Controlling chain conformation in conjugated polymers using defect inclusion strategies

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Abstract.

The Horner method was used to synthesize random copolymers of MEH-PPV that incorporated different backbone directing monomers. Single molecule polarization absorption studies of these new polymers demonstrate that defects that preserve the linear backbone of PPVtype polymers assume highly anisotropic configurations found in defect-free MEH-PPV. Rigid defects that are bent lower the anisotropy of the single chain, and saturated defects that provide rotational freedom for the chain backbone allow for a wide variety of possible configurations. Molecular dynamics simulations of model defect PPV oligomers in solution demonstrate that defect-free and linear defected oligomers are incapable of folding while the bent and saturated defects tend toward folded, more compact structures.

Introduction

With the increasing interest in conjugated polymers and their use in low cost, easily processed devices such as OLEDs, photovoltaics, and field effect transistors, understanding the role that morphology plays in the electronic properties and long term stability of these devices is critical to creating better materials.¹⁻³ Discerning how the structure of a single chain evolves from a single molecule to a thin film, a bulk heterojunction, or even a higher-order structure will lead to key insights for molecular design strategies. Single chain structure has long been a topic of interest.⁴⁻⁹ Over the course of the last decade, numerous studies have provided evidence that the prototypical conjugated polymer MEH-PPV, when isolated in a matrix of PMMA, can assume a myriad of configurations ranging from highly amorphous structures such as the "molten globule" and "defect cylinder" to highly ordered ones such as the "toroid" and "rod."¹⁰ Recent improvements in synthetic methods, polymer purification techniques and optical characterization have shown that MEH-PPV chains uniformly fold into a single, highly-anisotropic rod-like structure, as proposed previously.⁴

Recent work has demonstrated that synthetic strategies to incorporate saturated backbone defects can disrupt the nature of polymer backbone folding by acting as kinks in the rigid PPV chain. Polarization anisotropy measurements and simulations show that higher defect inclusion rates lower the anisotropy values measured for these conjugated systems.¹⁰ However in these previous studies, the vinyl linkages in the PPV backbone were randomly saturated resulting in a truncation of the chromophores in the chain. This leads to a blue shift of the solution absorption spectra by an amount dictated by the degree of backbone saturation and concomitantly limits the range of energy funneling that occurs in typical conjugated polymer molecules.¹¹ In comparison to recent results,⁴ the discrepancies between older synthetic efforts and today's commercially available materials deserves attention as well as more refined techniques aimed at polymer conformational control. It is natural to ask if, with proper synthetic techniques, one can controllably alter the conformation of a single polymer chain in a controlled and systematic manner characterizable by single molecule and theoretical methods. In this study, we measure the polarization anisotropy of single polymer chains with a variety of "morphology directing"

inclusions of different concentrations. These "defects" include groups that preserve the high anisotropy originally observed in MEH-PPV, rigid groups that result in very low anisotropy conformations, and a flexible group that allows for a broad distribution of observable anisotropies. Molecular dynamics simulations have been performed on long oligomers of "defected" MEH-PPV to provide insight into the role that defects play on the local folding of the polymer chain in solution. This collaborative effort thus demonstrates a powerful synthetic approach for polymer morphology control.

Materials and Methods

Materials. Poly [2-methoxy-5-((2'-ethylhexyl) oxy) 1,4-phenylenevinylene)] (MEH-PPV) and defected variants of MEH-PPV were synthesized using the Horner condensation polymerization (Scheme 1).¹² Details of the synthesis and characterization of the conjugated polymers used in this study are provided in the supporting information. In general, a di-phosphonate ester was mixed with varying ratios of a "linear dialdehyde" and a "defect dialdehyde". The

Scheme 1. Horner condensation polymerization with defect inclusion.



