, various processes have been implemented to control alignment in CP thin films, including mechanical rubbing, nanoimprinting, using patterned substrates, and the Langmuir–Blodgett technique.5,14,15 Interestingly, CPs with the capacity of hydrogen bonding have been found to assist in the bulk heterojunction morphology of OPVs.16 However, how these hydrogen bonding effects influence the solution self-assembly of CPs has yet to be reported.

Poly(3-alkylthiophenes) (P3ATs) are an extensively investigated class of CPs owing to their charge carrier mobility and low band gaps.17–19 These characteristics result from the alignment of polymer backbones, promoting charge transport through highly crystalline solid states.20 Factors such as solvent choice, solution temperature, and side-chain architecture have all been found to influence the self-assembled alignment of P3AT backbones.21–23 Although the so-called coil-to-rod conformation transition has been proposed to explain such self-organizations, the dynamics of this transition, with respect to intramolecular versus intermolecular origin, remains ambiguous.24 In our previous work, the supramolecular complexation of quaternary ammonium surfactants with poly(3-potassium-6-hexanoatethiophene)-2,5-diyl (P3K6T), a P3AT derivative, resulted in a dynamic coil-to-rod transition of intramolecular origin due to the long hydrocarbon side chains of surfactants.25,26 In contrast, intermolecular associations leading to polymer backbone coplanarity have been reported for the solution crystallization of poly(3-hexylthiophene) (P3HT).27,28 Although side-chain
functionality is known to have an effect on the solution-based assembly of P3ATs, how hydrogen-bonded moieties influence the coil-to-rod transition remains unknown.

Recently, new methods have been explored to improve charge transport in optoelectronic devices on basis of the self-assembly of lyotropic liquid crystals (LCs).\textsuperscript{11,29–31} Importantly, the promotion of smectic, columnar, and nematic LC phases is driven through the presence of rigid, high-aspect-ratio microstructures.\textsuperscript{32,33} As the concentration of the rodlike particle solution increases, the rotational component of entropy is minimized. To counteract this effect, the rodlike particles pack more efficiently to exclude solvent volume, minimizing the overall free energy of the system and forming the LC phase. In this way, ordered LC domains that span over hundreds of micrometers may be generated in thin films constructed from dilute rodlike particle solutions.\textsuperscript{34} Moreover, the alignment of LC domains that span even greater length scales may be achieved through external influences, such as mechanical shearing and electric or magnetics fields.\textsuperscript{35,36} There have been reports on the nematic LC phase in CP gels, and they are surmised to result from the presence of short-range interactions, such as those provided through hydrogen-bonded pendant groups.\textsuperscript{37} Additionally, the incorporation of these moieties supports thermally reversible cross-linking within the polymer matrix, enhancing plasticity of the gel and allowing for ease of alignment processes.\textsuperscript{38} Moreover, gelation of CPs has been reported to improve charge transport due to the formation of interconnected three dimensional (3-D) networks.\textsuperscript{39} Therefore, the capacity to foster hydrogen-bonded rodlike microstructures of P3AT solutions may provide a modest method for constructing 3-D gel networks of LC conjugated polymers with enhanced anisotropy.

In this work, we report on the assembly processing of carboxylic acid-functionalized poly(3-alkylthiophene)s from dilute and concentrated solutions to the solid state. In the dilute regime, the coil-to-rod transition is spectroscopically investigated as a function of alkyl-chain length, solvent choice, and temperature. When concentrated, the samples exhibit thermally reversible gelation accompanied by isotropic-to-LC phase transitions. We put forward arguments that explain quantitatively how hydrogen bonding as a strong intermolecular interaction influences the kinetics laws of the coil-to-rod transition and LC gelation. A balancing of mechanical and thermal stresses is noted to have an effect on the LC textures. Through the application of a mechanical shearing force, aligned films are obtained and preserved through the drying process. A significant anisotropy of optical and electrical properties in the aligned films is obtained. We believe these methodologies show promise in combining the alignment capabilities of LC phases with the processing potential of CP gels, allowing for a probable pathway to the construction of flexible high-performance optoelectronic devices.

