Absence of Electrostatic Rigidity in Conjugated Polyelectrolytes with Pendant Charges

Scott P. O. Danielsen,^{†,‡,§}[®] Emily C. Davidson,^{†,‡,||,⊥®} Glenn H. Fredrickson,^{*,†,‡,#®} and Rachel A. Segalman^{*,†,‡,#®}

[†]Department of Chemical Engineering, [‡]Materials Research Laboratory, and [#]Materials Department, University of California, Santa Barbara, California 93106, United States

Department of Chemical and Biomolecular Engineering, University of California, Berkeley, California 94720, United States

Supporting Information

ABSTRACT: The delocalization of electrons in conjugated polymers impacts their chain shape, affecting their local ordering, self-assembly, and ultimately charge transport. Conjugated polyelectrolytes introduce electrostatic interactions as a molecular design parameter to potentially tune chain rigidity by combining the π -conjugated polymer backbone with pendant ionic groups. In conventional polyelectrolytes, the self-repulsion of the bound charges induce extended rod-like chain configurations. Here, we leverage small-angle neutron scattering to measure the chain shapes of model conjugated polymers in dilute solution with controlled fractions of randomly distributed



pendant charges. We find these model polythiophenes are semiflexible, with a persistence length of approximately 3 nm, regardless of charge fraction, suggesting the effective absence of electrostatic rigidity in conjugated polyelectrolytes. While the overall persistence length is negligibly impacted by pendant charges, optical spectroscopy indicates that the pendant charges increase the backbone torsion between thiophene rings without significantly impacting the π -conjugation length (the length of electron delocalization along a nearly planar backbone) in dilute solution. These results indicate the effective decoupling of the pendant ionic charges from the overall chain conformation with implications for solution processing of organic semiconductors.

onjugated polyelectrolytes (CPEs), which combine a π - conjugated polymer backbone with pendant ionic groups, are versatile functional materials for not only traditional optoelectronic devices,¹ but also sensors and bioelectronics.²⁻⁴ The versatility arises from orthogonal control of both the aromatic backbone for tunability of optoelectronic properties and the ionic groups with charge compensating counterions for control over solution processability.^{1,5,6} The delocalization of electrons along the polymer enables the unique charge transport and optical properties, but also significantly alters the chain shape by stiffening the π -conjugated backbone due to the energetic preference for planar conformations between adjacent repeat units. The relative rigidity of conjugated polymers favors local rod-like behavior, $^{7-12}$ driving aggregation and crystallization as well as liquid-crystallinity,¹ ⁹ significantly altering their self-assembled structures and mechanical properties.²⁰⁻

The backbone rigidity of polymers is described by the persistence length l_p , which is the characteristic length scale for the exponential decay of the backbone tangent vector pair correlation function. When l_p is comparable to the monomer size, the chain behaves as a flexible coil, but, as for most conjugated polymers, if l_p is significantly larger than a monomer, the chain is semiflexible (Figure 1). Semiflexible chains are often stiff due to small backbone deflection angles θ .



Figure 1. Chain conformations are dictated by the ratio of the persistence length l_p to the contour length L_c . The persistence length is commonly impacted by steric or charge–charge interactions, degree of electron delocalization, and geometric factors.

The isomeric energy differences for conjugated polymers are typically only a few $k_{\rm B}T$, similar to polyethylene, yet conjugated polymers are significantly stiffer because the small deflection angles weaken the effects of dihedral rotations on the chain

 Received:
 July 19, 2019

 Accepted:
 August 20, 2019

 Published:
 August 22, 2019

conformation. As the deflection angles approach zero, the backbone orientation cannot be altered by dihedral rotations, and the polymer backbone behaves like a rigid rod.²⁴ Due to variations in the local conjugated polymer backbone structure, the degree of conjugated polymer rigidity, quantified by the persistence length, can vary widely from approximately 1 nm for regiorandom polythiophenes to over 40 nm for poly(pphenylenevinylene)s. The observed persistence lengths of conjugated polymers depend strongly on steric (or other interactions) between side chains, varying degrees of electron delocalization, and geometric factors such as bond angles between monomers.²³⁻²⁵ However, the connection between the chain shape of conjugated polymers and the presence of bound charges has thus far not been demonstrated, while in dilute solutions of classical polymers the repulsion of likecharges results in chain extension, a phenomenon termed electrostatic rigidity.^{26–30}