polymerization was initiated by the addition of potassium tert-butoxide. The number average molecular weight of all species studied was measured by gel permeation chromatography and found to be M_n 12-25 kDa with PDI ranging from 1.4 to 2.1. Glass coverslips were cleaned with piranha solution (1:3 hydrogen peroxide:sulfuric acid by volume) followed by rinsing in DI water. Isolated chains of the conjugated polymer were prepared in a PMMA (polymethylmethacrylate) matrix by dynamic spin-casting from a toluene solution of PMMA and dilute conjugated polymer. Sample solution concentrations were adjusted such that a typical

image yielded 15 fluorescent spots on average. The final thicknesses of these films were determined by atomic force microscopy (AFM) and found to be 200nm. Photooxidation of samples was prevented by packaging the sample using an epoxy resin (GC electronics, 2 Part Epoxy Glue) and another coverslip. Sample preparation and packaging was performed inside a glovebox (MBraun, O_2 and H_2O less than 5 ppm). Samples were investigated within a few days of preparation in order to avoid unwanted photooxidation.

Wide-Field Fluorescence Polarization Spectroscopy Apparatus. Samples were investigated using a 488-nm and 458-nm excitation wide-field fluorescence polarization spectroscopy microscope. The 488-nm microscope has been described in detail elsewhere,⁴ and the 457-nm microscope is based on the same principles. Briefly, the apparatus is based on an inverted microscope (Zeiss Axiovert 135TV) with a 0.9 NA objective lens (Zeiss Epiplan Neofluar 100X) and a wide-field detection scheme using an EMCCD detector (Andor iXon+ DU-897C). The excitation source is the 458-nm line of an Ar ion laser (Melles Griot, model IMA101040ALS). The polarization of the excitation beam was rotated around the axis of propagation of the laser using an electro-optic modulator (EOM, Fastpulse technology, model 3079-4), a voltage amplifier (Trek, model 601C), and a programmable function generator (Wavetek, model 29). The polarization ratio was measured to be greater than 20:1 at every polarization angle. The Gaussian illumination area was ~40µm at fwhm and the corresponding excitation power was 1.5 Wcm⁻². Scattered laser light was rejected by a long-pass dichroic mirror and a 458-nm notch filter (Chroma). Fluorescence intensities of single molecules were measured as a function of the polarization angle, θ . The intensities of individual molecules were calculated by integration over a 5 X 5 pixel area with the box centered on the most intense pixel and a local background subtraction for each molecule was performed. The intensities were synchronously time averaged over multiple polarization cycles in order to obtain better signal-to-noise ratios. All data analysis was performed using home written Matlab code.

Computational Modeling

Structures Examined. Five 15-unit MEH-PPV oligomers were designed with differing, randomly assigned, tacticities. Defects were then substituted into each of these chains in two different ways, resulting in a set of 10 oligomers for each designed defect, and a corresponding

five oligomers for the non-defected chain. Defects were inserted such that either every third MEH-PPV monomer was replaced by a defect or each MEH-PPV monomer was replaced by a defect with a 1/3 probability. The probabilistic determination of defect placement was performed just once for each of the five atactic oligomers, resulting in a consistent test set of matching oligomers for all the designed defects. Initial models were constructed using PyMOL,¹³ and all polymer linkages were made in the *trans* configuration.

Model. The OPLS2005 force field was used with a constant dielectric constant of 1.0 and no cutoffs in the potential.¹⁴ The Analytical Generalized Born plus Nonpolar (ABGNP)¹⁵ implicit solvent model was adjusted to approximate the effect of solvation in toluene by changing the dielectric constant, the surface tension, the density, and the Lennard-Jones parameters to appropriate values. We used a constant value of 0.7 for the fitting parameter α_i in¹⁵ to better approximate the self-solvation free energy of toluene.¹⁶

REMD. Using the program IMPACT,¹⁴ replica exchange molecular dynamics (REMD)¹⁷ was run from extended initial configurations with 8 replicas ranging in temperature from 300 to 377 Kelvin. MD time steps were 1 fs, replica exchanges were attempted every 250 steps, and each simulations ran for 5 ns. The replica exchange acceptance ratio was consistently ~40%. A Nosé-Hoover thermostat^{18,19} was used to sample the NVT ensemble, and results are shown for 300K.