**RESULTS AND DISCUSSION**

**Diluted Solutions.** The regioregular poly[3-(5-carboxyalkyl)thiophene-2,5-diyl], denoted P3CrTs (Figure 1), were prepared in dimethyl sulfoxide (DMSO) and diluted to a concentration of 25 μg/mL. The samples were left to equilibrate for 80 min. Figure 2 displays the UV–vis absorption spectra of P3CrTs in pure DMSO. Broad Gaussian-like absorption peaks are observed for both P3C3T and P3C4T with \( \lambda_{\text{max}} \)'s of 442 and 464 nm, respectively. In contrast, the absorption of P3C6T exhibits two peaks with narrow half-widths at 590 and 550 nm, corresponding to \( F_{0}^{0} \text{abs} \) and \( F_{0}^{1} \text{abs} \) vibronic transitions, respectively.\textsuperscript{40} These fine structures correspond to the Franck–Condon progression of C–C stretching within the thiophene ring.\textsuperscript{26} Interestingly, the spectrum of P3C5T presents the broad absorption of both \( F_{0}^{0} \text{abs} \) and \( F_{0}^{1} \text{abs} \) transitions apparent at 590 and 550 nm, respectively, and a primary \( \lambda_{\text{max}} \) at 500 nm. Therefore, the resulting spectra of P3CnTs collectively display a distribution of bathochromic and hypsochromic shifting as a function of alkyl-chain length. It is well understood that regioregular P3ATs form antico-planar arrangements of their thiophene rings, promoting rodlike structures that maximize backbone conjugation and minimize charge traps.\textsuperscript{41} Conversely, geometric frustrations between adjacent repeat units are ascribed to the coil-like disorder of the polythiophene backbone. This leads to defects in backbone conjugation, which manifests as broad hypsochromic peaks in the electronic spectra. Figure 2 clearly demonstrates that \( \lambda_{\text{max}} \)'s of P3CnTs gradually red-shift with increasing the length of their side chains, promoting absorption of vibronic fine structures. This effect may be explained through the increase of alkyl-chain steric factors between thiophene rings, in which longer side chains force coplanarity of the polymer backbone, encouraging \( \pi-\pi \) stacking and increased conjugation lengths.\textsuperscript{41} These findings are consistent with the theoretical calculations, suggesting that ordered crystalline structures and enhanced conjugation lengths may be achieved through the incorporation of long alkyl chains.\textsuperscript{42} Additionally, the absorption spectra of P3CrTs dissolved in DMSO have been reported previously.\textsuperscript{43} Although our results show consistency with the literature values, a notable exception can be observed in the absorption of P3C5T, which displayed diminished vibronic bands in the cited work.\textsuperscript{25} The disparity between the vibronic fine absorption of both \( F_{0}^{0} \text{abs} \) and \( F_{0}^{1} \text{abs} \) vibronic transitions, respectively.

**Figure 1.** Chemical structures of P3CnTs with \( n = 3, 4, 5, \) or 6 carbons.

**Figure 2.** UV–vis spectra of dilute P3CnTs in DMSO with varied alkyl-chain lengths \( (n = 3, 4, 5, \) and 6) after 80 min equilibration. The concentration of the solutions is 25 μg/mL.
structures of P3C5T may be justified by the 80 min equilibration time implemented in our study. This suggests that a time-dependent chromism is present in the absorption spectrum of P3C5T.25,26