In classical polymers, the simplest approximation of this behavior describes electrostatic repulsions via the Debye-Hückel potential; charged polymers with size (e.g., radius of gyration) much larger than the Debye length κ^{-1} would be expected to have a similar random coil structure as a neutral chain in a good solvent, while at length scales smaller than the Debye length the chain should adopt an extended, rod-like structure.²⁷ However, work by Odijk³¹ and Skolnick and Fixman,³² showed that due to local correlations in the electrostatic environment, rod-like conformations persist at length scales much larger than κ^{-1} for semiflexible polyelectrolytes. Accordingly, the persistence length can be described as the sum of two contributions: (1) a bare persistence length l_0 due to the intrinsic stiffness of the polymer backbone and (2) an electrostatic contribution $l_{\rm e}$ arising from the repulsion of bound neighboring charges, partially screened by the local electrostatic environment. This electrostatic contribution is highly dependent on both the solvent dielectric constant and the concentration of added salt; theoretical estimations of l_e have been proposed spanning fully flexible and fairly stiff semiflexible polyelectrolytes 27-29,31-36semiflexible polyelectrolytes.²⁷

Doped conjugated polymers, where the "bound" charges are along the π -backbone, have shown rod-like behavior in dilute solution at high levels of doping.³⁷ However, the interplay between doping and chain conformation has not been systematically studied as the doping process leads to chain aggregation that partially obfuscates determination of singlechain structure. Further, the charges introduced by doping are mobile along the backbone contour and alter the chemical structure, affecting the electron delocalization and monomer planarization.

Conjugated polyelectrolytes allow systematic studies on the electrostatic rigidity in contrast to doped conjugated polymers, yet still complicate the classical scaling ansatz through several molecular features: (1) the charges are commonly pendant to the main chain on aliphatic linkers, (2) the backbone repeat units are commonly large and composed of rings, where the rigidity arises from torsion rather than bond extension, and (3) solubility complications arise from the bulky and hydrophobic nature of the backbone balanced by the polarity requirements of a solvent necessary to dissociate the pendant group counterions. The common use of mixed solvents further modulates the local dielectric environment.

In this work, we systematically investigate the magnitude of electrostatic rigidity induced by pendant charges on conjugated polymers. Persistence lengths, measured by small-angle neutron scattering, of a model system of CPEs surprisingly show negligible increases in stiffness from increasing the fraction of charges along the chain. Optical spectroscopy indicates that the conjugation length is also nearly unchanged by the ionic interactions as charges induce mild twisting of the aromatic backbone, which minimize like-charge repulsion while maintaining π -conjugation.

A model system of polythiophenes containing controlled fractions of pendant ionic charges was synthesized (Figure 2,



Figure 2. Repeat units containing pendant charges can be spaced out randomly along the polymer chain, generating a series of P3BImHT:P3HT copolymers with differing charged fractions.

full synthetic details described in the Supporting Information). The copolymerization of 2,5-dibromo-3-hexylthiophene and 2,5-dibromo-3-(6-bromohexyl)thiophene following a Grignard metathesis polymerization route yields low dispersity, regioregular, random copolymers (P3BrHT:P3HT) with controllable ratios (Table 1).³⁸ After precipitation, P3BrHT:P3HT copolymers can be redissolved and functionalized according to a Menshutkin amine quaternization,^{39,40} yielding ionic liquid-like charge moieties randomly distributed along the polymers (P3BImHT:P3HT) at desired charge fractions (f_{ionic}) . Dilute solutions of the nearly monodisperse P3BImHT:P3HT copolymers of similar molecular weights (measured from both SEC and SANS, Table 1) are prepared (3 mg mL^{-1}) in deuterated solvents of marginal quality. Increasing the fraction of charged monomers along the polymer requires increasingly polar solvents for dissolution. The Bjerrum length $l_{\rm B}$ is the distance at which two elementary charges interact with energy comparable to the thermal energy $k_{\rm B}T$ and is a descriptor of the strength of electrostatic interactions in the studied dilute solutions. Note: All studied samples were carefully prepared in the absence of added salt. Trace salt levels may still affect chain shape due to increased electrostatic screening.