Analysis. Results are reported from the ensembles generated at 300 K. Radii of gyration are calculated from the coordinates of just the initial carbon atom from each monomer, as are the vectors representing the orientation of the chain between each monomer. A set of 15 atom coordinates is therefore used to calculate the center of mass and then the distances contributing to the radius of gyration for each structure, and a corresponding set of 14 vectors is used to determine the anisotropy for each structure. Statistics are calculated on 500 structures from each REMD run. An anisotropy order parameter, *A*, is also calculated.⁴ $A=(3S_c)/(2+S_c)$ and S_c , the order parameter of the polymer chain, is calculated as $S_c = 0.5\langle 3(\cos^2 \beta) - 1 \rangle$, where the angled brackets indicate an average over the full set of chain vectors for each structure and β is the angle between each chain vector and the principal internal axis of those vectors. A value of A = 1.0

indicates complete alignment of the chain vectors while a value of A = 0.0 indicates no alignment. Average values of the radius of gyration and the anisotropy order parameter are then calculated over the set of 5 unique polymer sequences for the non-defected MEH-PPV and over the set of 10 unique polymer sequences for the defected MEH chains.

Results and Discussion

Solution absorption and emission spectra. The chemical structures of MEH-PPV and the defect copolymers are shown in the left side of Figure 1(A-D) and each compound's corresponding solution phase absorption and emission spectra on the right side (Figure 1(E-H)), with (A)MEH-PPV, (B)para-terphenyl defected MEH-PPV (para-terphenyl MEH), (C)orthoterphenyl defected MEH-PPV (ortho-terphenyl MEH), and (D)1,2-diphenylethane defected MEH-PPV (saturated MEH). The para-terphenyl defect is a stiff linear molecule that is expected to maintain the linearity of the PPV backbone. The ortho-terphenyl defect is a highly kinked species that should disturb the ordering of the pristine polymer, and the saturated defect lends rotational flexibility to the polymer backbone. The absorption maximum of defect free MEH-PPV is 503 nm, in good agreement with previous work, while the 10% defected polymers each undergo substantial blue shifts (~20 nm) and the 30% demonstrating shifts up to 80 nm dependent on defect type. Previous studies have shown that the absorption spectra of PPV type polymers is sensitive to the concentration of saturated defects along the polymer backbone with increased defects blue shifting the absorption to higher energies, consistent with our results.¹¹ Solution emission spectra for all defected species show only modest change upon defect inclusion as shown in Figure 1. At 10% defect inclusion, emission spectra are almost identical to that of MEH-PPV, and even at 30% defect inclusion, the peak of emission is blue shifted by <10 nm. Spectra at 30% are also broadened, masking the vibronic band shoulder. The fact that the emission spectra of the defected polymers are not blue-shifted, suggests that even in the highly defected species there are still a subset of lower energy longer chromophores present in each polymer chain and energy transfer to these emitting sites remains efficient in solution.

NMR Analysis. MEH-PPV samples were prepared via the Horner condensation method, which has been shown to produce *trans* double bonds in preference to *cis* double bonds.²⁰ NMR characterization of the methylene resonances from the ethylhexyl group from 3.5-4.0 ppm provides a quantitative marker for determining the *cis:trans* ratio.^{21,22} The methylene protons

adjacent to *trans* double bonds arise at 3.9 ppm while the methylene protons adjacent to a *cis* double bond appear at 3.5 ppm. Using these characterization strategies, MEH-PPVs prepared by the Horner method have consistently reported *cis* inclusion rates of 2-5%.²⁰⁻²² Our synthesized MEH-PPV, without the incorporation of defect sites, showed a similar *cis* double bond inclusion of 5.3%. However, we have found that including engineered defect sites in the polymer backbone can dramatically disturb the *cis:trans* ratio in MEH-PPV. For example, when preparing MEH-PPV with ortho-terphenyl defect groups at 10% or 30% defect loading, the *cis* double bond inclusion rate was again high at 19.0% and 15.1%, respectively.