Previous reports of numerous P3AT systems have shown that their self-organization may be promoted through the addition of a poor or marginal solvent.44 In this way, unfavorable interactions between the polymer chains and poor solvent molecules drive self-assembly and aggregation.44 As such, the degree of assembly should be dependent on the amount of poor solvent present in the system. Figure 3a demonstrates such self-organizations of P3C5T upon initial dilution (t = 0 min) in varying ratios of DMSO/EtOH. In pure DMSO (10:0), P3C5T displays a Gaussian-like $\lambda_{\text{max}}$ at 460 nm and lacks vibronic fine structures, similar to those in P3C3T and P3C4T. Upon dilution of P3C5T in smaller ratios of DMSO/EtOH, the spectra gradually exhibit more red-shifted $\lambda_{\text{max}}$s accompanied by strongly absorbed vibronic structures at 550 and 590 nm. At lower ratios, the $I_0 - I_{\text{abs}}$ shifts slightly to higher wavelengths. These observations imply that the addition of EtOH enhances $\pi-\pi$ stacking between the thiophene rings, thereby promoting aggregation and extended conjugation lengths. Figure 3b shows the spectra of P3C5T dissolved in various ratios of DMSO/EtOH after storage in the dark for 24 h. In all cases, little to no pronounced Gaussian-like peak is observed at around 460 nm. Additionally, more pronounced absorption is detected for vibronic structures in the

- Figure 3. UV−vis spectra (a) upon and (b) 24 h after initial dilution of P3CST in varying ratios of DMSO/EtOH. The concentration of solutions is approximately 25 μg/mL.

- Figure 4. UV−vis spectra of P3CST thermochromism in (a) DMSO and (b) 8:2 DMSO/EtOH. The concentration of solutions is approximately 25 μg/mL.

- Figure 5. Room-temperature time-dependent chromism of dilute solutions of P3CST in (a) DMSO and (b) 8:2 DMSO/EtOH. The concentration of solutions is approximately 25 μg/mL.
550–600 nm range. This infers that greater assembly is upheld with time and that all solutions of P3CST in mixed solvents display time-dependent spectroscopic transitions.

Whereas the addition of marginal solvent to solutions of P3CST in DMSO yields an enhancement of backbone coplanarity, the thermochromism of P3ATs has been reported to decrease the conjugation length. Previous reports of P3AT systems indicate that such vibronic peaks at $\lambda = 590$ nm are associated with the quantity of rodlike structures in solution. As such, the method of initial rates was employed to measure the kinetics of the P3CST solution assembly. In this way, the initial slope of absorbance ($\lambda = 590$ nm) against aging time is accepted as the initial rate of the spectroscopic transition.47

From a theoretical standpoint, the scaling relationship between the transition rate and concentration is codified as $R \propto C^n$, where $R$ is the rate of transition, $C$ is the solution concentration, and $n$ signifies the reaction order, which is solely associated with the reaction mechanism. Figure 6 shows the kinetics of the P3CST solution assembly in DMSO and 8:2 DMSO/EtOH. In this instance, the initial rate scales with the concentration as $R \propto C^{2.05 \pm 0.05}$ and $R \propto C^{2.06 \pm 0.12}$ for P3CST in pure DMSO and 8:2 DMSO/EtOH, respectively. These results demonstrate no significant difference between reaction orders of the pure and mixed-solvent P3CST solutions. Therefore, no change in the dynamic mechanism of the P3CST assembly takes place subsequent to the addition of a poor solvent although the solubility of P3CST in the mixed solvents decreases considerably. Moreover, the second-order kinetics law in this work is in contrast to the inverse first order in P3AT complexes and the mixed fractional order in P3HT.

It is understood that the self-organization mechanism of P3AT assembly results from both a coil-to-rod conformational transition and adjacent rod–rod aggregations to form nanofibrils. Structurally, such nanofibrils are upheld through the formation of hairpinlike lamellae that propagate through the back-and-forth folding of polymer chains. In some cases, the coil-to-rod transition is thought to be the primary driver for assembly,