Small-angle neutron scattering (SANS) measurements in dilute solution can be used to measure polymer conformations and probe correlations along a single polymer chain. The neutron scattering contrast arises from a difference in the scattering cross section between the hydrogenous polymer chains and the deuterated solvent. For the purpose of modeling semiflexible chains such as the studied polythiophene copolymers, the wormlike chain model (WLC) provides a useful form factor (full details in the Supporting Information.) The WLC model details a chain of contour length, L_{c} as a sequence of locally stiff segments of persistence length, l_p . At high molecular weights ($L_c \gg l_p$), the WLC description can be mapped to a freely jointed chain model with Kuhn length, $b = 2 \cdot l_p$.^{41,42}

Remarkably, across a full range of charge fraction f_{ionic} and across multiple solvent environments, all the studied

$f_{\rm ionic}$	$M_{\rm n}^{\ a} \ ({\rm g \ mol}^{-1})$	$M_{\rm w}^{\ a} \ ({\rm g \ mol}^{-1})$	D^{a}	$M_{\rm w}^{\ b} ({\rm g \ mol}^{-1})$	l _p (nm)	solvent	$l_{\rm B}~({\rm nm})$
0					$(3.0 \pm 0.2)^{c}$	d-DCB	5.7
0.25	15700	19800	1.2	14100	3.0 ± 0.4	4:1 THF-d ₈ /CD ₃ OD	4.5 ^d
0.5	7600	9000	1.2	8000	3.3 ± 0.2	4:1 THF-d ₈ :CD ₃ OD	4.5 ^d
0.75	13800	17900	1.3	10200	3.1 ± 0.4	4:1 THF-d ₈ /CD ₃ OD	4.5 ^d
1	8700	9700	1.1	9200	3.4 ± 0.4	CD ₃ OD	1.7
1	8700	9700	1.1	8900	3.1 ± 0.3	D_2O	0.7

^aAs measured by SEC from the precursor P3BrHT/P3HT copolymer in THF. ^bAs measured from the zero-angle scattering extrapolation from SANS. ^cP3HT ($f_{ionic} = 0$) persistence length obtained from McCulloch et al. *Macromolecules*, **2013**.²⁵ ^dCalculated from the volume average weighted sum of dielectric constants of pure THF and MeOH.

polythiophenes are found to have nearly identical persistence lengths of approximately 3 nm (Table 1, Figures 3 and S2).



Figure 3. Persistence length of two distinct classes of conjugated polymers (P3ATs, P3BImHT:P3HT copolymers studied here, and PCPDTBTs,⁴³ poly(4-(4,4-dialkyl-4H-cyclopenta[1,2-b:5,4-b']-dithiophen-2-yl)-*alt*-benzo-[2,1,3]-thiadiazole)) is independent of the fraction of charged repeat units.

Furthermore, examining a class of donor-acceptor copolymers for which literature comparisons can be made at the $f_{ionic} = 0$ and 1 limits⁴³ suggests that this lack of electrostatic rigidity may be universal to conjugated polymers with pendant ionic groups. The observed persistence lengths are in agreement with semianalytical model predictions of 3.2 nm, accounting for the bond deflection angles and torsional potentials between monomers of an uncharged polythiophene.^{24,25} These models do not account for long-range interactions such as excluded volume or charge repulsion. While, it might be expected that such long-range interactions would be important in predicting the chain shape of conjugated polymers, our results suggest that chain shape is dominated by the intrinsic stiffness imparted from the bonded interactions.

To understand why the persistence length of polythiophenes across different charge fractions remains constant, it is useful to understand how both conjugation length and torsional disorder are impacted by the backbone configuration. Polythiophenes have two possible monomer conformations, syn- and anti- configurations. The anti-conformation is the lower energy state and is the conformation that would result in a completely rigid polymer backbone. However, the synconformation is a competitive state with an energy difference of only a few $k_{\rm B}T$. Furthermore, the dihedral potential has an accessible barrier, resulting in a Boltzmann distribution of both syn- and anti- states, along with a non-negligible amount of backbone torsion. Both the syn- and anti- states preserve conjugation along the backbone by retaining the planar geometry. There can also be small amounts of torsional disorder away from planarity without breaking π -conjugation.²⁵ Thus, flexibility of the polythiophene backbone arises from both a distribution of syn- and anti-conformations and finite torsion between repeat units.

Significant levels of backbone torsion would result in an increase in the optical band gap (shorter conjugation length) and decreased persistence length. Both the syn- and anticonformations are planar, and these conformations maintain conjugation along the backbone so a change in the distribution of syn- and anti- states alters the persistence length without affecting the conjugation length. Here we directly probe the conjugation length and degree of backbone torsion by optical absorption and fluorescence spectra to elucidate how monomer conformations and backbone torsion affect the final chain shape.^{25,39,44–48} Absorption and fluorescence spectra are consistent with all polymers having random coil-type configurations (Figure 4a), based on their featureless broad absorption and fluorescence peaks, as expected for dilute solution and seen in the neutron scattering (Figure S2).