The inclusion of para-terphenyl defects at 10% or 30% loading provided polymers with *cis* double bond inclusion rates of 5.8% and 7.6%, respectively, similar to that of the native MEH-PPV. We theorize the incorporated defects template the polymerization and influence the chemical reaction pathway (i.e., formation of *cis* or *trans* double bonds). The

Table 1. Incorporation of *cis* double bonds inMEH-PPV backbone

Polymer	% cis
MEH-PPV	5.3
10% ortho-terphenyl	18.7
30% ortho-terphenyl	13.1
10% saturated	19.0
30% saturated	15.1
10% para-terphenyl	5.8
30% para-terphenyl	7.6

para-terphenyl defect is a linear segment that does not undermine the linear *trans* double bonds of MEH-PPV and therefore we see little change to the amount of *cis* inclusion. In contrast to the linear defect, the ortho-terphenyl defect installs a 60° kink in the polymer backbone. This structural modification disorients the polymer segments away from linearity and templates a more globular assembly. To allow better intra-molecular chain packing, we suggest *cis* double bonds are incorporated at higher rates during polymerization to help re-adjust the polymer segments in the globular structure and reduce the overall energy. A similar result arises from incorporation of the conformationally flexible, saturated defect. During polymer growth the defects could provide a hinge-like segment that allows the polymer segments to back-bite and create more *intra*-molecular associations. A globular structure can result that would warrant the inclusion of more *cis* defects. Finally, the *cis* double bond inclusion was slightly greater in MEH-PPVs with 10% defect inclusion than in 30 % defect inclusion polymers. **Polarization Modulation Depth.** The absorption polarization modulation was measured for ensembles of single polymer chains of MEH-PPV with the conformation directing groups discussed above as well as "pure" MEH-PPV for comparison. This method has been discussed in detail in previous studies.^{4,10} In brief, using the microscope apparatus described above, linearly polarized excitation is modulated such that the angle of polarization is rotated 180 degrees. As the angle of the polarized light matches the orientation of a transition dipole in a fluorescent species, the increase in excitation rate becomes apparent from the increased fluorescence intensity. This interplay between fluorescence intensity and polarization angle, θ , is described by the following equation

$I(\theta) \propto 1 + M \cos 2(\theta - \phi)$

where ϕ is the orientation when the emission intensity is maximized. *M* is the polarization modulation depth. For a single dipole or a collection of dipoles with similar orientation, M = 1. For an isotropic distribution of dipoles where the spacing between dipoles is much smaller than the diffraction limit of light, M = 0, i.e. no modulation should be observed.

In the case of a conjugated polymer such as MEH-PPV, a single chain consists of multiple chromophore segments, each composed of a set of sequential monomers, that are capable of absorbing light.²³ Recent polarization modulation measurements of defect-free MEH-PPV reveal a single distribution of modulation values centered at ~0.7, suggesting that each individual polymer is folding into a well-ordered structure in which the majority of the chromophore dipoles are aligned.⁴ These results are qualitatively consistent with the picture that has emerged from coarse-grained Monte Carlo simulations of interacting beads on a chain.⁴

In this work 488-nm excitation was used to democratically interrogate the chromophores in the defect-free MEH-PPV as well as in the 10% defected MEH species, as this wavelength is near the peak of the solution absorption for these species (Figure 1). For the 30% defected MEH species, 488-nm excitation is on the red edge of the absorption spectrum, and is therefore likely excite only a lower-energy subset of chromophores, resulting in nondemocratic excitation of the polymer chain which artificially creates high anisotropy values (data shown in the supporting information, Fig. S1). Therefore 458-nm excitation was used to probe the 30% defected chains. Polarization modulation depth histograms for the defect-free MEH-PPV and the 10% defected compounds in this study are presented in Figure 2, and the modulation depth histograms for the three 30% defected MEH compounds studied are presented in Figure 3. Although Fig. 2 only presents results obtained with 488-nm excitation, excitation at 458 nm was also done, resulting in the same general trends for the modulation depth distributions with an ensemble average modulation depth slightly lower than that obtained at 488 nm (data shown in the supporting information, Fig. S2).