Figure 6. Assembly kinetics of diluted solutions of P3CST at 25 °C. (a) Time-dependent absorbance against aging time of P3CST in DMSO, (b) the initial rate versus polymer concentration of P3CST in DMSO, (c) time-dependent absorbance against aging time of P3CST in 8:2 DMSO/EtOH, and (d) the initial rate versus polymer concentration of P3CST in 8:2 DMSO/EtOH.
whereas in others, rod–rod aggregation dominates. Previous reports have shown the solution assembly of P3HT due to π–π stacking in a marginal solvent to be of a mixed fractional order, with an exponent of approximately 1.6.27,28 Such results may be explained through secondary nucleation theory, which states that the growth rate (G) is proportional to the total nucleation (S), such that \( G \propto S^{\gamma} \). As such, the variations between the growth rates of numerous P3AT systems may be explained by the total individual contributions of nucleation (\( S_i \)) from various elementary processes. Therefore, the total nucleation will result from differing weights of the following elementary components:

\[
S_{\text{total}} = \sum_i W_i S_i = W_{\text{coil\-rod}} S_{\text{coil\-rod}} + W_{\text{fold\-fold}} S_{\text{fold\-fold}} + W_{\text{agg\-agg}} S_{\text{agg\-agg}}
\]

where \( W_i \) is the weighing factor determining the intrinsic contribution of each term. Additionally, each contributor has a fundamental scaling relationship associated with the physical process it represents. For the only coil-to-rod transition, our previous work shows kinetics that demonstrates inverse first-order behavior (\( S_{\text{coil\-rod}} \propto C^{-1} \)) in the P3AT supramolecular complexes.25 For the sole rod–rod aggregation, scaling establishes a nucleation rate that is proportional to the concentration raised to the second power (\( S_{\text{agg\-agg}} \propto C^2 \)).50 In contrast, the chain-folding process reveals the kinetics of a fractional order. Therefore, the overall kinetics is determined by the relative contributions of the nuclei of each primary process.

The previous report on a mixed fractional order of \( \sim 1.6 \) in P3HT demonstrated that the nucleation of π–π stacking-induced rod–rod aggregation contributed more than that of coil-to-rod and chain-folding processes.27,28 In this work, the second-order growth kinetics of P3CST indicates that the rod–rod aggregation is the main process driving the solution assembly and the other two processes are negligible. The discrepancy between the assembly mechanism of P3HT and that of P3CST may be explained through variations in their chemical structures. The carboxylic acid alkyl-chain end group of P3CST has the potential to act as both a hydrogen bond donor and an acceptor.51 Accordingly, intermolecular hydrogen bonding is possible between chains of P3CST but not between those of P3HT. Such short-range strong intermolecular interactions may act to accelerate rod–rod aggregations of P3CST chains, resulting in the aforementioned second-order growth kinetics. Moreover, second-order spectrokinetic measurements have been reported for another P3AT derivative with the potential for hydrogen bonding.52 The fact that P3CST exhibits the second-order kinetics in both DMSO and 8:2 DMSO/EtOH indicates that hydrogen bonding, when it is present, is a predominant factor over π–π stacking to control the assembly process.

**Concentrated Solutions.** A consequence of conjugated backbone aggregation influencing the solution assembly of P3CST is the formation of hydrogen-bonded 3-D networks at higher concentrations, leading to a sol–gel transition. Additionally, the use of low-volatility solvents, similar to DMSO, has been found to promote P3AT gelation.53 The Fourier transform infrared (FT-IR) spectra of P3CST solid films and gels (30 wt % in DMSO and DMSO/EtOH) were evaluated to determine the extent of hydrogen bonding (Figure S1, Supporting Information). In both the solid film and gel, broad bands and sharp peaks are present within the hydroxyl and carbonyl regions of the FT-IR spectra, respectively. In this regard, sharp carbonyl peaks are used to evaluate hydrogen bonding. In the solid state, the carbonyl vibrations present at 1697 cm\(^{-1}\) are indicative of low-energy hydrogen bonding.54 Reports of P3CnT’s have indicated that carbonyl peak positions at approximately 1735 cm\(^{-1}\) are suggestive of free C=O stretching.55 In the gelated state, P3CST shows carbonyl peaks at roughly 1716 cm\(^{-1}\), which suggests that degrees of hydrogen bonding are present in the gel. As the carbonyl peak shift in the gel is associated with the strength of hydrogen bonding,54 the higher-energy wavenumber peak indicates the weaker hydrogen bonding of the gel. Interestingly, redrying of P3CST gels shifts carbonyl peaks back to lower-energy wavenumbers, signifying complete restoration of solid-state hydrogen bonding.