All the polymers (except for $f_{\rm ionic} = 1$ in H₂O, discussed below) have nearly the same conjugation lengths irrespective of their charge fraction or solvent (Figure 4a, Table 2). While it might have been expected that repulsion of like charges would splay the side chains apart, causing significant backbone torsion, this result is consistent with the minimal steric effects of side chain length and branching on conjugation length observed in neutral poly(3-alkylthiophene)s.²⁵ It is also possible that repulsions between side chains of adjacent thiophene units, due to steric bulk or charges, cause a slightly higher population of anti-configurations, but are offset by a slight increase in backbone torsion. This would result in the observed relatively unchanged persistence and conjugation lengths.

Time-resolved measurements of the fluorescence lifetime, the amount of time the exciton stays in the excited state, can provide higher sensitivity information about potential backbone torsion or disorder of the π domains.^{39,46,47,49} Vibrational relaxations, frequently from the induced exciton encountering a break in conjugation or through other disorder of the π orbitals,^{48,50} cause a loss of energy in the excited state resulting in the molecule returning to the ground state and the emission



Figure 4. Conjugation length (in both ground and excited states) is affected by solvent choice, but is nearly independent of the fraction of charged repeat units. Rather than extending the π -conjugation and overall chain size, increasing the charge along the polymer generates additional backbone torsion, twisting the chain contour. (a) Absorbance (low-wavelength curves) and photoluminescence (high-wavelength curves) shown normalized to their peak absorption and emission, respectively. (b) Photoluminescence decays as a function of charged fraction, showing faster decay as the percent of charge is increased. Symbols are measured data and lines are corresponding exponential fits.

Table 2. Photophysical Properties of Studied PSDIMHT: PSHT Copolyment	Table	e 2.	Photoph	nysical	Properties	of Studied	P3BImHT:P3HT	Copolymer
---	-------	------	---------	---------	------------	------------	--------------	-----------

$f_{\rm ionic}$	solvent	$\epsilon_{ m r}$	$E_{\rm g,opt}^{c}$ (eV)	$t_{\rm fast}/\epsilon_{\rm r}~({\rm ps})$	$f_{ m slow}$	$t_{\rm slow}/\epsilon_{\rm r}~({\rm ps})$
0	THF	7.58	2.27		1	76.4 ± 0.34
0.25	4:1 THF/MeOH	12.6 ^b	2.27	38.8 ± 7.97	0.711 ± 0.109	45.3 ± 5.28
0.5	4:1 THF/MeOH	12.6 ^b	2.27	15.7 ± 1.24	0.754 ± 0.023	45.1 ± 0.67
0.75	4:1 THF/MeOH	12.6 ^b	2.27	9.88 ± 0.57	0.738 ± 0.012	41.7 ± 0.45
1	MeOH	32.7	2.27	4.00 ± 0.21	0.813 ± 0.007	20.5 ± 0.13
	H ₂ O	78.6	2.08	2.41 ± 0.08	0.424 ± 0.012	10.8 ± 0.20

 ${}^{a}\epsilon_{r}$ is the relative dielectric constant of the solvent; $E_{g,opt}$ is the optical bandgap; t_{fast} is the short photoluminescence lifetime; t_{slow} is the relative fraction of the total photoluminescence attributable to the long lifetime process. b Taken to be the volume average weighted sum of dielectric constants of pure THF and MeOH. ^cCalculated from the onset of absorption.

of a photon. P3HT in THF has only one such process due to the loss of π -conjugation from torsional fluctuations along the flexible backbone resulting in a monoexponential photoluminescence decay with a time constant of (579.3 ± 2.6) ps.

All the charge-containing conjugated polyelectrolytes are observed to have biexponential photoluminescence decays with two characteristic time constants, presumably due to increased levels of dihedral disorder along the conjugated polymer backbone.^{39,46–48} The long lifetime component t_{slow} of the CPEs is comparable to that of the P3HT lifetime. However, with increasing charge fraction, a new short lifetime t_{fast} appears, likely attributable to increased torsional relaxations due to charge-charge repulsions.⁵⁰ It is proposed that the electrostatic repulsions increase the energy of the syn and anti conformations, while the energetic barrier is relatively unperturbed, resulting in broader shallower energetic minima around 0° and 180°. Some energy is stored in torsion around the lowest energy planar conformers such that thermal fluctuations can more easily break conjugation and emit a photon. The charge-charge repulsions thus likely affect the backbone torsion dynamically without significantly altering the

overall dihedral distribution, decreasing the short photoluminescence lifetime while preserving the conjugation and persistence lengths.

