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Synthesis and Folding Behaviour of Poly-(*p*-phenylene vinylene)-based β-sheet Polychromophores

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Supporting Information

Materials and Methods. All chemicals were purchased from Sigma Aldrich, Alfa Aesar, or TCI America, and used as received unless otherwise indicated. NMR spectroscopic characterization was conducted on a Bruker Avance 500 or 600 MHz spectrometer using $CDCl_3$ unless otherwise indicated. Chemical shifts are reported in ppm, and referenced to residual $CHCl_3$. Polymer molecular weights and dispersities were measured using an Agilent 1200 gel-permeation chromatograph (GPC, Agilent Technologies) and operated using a ChemStation program equipped with ASTRA V program. An Agilent 1200 series isocratic pump coupled with a UV detector and the Optilab rEX differential refractive index detector (Wyatt Technology Corporation; Santa Barbara, CA) were calibrated with poly(styrene) standards. The column and guard column utilized were pre-packed (AM GPC Gel, $CHCl_3$; American Polymer Standards) and the column temperature was maintained at 40 °C. All samples were measured with a mobile phase consisting of chloroform. The injection volume was 100 μL and the flow rate was 1 mL min^{-1}. The concentrations utilized for GPC measurements are ca. 1-3 mg mL^{-1}, owing to aggregation of the PPV systems in more concentrated solutions through the duration of the measurements. Data obtained from the UV and RI detectors were in agreement. X-ray diffraction data was collected on a Bruker D8 DISCOVER GADDS microdiffractometer equipped with a VÅNTEC-2000 area detector. X-rays were generated with a sealed Cu tube, monochromated by a graphite crystal, and collimated by a 0.5 mm MONOCAP (λ = 1.54178 Å). Samples for WAXS were measured as thin films in bulk, and compared to the parent polymers. Measurements were collected at room temperature via mounting of the polymer films onto a silicon wafer.

Single Molecule Spectroscopy:

Steady-state absorption and emission spectroscopy

Polymer solutions were prepared in chloroform (Fisher). Absorption and emission measurements were performed with Agilent 8453 UV-visible spectrophotometer (Agilent Technologies Inc.) and Fluorolog-3 spectrofluorometer (Jobin-Yvon), respectively. All polymer solutions were excited at 488 nm, and fluorescence emission was measured from 500-700 nm.

Sample preparation. Single molecule samples were prepared by creating ultra-dilute polymer solutions in 2 wt% PMMA/chloroform and spin-casting onto piranha cleaned coverslips with resulting PMMA/polymer films ~200 nm thick.

Excitation polarization study. During all single molecule experiments, samples were protected with a flow of N_2 gas and held at ambient temperature. An electro-optical modulator (Fastpulse Technology, model 3079-4) was used to generate a linearly rotating 488 nm excitation beam (Melles Griot, model 35-IMA-040-208). A high numeric aperture objective (Zeiss, Achrostigmat, x100, oil immersion, N.A. 1.25) was used in a wide-field optical microscope (Zeiss, Axiovert 200) in order to expose the sample plane to a collimated laser beam during fluorescence excitation polarization measurements. Methods are described in further detail elsewhere (Adachi 2010 J phys chem). Fluorescence signals were captured with an EMCCD detector (Andor, model iXon+ DU-897E).

Single molecule spectra. Fluorescence emission spectra were collected under a confocal scheme in which the laser beam was focused to a diffraction limited spot on the sample with an intensity of ~30 W cm^{-2}. A home-written LabView program (National Instruments) was used to control the piezo stage. Emitted light was filtered through a 496 nm long pass edge filter (Semrock) and directed onto the spectrograph (Princeton Instrument, Acton SP-150) that was coupled to a liquid N_2 CCD detector. Three consecutive spectra, each taken with an integration time of 15 s, were averaged to increase the signal-to-noise ratio.

Polymerizations

ROMP – PPV homopolymer:

ROMP is conducted at 50 °C, and monitored via ^{1}H NMR spectroscopy for conversion. After the reaction is completed, the polymerization mixture is added to a dichloromethane solution with the desired CT (4.0 eq., relative to initiator used), and allowed to stir at room temperature over a period of 16 hours. The polymer solution after quenching is purified using reprecipitation into methanol and acetone. The polymer Dp was confirmed through ^{1}H NMR spectroscopic end group analysis.

