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Supplementary Information



Figure S1. NMR spectrum of RRa-P3HT 60mers (a) and P3HT-H14 41mers (b). Gaussian fits of peaks correspond to different head-tail trimer configurations, as outlined in Chen et al.¹ NMR spectrum was acquired from Rieke Metals for RRa-P3HT. Simulated regio-random chains could then be constructed to have the same relative ratios of head-to-tail configurations. For P3HT-D13, the same distribution as P3HT-H14 was used in simulations.



Figure S2. DSC thermograms of (a) RRa-P3HT (60mer) and of (b) P3HT-H14/-D13 (41mers) taken at a rate of 5 K/min. Glass transition temperatures have been noted on the plot for all materials.



Figure S3. Normalized weight fraction calculated from SEC data versus molecular weight (in number of P3HT monomers) for RRa-P3HT (60mers). SEC was run using a universal method with polystyrene MW standards; data was acquired from Rieke Metals.

Liu et al. has shown that SEC run with a polystyrene standard overestimates the MW of regioregular P3HT by a factor ranging from 1.5 to 2.² In this work, we have chosen to apply this correction to all of our regiorandom samples to more accurately represent the molecular weight *in-silico*. The normalized molecular weight distribution as a function of the number of P3HT monomers after correcting for the overestimation of MW is also provided in Figure S3 for RRa-P3HT. After correcting the number averaged molecular weights for all materials, monomer lengths of 60 and 41 were used for simulations of RRa-P3HT and P3HT-H14-D13.



Figure S4. (a) Comparisons of I(q,t) calculated using the Moreno FF2³ force field with different molecular weights. (b) Backbone dihedral autocorrelation function (DACF) for the same systems. (c) For the 20mer system, the overall backbone DACF, backbone DACF for the last four monomer-monomer bonds on either end of each chain, and backbone DACF for the remaining monomer-monomer bonds in the middle of each chain. All simulations were run at 473 K.

We investigated the effect of molecular weight on the structure and dynamics of the MD simulations. While calculations of the static structure factors for each of these simulations revealed no significant differences (Figure 5 in the main text), we expected discrepancies in the dynamics, as it is well established that the viscosity of polymer systems above the glass transition temperature is influenced by the polymer molecular weight.⁴ Figure S4a shows that molecular weight indeed has a large impact on the I(Q,t) calculated from MD simulations. A clear shift is observed between the 40-mers system and the 20-mers system, while the shift observed between the 60-mers system and the 40-mers system is less pronounced. This implies a nonlinear dependence of the dynamics of the simulated system with respect to molecular weight. There is a crossover molecular weight between 20-mers and 40-mers, after which increasing molecular weight has a minimal effect on I(Q, t) over this time window. A primary contributor to the accelerated dynamics for the 20-mers system is increased backbone torsion (α) as can be seen in Figure S4b and Figure S4c. The discrepancy between DACFs for backbone torsion at the ends of each chain versus backbone torsion in the middle of the chain for the 20-mers simulation is clear. Here we define 'End Group' segments as those located four or less monomer units from a chainend. Backbone torsional motions along α -bonds are much faster for the end group segments in the chain versus the mid-chain segments. This trend was also observed for the 60-mers and 40mers systems but the overall concentration of end groups is much lower. For 20-mers, 42% of each chain is comprised of end groups as defined in this work, which is lower when compared to high molecular weight chains where only 21% and 14% of segments correspond to end groups for 40-mers and 60-mers respectively.

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Figure S5. (a) Comparisons of the static structure factor calculated from MD simulations run using the Mod. Bhatta FF⁵ to WAXS data of RRa-P3HT (60mers). One simulation (red) was initialized using a Monte Carlo algorithm to determine its initial backbone torsion angle distribution, and the other (blue) was initialized with a completely *trans* distribution. (b) The normalized torsion populations for each simulation.

A key factor to consider when equilibrating these systems is the relative population of *cis* and *trans* conformations of the backbone. The high energetic barriers for backbone torsion

necessitate an exceedingly long equilibration period to accurately reflect a system with torsion populations suggested by the backbone torsion potential calculated from DFT. This means that, starting from an all trans configuration, a standard equilibration method will provide a backbone torsion population that is inaccurately biased towards trans configurations. To solve this issue, we implemented a Monte Carlo algorithm with a Metropolis criterion to set the initial distribution of backbone dihedral angles as indicated by the backbone torsion potentials of each force field. Figure S5 shows the effect that implementing this algorithm had on the structure and final torsion population of MD simulations run using the Mod. Bhatta FF. While there is no clear change in the calculated structure factors, the backbone torsion population shows a clear increase in the number of *cis* configurations. It is important to note that even when equilibrating at high temperature and low initial density, the polymer chains were still biased towards adopting more trans configurations. The problem would likely be more exacerbated if the system was initialized with a higher initial density or a crystalline configuration. In this scenario, increased sterics would further prevent trans to cis flips from occurring, causing differences more dramatic than those seen in Figure 9 of the main text. This is particularly significant when running combined MD-DFT experiments, as both orbital structure and conjugation length are affected by introducing *cis* conformations to a chain⁶.



Equilibration Method

Figure S6. (a) Static structure factors calculated from MD simulations of RRa-P3HT (60mer) equilibrated using different ensembles using the Mod. Bhatta⁵ force field. The initial packing density is shown in parentheses. In some cases, isotropy of the simulation cell is enforced, and in others, no such constraint is added, causing the equilibrated cell to become anisotropic, with the longest dimension corresponding to the direction along the chain backbones. (b) The average radii of gyration for chains are plotted for each method. Images of representative chains are included for the isotropic NVT, isotropic NPT at 473 K, and isotropic NPT at 600 K

(green, red, and yellow markers) equilibration methods.