The short and long lifetimes depend on both the charge fraction and solvent due to a convolution of structural changes and dielectric constant changes. Photon emission involves a dipolar relaxation and is sensitive to the local dielectric medium and thus the dielectric constant of the suspending solvent even without structural changes;⁴⁸ the photoluminescence lifetimes increase with increasing dielectric constant (dramatically so upon the large dielectric constant increase from methanol to water for $f_{\text{ionic}} = 1$), potentially obscuring the chain shape data for polymers in different solvents. Furthermore, the relatively low dielectric constants and thus long Bjerrum lengths of organic and mixed solvents may impart significant ion condensation,⁵¹ increasing the effective charge spacing to ~ l_{B} , which may contribute to the weak effects of electrostatics on the chain shape.

Structural changes of the conjugated polyelectrolytes are at first order deconvoluted from these subtle dielectric effects by scaling the lifetimes with the solvent dielectric constant and through use of a common solvent (4:1 THF/MeOH) across a wide charge fraction ($f_{\rm ionic} = 0.25-0.75$); the photoluminescence lifetime differences in that series are attributable solely to chromophore structural changes that result from fine differences in the overall chain conformation (Figure 4b, Table 2). The photoluminescence lifetimes decrease with an increasing fraction of charges, reinforcing the likely increase of torsional disorder as the charge content along the polymer increases. Since the conjugation length is constant, the twisting of the chromophores is likely gentle, allowing weaker, but persistent, π -conjugation.⁴⁸ This is consistent with a nearly unchanged conjugation length, but a reduction in the photoluminescence lifetime. Thus, the repulsions between pendant like-charges result in subtle twisting of the backbone instead of extension of conjugation or persistence lengths.

In summary, we have shown the effective absence of electrostatic rigidity in dilute solutions of conjugated polyelectrolytes with pendant charges. A model system of polythiophenes with different fractions of charged side chains were all found, via small-angle neutron scattering, to have nearly identical persistence lengths of approximately 3.0 nm. This trend was found to be true in a class of donor-acceptor copolymers, PCPDTBTs, as well, where the 100% charged polymer has only a very minor increase in chain stiffness from the uncharged case. The lack of electrostatic rigidity is in contrast to theories such as the OSF theory^{31,32} or experimental evidence in conventional polyelectrolytes. The deviation from more traditional charge-containing polymers is attributed to several unique molecular features of conjugated polymers: the already low deflection angles from near-planar rings in backbone, the location of charges farther away from the backbone on pendant flexible linkers, and the long Bjerrum lengths of commonly used solvents. Photophysical interrogation of the studied conjugated polymers further suggests that increasing the charge fraction increases torsional disorder, but only weakly, and thus the polymers maintain equivalent π conjugation and persistence lengths. It is likely that the architecture of the side chains (where the charges are chemically bound, how they are reoriented and the ability to reorient to minimize the electrostatic repulsion) will significantly impact the rigidity of the chain. Future studies into the chain conformations of conjugated polyelectrolytes should focus on how interactions, particularly combining both ionic and steric interactions, between side chains can be designed to manipulate overall chain stiffness for control of self-assembly and optoelectronic properties.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacro-lett.9b00551.

Experimental details, characterization data, and SANS fit parameters (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: ghf@ucsb.edu.

*E-mail: segalman@ucsb.edu.

ORCID [©]

Scott P. O. Danielsen: 0000-0003-3432-5578 Emily C. Davidson: 0000-0001-5819-9233 Glenn H. Fredrickson: 0000-0002-6716-9017

Rachel A. Segalman: 0000-0002-4292-5103

Present Addresses

[§]Department of Mechanical Engineering and Materials Science, Duke University, Durham, NC 27708, U.S.A.

[⊥]John A. Paulson School of Engineering and Applied Sciences, Wyss Institute for Biologically Inspired Engineering, Harvard University, Cambridge, MA 02138, U.S.A.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors gratefully acknowledge support from the Department of Energy (DOE) Office of Basic Energy Sciences under Grant No. DE-SC0016390. A portion of this research used neutron research facilities at the Spallation Neutron Source, a DOE Office of Science User Facility operated by the Oak Ridge National Laboratory and the National Institute of Standards and Technology, U.S. Department of Commerce, supported in part by the National Science Foundation (NSF) under Agreement No. DMR-1508249. The Materials Research Laboratory Shared Experimental Facilities are supported by the Materials Research Science and Engineering Centers Program of the NSF under Award No. DMR 1720256; a member of the NSF-funded Materials Research Facilities Network. The authors thank Dr. Alexander Mikhailovsky (UCSB) for assistance in obtaining the time-resolved photoluminescence spectroscopy measurements and Dr. Rachel Behrens (UCSB) for assistance in polymer characterization and analysis.