**Figure 7** illustrates the bulk and thermal properties of concentrated P3CST–DMSO thermally reversible gels. The concentration of thin films is 23 wt %.

P3CST solutions maintain fluidity up to concentrations as high as 15 wt % at room temperature (**Figure 7a**). Above a critical concentration (~21 wt %), the percolation threshold is reached and the gels form. Slight color changes may be observed between the less-concentrated solutions and the P3CST gel, providing further evidence for the formation of an interconnected 3-D network. With heating, gel films of P3CST display a color change from dark purple to bright orange (**Figure 7b**). Upon cooling back to room temperature, the dark purple color of the films gradually restored and fluidity is no longer present. These observations imply that the gelation process of P3CST is thermally reversible and supported through a network of hydrogen-bonding interactions.58 Moreover, air-drying of P3CST produces solid films with a metallic sheen that can be carefully peeled off from glass substrates.

Upon sandwiching the P3CST gel between a clean glass slide and a coverslip, the gel exhibits characteristic phenomena related to birefringent media. When the samples are placed under a polarized optical microscope (POM), double diffraction is observed in the form of light and dark contrasting regions. Furthermore, the domains change alternatively upon rotating the sample through a 45° angle in between the microscope crossed polarizers. These observations indicate the construction of a liquid crystal (LC), with Schlieren textures resembling that of a typical nematic phase.52 Both small-angle and wide-angle X-ray scattering measurements show no scattering peaks, indicating no smectic LC phases or crystalline structures (**Figures S2 and S3**, Supporting Information). **Figure 8** illustrates the onset of such nematic LC formation as a function of concentration. The presence of the nematic LC phase suggests that P3CST chains maintain rigid rodlike conformations due to their net anisotropic...
of carboxylated polythiophenes in this work is di noted that the hydrogen-bonding-induced nematic LC gelation hexagonal LC phases of P3AT complexes without gelation and supported through short-range hydrogen bonding. It should be the LC gels may form through a network of interconnected rods formation is of the same order as the threshold of gelation. Thus, Interestingly, this critical concentration of the nematic LC textures. The period of a single band is approximately 64 μm (Figure 9b), denoting significant evidence that the LC director’s azimuthal angle is not degenerate but rather well-defined over thousands of micrometers within the substrate plane.

Figure 11 shows the quantified in-plane optical anisotropy of the aligned P3CST LC gels. The degree of order inherent in the system was determined through the distribution symmetry of transmission intensity plots. Through rotation of the P3CST films in 15° increments, gradual alterations of the transmission intensity are observed (Figure 11a). As such, the intensity of these images is plotted as a function of rotational degrees in Cartesian coordinates (Figure 11b). The resultant plot supports an overall Gaussian-like symmetry and displays minimal transmission intensity with the P3CST long axis parallel and perpendicular to the polarizer (0 or 90°). A maximum intensity is reached at an angle of 45°. These findings are consistent with previous observations made regarding Figure 10. To further demonstrate the optical anisotropy of the aligned P3CST films, transmission intensity plots were constructed in polar coordinates over a rotational range of 360°. A characteristic and highly symmetric flower pedal shape is observed (Figure 11c), denoting significant optical anisotropy of the system. Promotion of LC gelation provides a facile way to foster the large-area thin-film alignment of conjugated polymers with enhanced anisotropic properties for up and coming electronic and energy applications. After air-drying of the sheared P3CST gel films, aligned LC monodomains were maintained. Electrical

effects may play a key role in their materialization. Further investigation is warranted in this context.