ROMP – PPV-PNB$_{Ph}$-PNB$_{PFP}$-PPVs:

The above procedure is utilized except that upon completion of ROMP, the polymer solution is transferred back to the glove box, and 5-*exo*-norbornene carboxylic acid, phenyl ester (NB-Ph) is added and polymerized at room temperature for 15 minutes, followed by 5-*exo*-norbornene carboxylic acid, perfluorophenyl ester (NB-PFP), which is also polymerized for 15 minutes at room temperature. After incorporation of the interior PNB blocks, a fresh equivalent of pCpd was added. After completion, an aliquot of the polymer is subsequently quenched while further equivalents of the PNB blocks (and pCpd) are added. As the series of polymers was sequentially polymerized and quenched from a single pot, the general procedure is as follows:
1T) 50 mg (0.0001085 mol) of pCpd was dissolved in 0.5 mL of $CDCl_3$, with Hoveyda-Grubbs II initiator (6.2 mg, $CDCl_3$ solution) then introduced. Polymerization was conducted at 50 °C. Upon complete consumption, the desired amount of NB-Ph was added and polymerized, followed by NB-

PFP. An equal equivalent of pCpd ((0.0001085 mol) was then added and polymerized. Upon completion, 1/5th of the overall solution was drawn and quenched with ethyl vinyl ether (EVE) overnight, affording 1T.

2T) The remaining solution was utilized for subsequent polymerizations, wherein the desired amount of NB-Ph and NB-PFP were polymerized in sequence, followed by pCpd (0.0000868 mol). Upon completion, 1/4th of the overall solution was drawn and quenched with EVE overnight, affording 2T.

3T) The remaining solution was utilized for subsequent polymerizations, wherein the desired amount of NB-Ph and NB-PFP were polymerized in sequence, followed by pCpd (0.0000651 mol). Upon completion, 1/3rd of the overall solution was drawn and quenched with EVE overnight, affording 3T.

4T) The remaining solution was utilized for subsequent polymerizations, wherein the desired amount of NB-Ph and NB-PFP were polymerized in sequence, followed by pCpd (0.0000434 mol). Upon completion, ½ of the overall solution was drawn and quenched with EVE overnight, affording 4T.

5T) The remaining solution was utilized for subsequent polymerizations, wherein the desired amount of NB-Ph and NB-PFP were polymerized in sequence, followed by pCpd (0.0000217 mol). Upon completion, the solution was drawn and quenched with EVE overnight, affording 5T.