REFERENCES

(1) Hoven, C. V.; Garcia, A.; Bazan, G. C.; Nguyen, T. Q. Recent Applications of Conjugated Polyelectrolytes in Optoelectronic Devices. *Adv. Mater.* **2008**, *20*, 3793–3810.

(2) Rivnay, J.; Inal, S.; Salleo, A.; Owens, R. M.; Berggren, M.; Malliaras, G. G. Organic Electrochemical Transistors. *Nat. Rev. Mater.* **2018**, *3*, 170861–1708614.

(3) Rivnay, J.; Owens, R. M.; Malliaras, G. G. The Rise of Organic Bioelectronics. *Chem. Mater.* **2014**, *26*, 679–685.

(4) Rivnay, J.; Inal, S.; Collins, B. A.; Sessolo, M.; Stavrinidou, E.; Strakosas, X.; Tassone, C.; Delongchamp, D. M.; Malliaras, G. G. Structural Control of Mixed Ionic and Electronic Transport in Conducting Polymers. *Nat. Commun.* **2016**, *7*, 11287.

(5) Pinto, M. R.; Schanze, K. S. Conjugated Polyelectrolytes: Synthesis and Applications. *Synthesis* **2002**, *9*, 1293–1309.

(6) Jiang, H.; Taranekar, P.; Reynolds, J. R.; Schanze, K. S. Conjugated Polyelectrolytes: Synthesis, Photophysics, and Applications. *Angew. Chem., Int. Ed.* **2009**, *48*, 4300–16.

(7) Sirringhaus, H.; Wilson, R. J.; Friend, R. H.; Inbasekaran, M.; Wu, W.; Woo, E. P.; Grell, M.; Bradley, D. D. C. Mobility Enhancement in Conjugated Polymer Field-Effect Transistors through Chain Alignment in a Liquid-Crystalline Phase. *Appl. Phys. Lett.* **2000**, 77, 406–408.

(8) Zhu, Z. G.; Swager, T. M. Conjugated Polymer Liquid Crystal Solutions: Control of Conformation and Alignment. *J. Am. Chem. Soc.* **2002**, *124*, 9670–9671.

(9) Bridges, C. R.; Ford, M. J.; Popere, B. C.; Bazan, G. C.; Segalman, R. A. Formation and Structure of Lyotropic Liquid Crystalline Mesophases in Donor-Acceptor Semiconducting Polymers. *Macromolecules* **2016**, *49*, 7220–7229.

(10) Bridges, C. R.; Ford, M. J.; Thomas, E. M.; Gomez, C.; Bazan, G. C.; Segalman, R. A. Effects of Side Chain Branch Point on Self Assembly, Structure, and Electronic Properties of High Mobility Semiconducting Polymers. *Macromolecules* **2018**, *51*, 8597–8604.

(11) Bridges, C. R.; Ford, M. J.; Bazan, G. C.; Segalman, R. A. Molecular Considerations for Mesophase Interaction and Alignment of Lyotropic Liquid Crystalline Semiconducting Polymers. *ACS Macro Lett.* **2017**, *6*, 619–624.

(12) Martin, J.; Davidson, E. C.; Greco, C.; Xu, W. M.; Bannock, J. H.; Agirre, A.; de Mello, J.; Segalman, R. A.; Stingelin, N.; Daoulas, K. C. Temperature-Dependence of Persistence Length Affects Phenomenological Descriptions of Aligning Interactions in Nematic Semiconducting Polymers. *Chem. Mater.* **2018**, *30*, 748–761.

(13) Yang, S. H.; Hsu, C. S. Liquid Crystalline Conjugated Polymers and Their Applications in Organic Electronics. J. Polym. Sci., Part A: Polym. Chem. 2009, 47, 2713–2733.

(14) Zhu, Z. G.; Swager, T. M. Conjugated Polymer Liquid Crystal Solutions: Control of Conformation and Alignment. *J. Am. Chem. Soc.* **2002**, *124*, 9670–9671.