Molecular Dynamics. REMD¹⁷ was used to probe the canonical ensemble of structures at 300 K for a set of ten oligomer variants for each type of defect as well as five oligomer variants for the defect-free MEH-PPV. Representative structures for the various chains, chosen to display a range of anisotropies, are shown in Figure 4, as are calculated average radii of gyration and anisotropy order parameters, and two particularly noteworthy structures are shown in Figure 5. The simulations were done both in implicit toluene and in the gas phase (data not shown), and the resulting structures were quite similar. This suggests that mean field solvation effects do not greatly influence the stability and internal alignment of these collapsed oligomers at 300 K. However, it is important to note that both toluene and gas-phase simulations neglect the effect of PMMA, the carrier polymer, as well as the entire spin-casting process, on the final morphology of the spin-castconjugated polymers. Such effects are not negligible, especially in light of recent work demonstrating significant changes in polymer morphology when toluene solvent vapor annealing isperformed on single molecule MEH-PPV/PMMA systems.⁹

Defect-free MEH-PPV. Figure 2A presents modulation depth data for 16kDa (~60 monomer length chain) MEH-PPV without defects present. Consistent with previous results from studies done on MEH-PPV with a higher molecular weight, modulation depths for these shorter, defect-free, MEH-PPV chains are distributed around a single value with an average modulation depth of 0.67. One important difference to note in this work as compared to the previous studies on longer MEH-PPV chains is the increased signal-to-noise ratio for these very low molecular weight chains. As more error is introduced into the measurement, the modulation depth histograms become broader, as can be seen in the increased number of molecules with modulation depths above the physically realistic value of one as compared to previous studies.^{4,9-}

¹¹ As can be seen in Fig. 4A, the defect-free MEH-PPV oligomer demonstrated no propensity to fold during the course of the REMD simulations, adopting instead an elongated conformation with only slight fluctuations away from linear configuration. The resulting radius of gyration is

rather large, at 28.0 Å, and the anisotropy order parameter is also quite high, with a value of 0.91. Such stiff chains will still fold at longer chain-lengths,¹⁰ and the stiffness demonstrated in these oligomers suggest that it will be favorable for these molecules, even once folded, to adopt a set of highly ordered, mostly anisotropic, configurations qualitatively consistent with the single molecule data shown above.

Para-terphenyl MEH. This linear defect preserves the extended, stiff backbone configuration common to PPV polymers, and is not expected to introduce dramatic changes in the polymer's overall morphology. Indeed, the modulation depth histograms of both10% and 30% paraterphenyl MEH (Figures 2B& 3A) present nearly identical distributions in both their shape and average modulation depth (0.67 and 0.74, respectively) to that of the defect-free MEH-PPV, although the 30% para-terphenyl MEH, at 0.74, has the highest average modulation depth in this study. Likewise, the structures that are observed during our simulations of 33% para-terphenyl MEH (Figure 4B) are also quite similar to those for the defect-free MEH-PPV, although elongated since a single para-terphenyl group is longer than the corresponding MEH-PPV monomer. The radius of gyration (37.9 Å) is therefore greater, but the anisotropy order parameter (0.90) is nearly the same. These results together confirm our hypothesis that a stiff, linear defect would preserve the highly anisotropic nature of the single-molecule MEH-PPV morphology. The only observed effect of the para-terphenyl defect inclusion in our study, namely the shift in peak absorption, can be attributed to the corresponding disruption to the average conjugation length, since the π conjugation is reduced by the non-planar geometry of the phenyl rings in the terphenyl group.²⁴

Ortho-terphenyl MEH. Ortho-terphenyl MEH demonstrates the largest deviation in modulation depth as compared to MEH-PPV (see Figures 2C & 3B). The average value of the modulation for the 10% ortho-terphenyl MEH is still relatively high at 0.56, but the distribution of values is now much broader, with an almost equal probability of a polymer chain having a modulation depth anywhere from 0.1 to 1. This wide range of modulation depths suggest that, at 10% defect incorporation, the polymer chain can assume a wide variety of conformations ranging from nearly amorphous to highly folded.