A sufficiently swollen and oriented P3AT gel can provide a worthwhile preliminary material for doping of electrically conductive films. Moreover, the presence of the LC phase implies that enhanced alignment of the P3CST gel network may be possible. Estimates of the LC phase boundary and minimum gelation concentration show both of these values to be of similar order (~21 wt %). As a result, any P3CST solution of high-enough concentration to form a nematic LC phase will simultaneously form a gel. After heating and subsequent slow cooling of the P3CST gel, a shear force was applied across the still-wet polymeric samples. Figure 10 displays the alignment of P3CST gelled thin films in response to an applied mechanical shear force. At the lowest magnification, POM images of sheared P3CST thin films illustrate the existence of planar alignment in the LC domains. When the shear direction is in line with the crossed polarizers, minimal transmission intensity is detected through the POM (Figure 10a). After rotation of the microscope stage by 45°, the transmission intensity of the sample is augmented (Figure 10b). This provides significant evidence that the LC director’s azimuthal angle is not degenerate but rather well-defined over thousands of micrometers within the substrate plane.

Figure 11 shows the quantified in-plane optical anisotropy of the aligned P3CST LC gels. The degree of order inherent in the system was determined through the distribution symmetry of transmission intensity plots. Through rotation of the P3CST films in 15° increments, gradual alterations of the transmission intensity are observed (Figure 11a). As such, the intensity of these images is plotted as a function of rotational degrees in Cartesian coordinates (Figure 11b). The resultant plot supports an overall Gaussian-like symmetry and displays minimal transmission intensity with the P3CST long axis parallel and perpendicular to the polarizer (0 or 90°). A maximum intensity is reached at an angle of 45°. These findings are consistent with previous observations made regarding Figure 10. To further demonstrate the optical anisotropy of the aligned P3CST films, transmission intensity plots were constructed in polar coordinates over a rotational range of 360°. A characteristic and highly symmetric flower pedal shape is observed (Figure 11c), denoting significant optical anisotropy of the system. Promotion of LC gelation provides a facile way to foster the large-area thin-film alignment of conjugated polymers with enhanced anisotropic properties for up and coming electronic and energy applications. After air-drying of the sheared P3CST gel films, aligned LC monodomains were maintained. Electrical
conductivities of the solid films were measured at room temperature in a four-point probe configuration. Figure 12 presents $I−V$ curves of P3C5T solid films and conductivity values with probes parallel and perpendicular to the shear direction. The slight non-Ohmic behavior of the conductivities indicates some characteristic of the capacitive interface in the current−voltage measurements. Directional conductivity measurements of the P3C5T films demonstrate a clear electronic anisotropy. Careful calculations show values of the electrical conductivities both parallel and perpendicular to the direction of shear to be $(5.2 ± 1.8) \times 10^{-3}$ and $(2.3 ± 0.8) \times 10^{-3}$ S/m, respectively. As the long axis (conjugated backbone) of P3C5T chains is oriented
parallel to the shear direction, greater charge transport is observed through the intramolecular pathways as opposed to intermolecular hopping through π-π stacking. The error in the conductivity values is associated with instrumental limitations for measuring film thickness. Nevertheless, the uniformity in relative film thickness between measurements suggests that the difference in conductivity between the parallel and perpendicular orientations is accurate. Moreover, these results show conductivities comparable to those of P3HT unaligned films at $2.8 \times 10^{-3}$ S/m.\(^{59}\)

### CONCLUSIONS

In summary, we have reported on the hydrogen-bonding-directed ordered assembly of carboxylic acid-functionalized poly(3-alkylthiophene) derivatives in diluted and concentrated solutions as well as solid films. In dilute solutions, a combination of good and poor solvents is found to promote self-assembly from disordered coil-like to ordered rod-like structures. With increasing temperature, such self-organizations are thermodynamically hindered, indicating that the solution assembly process is thermally reversible. Spectroscopic transitions display second-order growth kinetics, signifying that the solution assembly involves an intermolecular mechanism promoted through the presence of hydrogen-bonded carboxyl acid side chains. In concentrated solutions, hydrogen bonding promotes thermally reversible nematic LC gelation above a critical concentration. Under an appropriate balance of mechanical and thermal stresses, mechanical shearing of LC gels induces the alignment of polymer chains at macroscopic scales. The aligned films display a significant anisotropy of optical and electrical properties, with more than 2 times faster charge transport along the backbone alignment direction compared to that in the perpendicular direction. We believe our work may provide a facile methodology to combine the alignment capacity of LCs with the processing potential of conjugated polymer gels, allowing for the improved production of high-performance electronic devices.