(15) Kim, B. G.; Jeong, E. J.; Chung, J. W.; Seo, S.; Koo, B.; Kim, J. S. A Molecular Design Principle of Lyotropic Liquid-Crystalline Conjugated Polymers with Directed Alignment Capability for Plastic Electronics. *Nat. Mater.* **2013**, *12*, 659–664.

(16) Sirringhaus, H.; Tessler, N.; Friend, R. H. Integrated Optoelectronic Devices Based on Conjugated Polymers. *Science* **1998**, 280, 1741–1744.

(17) Sirringhaus, H.; Wilson, R. J.; Friend, R. H.; Inbasekaran, M.; Wu, W.; Woo, E. P.; Grell, M.; Bradley, D. D. C. Mobility enhancement in conjugated polymer field-effect transistors through chain alignment in a liquid-crystalline phase. *Appl. Phys. Lett.* **2000**, 77, 406–408.

(18) Olsen, B. D.; Segalman, R. A. Self-Assembly of Rod-Coil Block Copolymers. *Mater. Sci. Eng.*, R 2008, 62, 37–66.

(19) Rivnay, J.; Mannsfeld, S. C. B.; Miller, C. E.; Salleo, A.; Toney, M. F. Quantitative Determination of Organic Semiconductor Microstructure from the Molecular to Device Scale. *Chem. Rev.* **2012**, *112*, 5488–5519.

(20) Mollinger, S. A.; Krajina, B. A.; Noriega, R.; Salleo, A.; Spakowitz, A. J. Percolation, Tie-Molecules, and the Microstructural Determinants of Charge Transport in Semicrystalline Conjugated Polymers. *ACS Macro Lett.* **2015**, *4*, 708–712.

(21) Noriega, R.; Salleo, A.; Spakowitz, A. J. Chain Conformations Dictate Multiscale Charge Transport Phenomena in Disordered Semiconducting Polymers. *Proc. Natl. Acad. Sci. U. S. A.* **2013**, *110*, 16315–16320.

(22) Noriega, R.; Rivnay, J.; Vandewal, K.; Koch, F. P.; Stingelin, N.; Smith, P.; Toney, M. F.; Salleo, A. A General Relationship Between Disorder, Aggregation and Charge Transport in Conjugated Polymers. *Nat. Mater.* **2013**, *12*, 1038–44.

(23) Kuei, B.; Gomez, E. D. Chain Conformations and Phase Behavior of Conjugated Polymers. *Soft Matter* **2017**, *13*, 49–67.

(24) Zhang, W. L.; Gomez, E. D.; Milner, S. T. Predicting Chain Dimensions of Semiflexible Polymers from Dihedral Potentials. *Macromolecules* **2014**, *47*, 6453–6461.

(25) McCulloch, B.; Ho, V.; Hoarfrost, M.; Stanley, C.; Do, C.; Heller, W. T.; Segalman, R. A. Polymer Chain Shape of Poly(3alkylthiophenes) in Solution Using Small-Angle Neutron Scattering. *Macromolecules* **2013**, *46*, 1899–1907.

(26) Tricot, M. Comparison of Experimental and Theoretical Persistence Length of Some Polyelectrolytes at Various Ionic Strengths. *Macromolecules* **1984**, *17*, 1698–1704.

(27) Barrat, J. L.; Joanny, J. F. Theory of Polyelectrolyte Solutions. *Adv. Chem. Phys.* **1996**, *94*, 1–66.

(28) Dobrynin, A. V.; Colby, R. H.; Rubinstein, M. Scaling Theory of Polyelectrolyte Solutions. *Macromolecules* **1995**, *28*, 1859–1871.

(29) Dobrynin, A. V. Electrostatic Persistence Length of Semiflexible and Flexible Polyelectrolytes. *Macromolecules* **2005**, *38*, 9304–9314.

(30) Murnen, H. K.; Rosales, A. M.; Dobrynin, A. V.; Zuckermann, R. N.; Segalman, R. A. Persistence Length of Polyelectrolytes with Precisely Located Charges. *Soft Matter* **2013**, *9*, 90–98.

(31) Odijk, T. Polyelectrolytes Near the Rod Limit. J. Polym. Sci., Polym. Phys. Ed. 1977, 15, 477–483.

(32) Skolnick, J.; Fixman, M. Electrostatic Persistence Length of a Wormlike Polyelectrolyte. *Macromolecules* **1977**, *10*, 944–948.

(33) Ha, B. Y.; Thirumalai, D. Electrostatic Persistence Length of a Polyelectrolyte Chain. *Macromolecules* **1995**, *28*, 577–581.