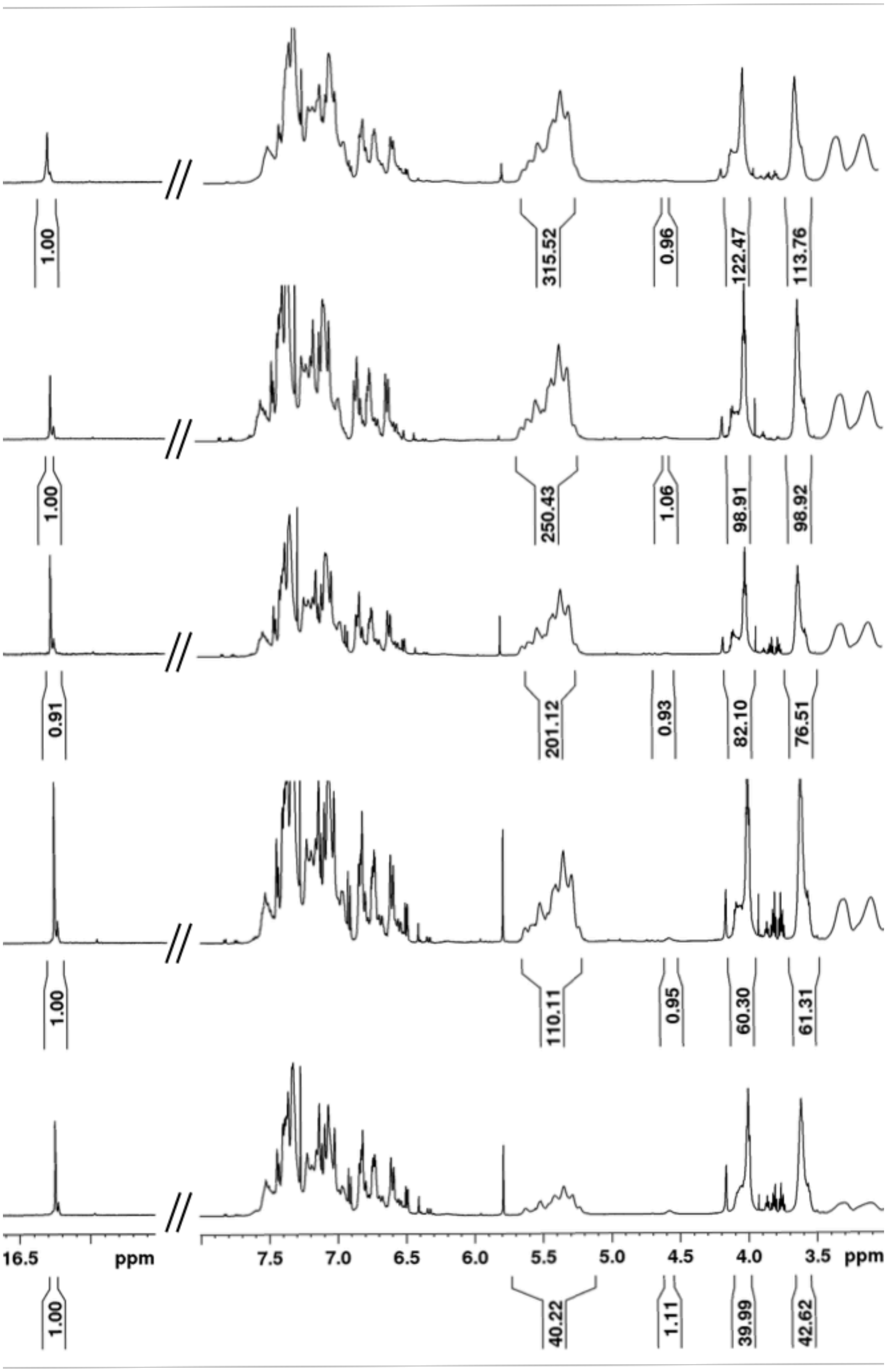

Figure S-1: ^{1}H NMR spectral overlay of PPV-PNB$_{Ph}$-PNB$_{PFP}$-PPV series *in situ*.

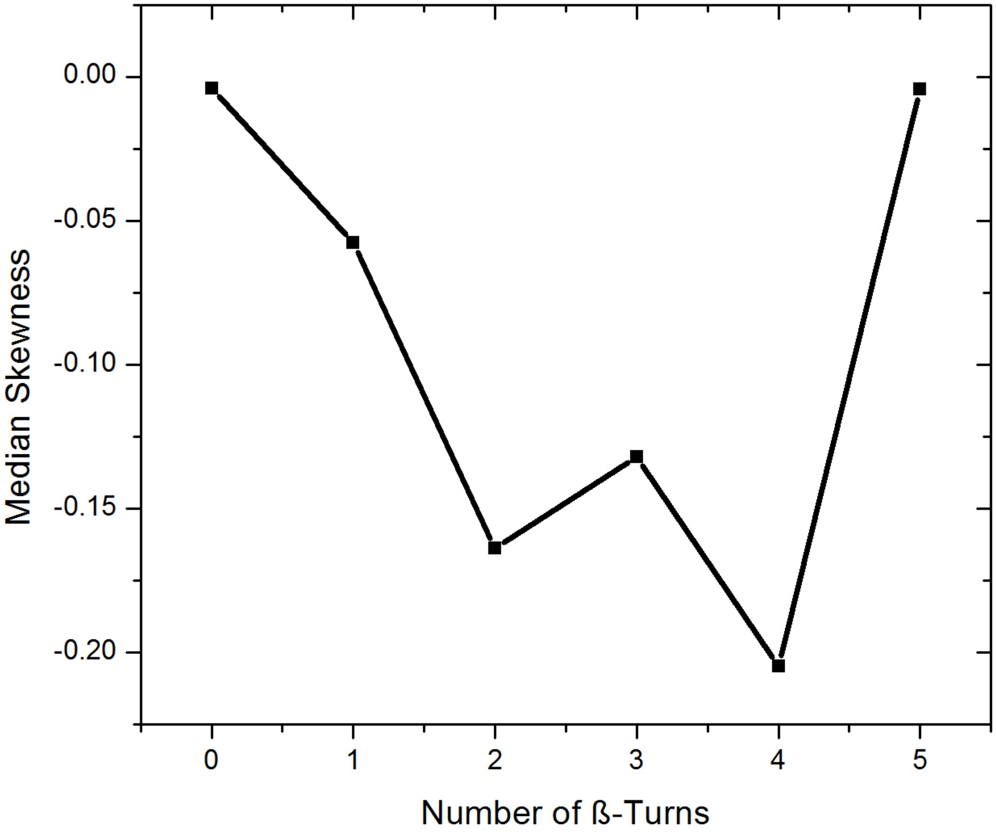

Figure S-2: Plot of median skewness vs the number of β-turns in the sample extracted from the data presented in figure 6. The plot shows a nearly gaussian distribution for the homopolymer, with an increasing skewness as β-turns increase before returning to nearly gaussian for the 5 β-turn sample.

Reference:

1. Yu, C. Y.; Helliwell, M.; Raftery, J.; Turner, M. L. *Chem. Eur. J.* **2011**, *17*, 6991-6997.