### EXPERIMENTAL SECTION

**Materials and Methods.** Regioregular (90−95% head-to-tail) poly[3-(5-carboxypentyl)thiophene-2,5-diyl] (P3C5T, average $M_w = 56$ kg/mol, Rieke Metals Inc.), regioregular (90−95% head-to-tail) poly[3-(5-carboxyhexyl)thiophene-2,5-diyl] (P3C6T, average $M_w = 50$ kg/mol, Rieke Metals Inc.), regioregular (90−95% head-to-tail) poly[3-(5-carboxybutyl)-thiophene-2,5-diyl] (P3C4T, average $M_w = 30$ kg/mol, Rieke Metals Inc.), regioregular (90−95% head-to-tail) poly[3-(5-carboxypropyl)thiophene-2,5-diyl] (P3C3T, average $M_w = 15$ kg/mol, Rieke Metals Inc.), dimethyl sulfoxide (DMSO, Fisher Scientific), and ethanol (EtOH, BDH 95% reagent grade) were used as received in the preparation of stock solutions (2.5 mg/mL, unless otherwise stated). All samples of the P3CnT stock solutions were first prepared in DMSO. For dilute samples containing a mixture of DMSO and EtOH solvents, the stock solution was diluted to an appropriate concentration in DMSO. The dilute sample was then heated until it displayed a bright orange color, indicating complete dissolution. The sample was removed from the heat source and an appropriate amount of EtOH was added dropwise to the solution.

**Characterization.** Fourier transform infrared (FT-IR) spectra of the concentrated solution and solid film samples were gathered on a Nicolet iS10 FT-IR spectrometer with an attenuated total reflection mode at a resolution of 4 cm$^{-1}$ of 1000 scans. Spectroscopic measurements of dilute solutions were performed on a Cary-Win UV−vis spectrophotometer. The temperature controller was set to 25 °C, and the samples were closed from ambient air atmosphere. Typically, samples were heated to 70 °C in a temperature-controlled water bath just prior to spectroscopy measurements. The samples were then quickly transferred and further diluted into a cuvette, which was preset at 25 °C. LC textures of concentrated solutions were characterized with a Leica DM2500P polarized optical microscope (POM). A Leica ICC50 high definition video camera was used to capture the images, and ImageJ software was used to process the transmission intensities. To prepare LC textured samples, a small aliquot of the concentrated solution was cast onto a clean glass slide. A coverslip was then applied atop the sample. To induce polymer alignment, a small aliquot of the LC solution was cast onto a clean glass slide. A coverslip was then applied on top of the sample with minimal pressure. The glass slide was then placed on a Linkam LTS420 hot stage. The hot stage was programmed using Linksys32 software to control the temperature. The sample was then heated to 80 °C at a rate of 5 °C/min or until a color change from dark purple to orange was observed. The sample was left to equilibrate under these conditions for 10 min. Cooling of the sample to room temperature was performed at a rate of 5 °C/min. A color change from orange to dark purple was observed, and the sample was then quickly removed from the hot stage and rapidly sheared at a high moving speed. Room-temperature conductivity measurements of dried films (~3 μm thickness) were carried out on a Keithley Instrument 2400 SourceMeter in a four-point probe configuration. Voltage sweeps were run in triplicate, with the average of the sweeps being taken as the slope of their respective $I-V$ curves.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01361.

FT-IR, SAXS, and WAXS (PDF)

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**Notes**

The authors declare no competing financial interest.

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