(34) Everaers, R.; Milchev, A.; Yamakov, V. The Electrostatic Persistence Length of Polymers Beyond the OSF Limit. *Eur. Phys. J. E: Soft Matter Biol. Phys.* **2002**, *8*, 3–14.

(35) Nguyen, T. T.; Shklovskii, B. I. Persistence Length of a Polyelectrolyte in Salty Water: Monte Carlo Study. *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.* **2002**, *66*, 021801.

(36) Ullner, M. Comments on the Scaling Behavior of Flexible Polyelectrolytes Within the Debye-Huckel Approximation. J. Phys. Chem. B 2003, 107, 8097-8110.

(37) Aime, J. P.; Bargain, F.; Schott, M.; Eckhardt, H.; Miller, G. G.; Elsenbaumer, R. L. Structural Study of Doped and Undoped Polythiophene in Solution by Small-Angle Neutron-Scattering. *Phys. Rev. Lett.* **1989**, *62*, 55–58.

(38) Palermo, E. F.; McNeil, A. J. Gradient Sequence π -Conjugated Copolymers. ACS Symp. Ser. 2014, 1170, 287–299.

(39) Danielsen, S. P. O.; Nguyen, T. Q.; Fredrickson, G. H.; Segalman, R. A. Complexation of a Conjugated Polyelectrolyte and Impact on Optoelectronic Properties. *ACS Macro Lett.* **2019**, *8*, 88– 94.

(40) Pipertzis, A.; Muhlinghaus, M.; Mezger, M.; Scherf, U.; Floudas, G. Polymerized Ionic Liquids with Polythiophene Backbones: Self-Assembly, Thermal Properties, and Ion Conduction. *Macromolecules* **2018**, *51*, 6440–6450.

(41) Kratky, O.; Porod, G. Diffuse Small-Angle Scattering of X-Rays in Colloid Systems. J. Colloid Sci. 1949, 4, 35–70.

(42) Saito, N.; Takahashi, K.; Yunoki, Y. Statistical Mechanical Theory of Stiff Chains. J. Phys. Soc. Jpn. 1967, 22, 219–226.

(43) Danielsen, S. P. O.; Sanoja, G. E.; McCuskey, S. R.; Hammouda, B.; Bazan, G. C.; Fredrickson, G. H.; Segalman, R. A. Mixed Conductive Soft Solids by Electrostatically Driven Network Formation of a Conjugated Polyelectrolyte. *Chem. Mater.* **2018**, *30*, 1417–1426.

(44) Klaerner, G.; Miller, R. D. Polyfluorene Derivatives: Effective Conjugation Lengths from Well-Defined Oligomers. *Macromolecules* **1998**, *31*, 2007–2009.

(45) Meier, H.; Stalmach, U.; Kolshorn, H. Effective Conjugation Length and UV/vis Spectra of Oligomers. *Acta Polym.* **1997**, *48*, 379–384.

(46) Nguyen, T. Q.; Schwartz, B. J. Ionomeric Control of Interchain Interactions, Morphology, and the Electronic Properties of Conjugated Polymer Solutions and Films. *J. Chem. Phys.* **2002**, *116*, 8198–8208.

(47) Nguyen, T. Q.; Doan, V.; Schwartz, B. J. Conjugated Polymer Aggregates in Solution: Control of Interchain Interactions. *J. Chem. Phys.* **1999**, *110*, 4068–4078.

(48) Simine, L.; Rossky, P. J. Relating Chromophoric and Structural Disorder in Conjugated Polymers. *J. Phys. Chem. Lett.* **2017**, *8*, 1752–1756.

(49) Dominguez, S. E.; Cangiotti, M.; Fattori, A.; Aaritalo, T.; Damlin, P.; Ottaviani, M. F.; Kvarnstrom, C. Effect of Spacer Length and Solvent on the Concentration-Driven Aggregation of Cationic Hydrogen-Bonding Donor Polythiophenes. *Langmuir* 2018, 34, 7364–7378.

(50) Ferreira, B.; da Silva, P. F.; Seixas de Melo, J. S.; Pina, J.; Macanita, A. Excited-State Dynamics and Self-Organization of Poly(3-hexylthiophene) (P3HT) in Solution and Thin Films. *J. Phys. Chem. B* **2012**, *116*, 2347–2355.

(51) Manning, G. S. Limiting Laws and Counterion Condensation in Polyelectrolyte Solutions. I. Colligative Properties. *J. Chem. Phys.* **1969**, *51*, 924–933.