Given the random nature of the chain-growth synthesis coupled with the low molecular weights of the compounds studied, the population of single molecules with high modulation depths may consist mainly of molecules with few, if any, defects. It is also possible that the 120° bend from the linear PPV backbone provided by the ortho-defect might enhance the ability of the chain to fold into a more compact, but still highly aligned structure. An example of such a structure can be seen in Figure 4C, where the regular placement of the ortho-terphenyl defects promotes alignment in the folded structure.

However, in longer chains or at higher defect concentrations, it would be less likely that the random placement of these "kinks" would allow for such alignment. Indeed, the 30% orthoterphenyl MEH compound demonstrated the lowest average modulation depth measured in this study, with a value of 0.40 (see Figure 3B). The distribution of modulation depth values is almost the exact opposite of the distribution of the 30% para-terphenyl MEH, with the majority of modulation depth values below 0.5. At 30% defect concentration, the majority of polymer chains now appear incapable of folding into the highly anisotropic structures that have been reported here and elsewhere. While most structures are likely to be adopting a more amorphous collapsed structure similar to a "molten globule" type conformation (see the first structure in Figure 4C), the modeled structure shown in Figure 5A demonstrates another possibility, wherein significant alignment in differing directions could offset one another.

In the simulations of 33% ortho-terphenyl MEH we observe an average radius of gyration of 11.1Å, which is significantly lower than that of either the defect-free MEH-PPV or the paraterphenyl MEH. The anisotropy order parameter is similarly reduced, to a value of 0.6. The observed trend of higher ortho-terphenyl defect concentrations to have lower modulation depths, more compact structures, and lower anisotropy values generally confirms our expectation that at a high enough number of defects per chain, the folding MEH-PPV into a highly aligned, anisotropic structure is disrupted.

Saturated Defect MEH. Results from the 10% saturated defect polymer (see Figure 2D) gives an average modulation depth nearly identical to that measured for the defect-free MEH-PPV (0.69), however, the measured distribution is much sharper suggesting a more uniform distribution of conformations. Contrary to previous studies, our results suggest that the inclusion of a saturated backbone site at modest inclusion rates does not hinder highly anisotropic polymer

folding,¹¹ and may in fact enhance it in small quantities by adding a flexible hinge that enables the chain to fold into highly anisotropic rods.

In contrast, the modulation depth values for 30% saturated MEH (see Figure 3C) display a very broad and nearly static distribution between 0.2 and 0.9, with an average modulation depth value of 0.54. This distribution is quite similar to that of the 10% ortho-terphenyl MEH and characteristic of chains that adopt a wide array of morphologies. The data suggests that even at this high level of defect inclusion, it is still possible for chains to anisotropically fold, however it is equally likely for chains to adopt a more disordered, isotropic conformation. This can be seen in the range of structures from the simulation shown in Figure 4D, where both a disordered collapsed structure and a highly anisotropic folded structure are shown. For these \sim 33% saturated defect MEH structures, the average radius of gyration is 21.5 Å, falling in between that of the ortho-terphenyl defect and the defect-free chain. The average anisotropy value is 0.88, which is slightly higher than expected, however the short chains explored in this simulation most likely bias the results towards more aligned structures.

The two-fold ability of this defect either to bend or to continue the linear chain is highlighted in Figure 5B, where four different saturated defects are circled. These defects show the range possible effects on the overall morphology. On the far left, a saturated defect induces a kink in the chain, enabling it to fold back on itself while still preserving the aligned nature of the straight chain. In the middle of the structure, there is a saturated defect in the top chain that is able to maintain its interaction with the defect-free segment of the lower chain, enhancing the stability of the anisotropic configuration. On the right, two saturated defects, one on each chain, have associated themselves such that the chains do not need to bend in order for them to continue their chain-to-chain association on the other side of the defects. Given this range of possible configurations for the saturated defect, short segments with even high proportions of saturated defects may remain highly anisotropic. However, when the alignment of the defects is less favorable, disordered structures, such as that shown on the left in Figure 4D, may result.