All equilibration steps shown in Figure S6 were followed by an NPT production run of 5 ns. In addition to ensemble type (NVT vs. NPT), we investigated the effects of forcing cell isotropy. We also examined the effect of starting the equilibration process at an elevated temperature (600 K). For the NVT case in which simulation cell isotropy was enforced during the production run (green curve), a low initial density coupled with the "kinks" in the polymer caused the chains to fold onto themselves to form oblong clumps that were packed next to each other as the box volume is reduced. The sharp diffraction peak at low Q for this system correspond to the packing of these clumps (Figure S6a). This was also reflected in the average radius of gyration for this system, which was the lowest out of all methods used. In the NPT case where isotropy was not forced the simulation cell became anisotropic along the direction of the polymer backbones. This caused the shortest cell dimension to approach the distances corresponding to low Q in Figure S6, which could lead to an overestimation in the pair correlations at low Q. Given these observations, for all subsequent calculations, we opted to use an isotropic NPT ensemble with a moderately increased initial density (0.0671 g/cm³) and an initial temperature of 600 K that was gradually reduced while equilibrating the system.



Figure S7. Density of 41mer P3HT-H14 MD simulations with extended equilibration procedures. Simulations utilized the force field developed by Moreno and coworkers³ (FF2 variant only). (a) Density has been averaged over steps in the cooling procedure with a rate of 10 K every 200 ps as well as during the 5 ns production runs at temperatures of 273, 373, and 473 K. (b-d) Density is reported at simulation time steps during the equilibration, cooling and production pieces of the MD simulations.

Figure S8. (a) Schematic showing the vectors used for the P_1 calculation done for five MD simulations of amorphous RRa-P3HT (60mers) run with different force fields. (b) The results of the P_1 autocorrelation calculations for the same simulations.

Given that the QENS signal was dominated by the motions of the alkyl side-chains, it was necessary to determine the extent to which these motions were influenced by the motions of the thiophene backbone. We calculated the reorientational autocorrelation function P_1 using the following formula:⁷

$$P_1(t) = \langle Cos(\theta(t)) \rangle \tag{S1}$$

given that

$$Cos(\theta(t)) = \vec{r}(t) * \vec{r}(t=0)$$
(S2)

Here, \vec{r} refers to the vector starting from the alkyl-substituted carbon (atom C2 in Figure 3b of the main text) at a given time, t, as seen in Figure S9a. The results are shown in Figure S9b. The Mod. Bhatta FF had the slowest P1 relaxation because it had the strongest side-chain torsion potentials out of all the force fields investigated, and it also showed reduced backbone torsional motions (Figure 10b in the main text). The Huang FF and Moreno FF2 show nearly the same relaxation. This could suggest that the lack of the first side-chain torsion potential in the Huang FF is offset by its relatively stronger backbone torsion potential, when compared to Moreno FF2. Finally, when looking at the three Moreno force fields, which only differ in the atomic partial charges applied to the thiophene rings, there is a clear downward shift in the relaxation when going from Moreno FF2 to Moreno FF1 (and passing through Moreno FF3, which has the averaged partial charges of the other two Moreno force fields). By only tuning a single parameter related to the conjugated backbone, the atomic partial charges, a noticeable impact was observed on the motions of the hexyl side-chains. This clearly demonstrates that the backbone and side-chain motions are linked, and it is insufficient to parameterize force fields without accounting for this interdependence to a certain extent.

Figure S9. Torsion potentials for the side-chain carbon-carbon bonds (dihedrals β_{2-5} in Figure 3b of the main text) for Bhatta FF⁵ (solid colored lines) and Mod. Bhatta FF⁵ (dotted colored lines) as well as the torsion potential for polyethylene from the base OPLS-AA⁸⁻¹⁰ force field (black), which was used for the Moreno FFs³ and Huang FF¹¹.

Figure S10. Comparisons of the dynamic structure factor I(Q,t) from MD simulations of RRa-P3HT (60mers) using the Bhatta and coworkers⁵, Huang and coworkers¹¹, and Moreno and coworkers³ force fields compared with experimental QENS data at 273 K. Experimental error bars are not shown for clarity, and are smaller than the symbols except at very long times (see Figure S13 in the supplementary information). In addition, the upturn at high times and low Qvalues of experimental data are an artifact of instrument detectors.

Figure S11. Comparisons of the dynamic structure factor I(Q,t) from MD simulations of RRa-P3HT (60mers) using the Bhatta and coworkers⁵, Huang and coworkers¹¹, and Moreno and coworkers³ force fields compared with experimental QENS data at 373 K. Experimental error bars are not shown for clarity, and are smaller than the symbols except at very long times (see Figure S13 in the supplementary information). In addition, the upturn at high times and low Qvalues of experimental data are an artifact of instrument detectors.

Figure S12. Comparisons of the dynamic structure factor I(Q,t) from MD simulations of RRa-P3HT (60mers) using the Bhatta and coworkers⁵, Huang and coworkers¹¹, and Moreno and coworkers³ force fields compared with experimental QENS data at 423 K. Experimental error bars are not shown for clarity, and are smaller than the symbols except at very long times (see Figure S13 in the supplementary information). In addition, the upturn at high times and low Qvalues of experimental data are an artifact of instrument detectors.

Figure S13. Comparisons of the dynamic structure factor I(Q,t) from a MD simulation of RRa-P3HT (60mers) using the Moreno and coworkers³ force field (FF2) compared with experimental QENS data at 423 K. Experimental error bars are shown here for reference and are representative of the error bars not shown on Figure 6 in the main text and in Figure S10, Figure S11, and Figure S12 in the supplementary information.

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