Cis defects. The substantial increase in *cis* defects in the ortho-terphenyl MEH and saturated MEH compounds as compared to the defect-free MEH-PPV and para-terphenyl MEH suggests some kind of templating of the *cis* defect occurs during the chain growth synthesis of polymers with these two defects, due perhaps to the steric constraints imposed by these designed defects.

The result is a decrease in the linearity of the backbone of the polymer, which is likely to then enhance the expected isotropic nature of these defected polymers. Thus the polarization modulation depths reported in this work are most likely a convolution of the synthetic and the *cis* defects. Interestingly, even with the increase in *cis* defects, the 10% saturated MEH demonstrates remarkably high anisotropy. The ability to maintain a highly oriented structure could perhapsbe due to some bias in the generally random *cis* defect inclusion during synthesis. The computational modeling in this paper neglects *cis* defects, but their inclusion could prove instructive, in particular if the probability of their occurrence depends on their morphological positionin the chain during polymerization.

Conclusions

In summary, the linear nature of the para-terphenyl defects do not hinder efficient folding of the PPV chain and may in fact improve the alignment of the chromophores in the polymer at higher inclusion rates. The ortho-terphenyl defects provided the largest changes to the modulation depth data suggesting that even at mild inclusion rates, these defects hinder chain alignment and at higher inclusion rates dramatically shift the single chain distribution towards less-ordered structures with lower anisotropies. The effect of the saturated defect, biphenylethane, on the single molecule anisotropy was surprisingly concentration-dependent; a low inclusion ratio results in a conformations with higher and more uniform anisotropies, while a high inclusion ratio results in a nearly equal probability of both low and high anisotropy conformations.

By combining synthetic, spectroscopic, and theoretical approaches we have laid the ground-work for being able to design polymer morphology design whereby the addition of different directing groups to the chain would influence the single molecule conformation of the conjugated polymer MEH-PPV in the manner desired. Single molecule measurements demonstrate that defect-free MEH-PPV and a linear defect that preserves the backbone geometry of PPV-type polymers results in highly anisotropic single molecule conformations, a highly bent defect results in a more isotropic conformation, and a defect that allows for rotational freedom of the backbone yields a concentration dependent effect. At low concentrations, this defect still allows for anisotropic conformations. However, at higher concentrations it leads to chains that can adopt a wide range of conformations. Molecular dynamics simulations on model oligomeric

systems show qualitative agreement with the experimental results, providing insight into the local folding induced by the different types of defects used in this study.

Acknowledgements. This work was supported as part of the program "Molecular Tools for Conjugated Polymer Analysis and Optimization", a Center for Chemical Innovation (CCI, phase 1) under NSF award no. CHE-0943957. We would like to thank Emilio Gallicchio for helpful conversations regarding the adjustment of the AGBNP potential for toluene.

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Figure 1. (A-D) Chemical structures of the conjugated polymers: MEH-PPV, para-terphenyl MEH, ortho-terphenyl MEH, and saturated MEH, respectively. (E-H) Absorption and emission spectra of the corresponding polymers shown to the left. In (F-H), 10% defect inclusion is represented in black lines and 30% defect inclusion is represented in green lines.



Figure 2. Experimental histograms of modulation depth, M, obtained with 488-nm excitation of (A) MEH-PPV (981 molecules), (B) 10% para-terphenyl MEH (424 molecules), (C) 10% orthoterphenyl MEH (454 molecules), and (D) 10% saturated MEH (524 molecules).



Figure 3. Experimental histograms of modulation depth, M, obtained with 457-nm excitation of (A) 30% para-terphenyl MEH (362 molecules), (B) 30% ortho-terphenyl MEH (862 molecules), and (C) 30% saturated MEH (1033 molecules).



Figure 4. Representative molecular structures from REMD simulations of short 15 unit oligomers of (A) MEH-PPV, (B) ~33% para-terphenyl MEH, (C) ~33% ortho-terphenyl MEH, and (D) ~33% saturated MEH. The corresponding radius of gyration and anisotropy order parameter are also shown. See Methods for details.



Figure 5. Additional structures of (A) ~33% ortho-terphenyl MEH and (B) ~33% saturated MEH. Saturated defects discussed in the text are circled in (B).