Supporting Information for:

Local Structuring of Diketopyrrolopyrrole (DPP)-based Oligomers from Molecular Dynamics Simulations

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Force Field

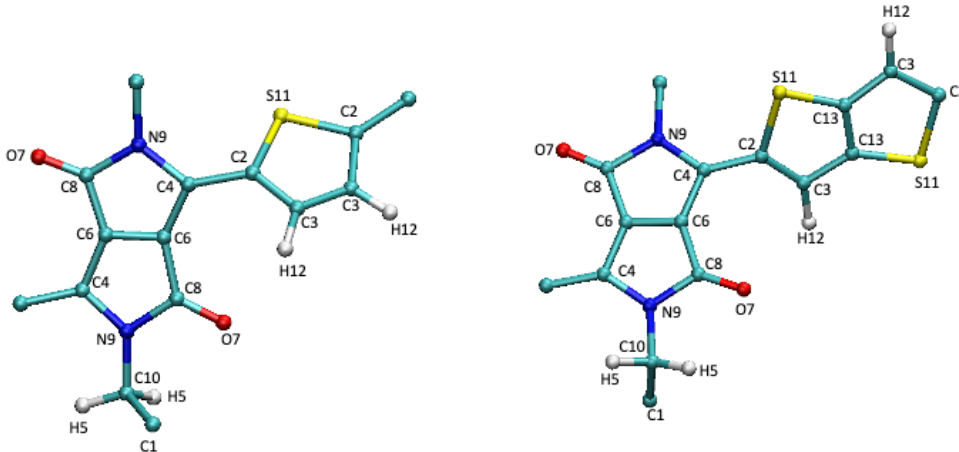Atom types assigned to each atom position are shown in Figure 1.

Figure 1: Atoms types

Non-bonded van der Waals (vdW) parameters based on 6-12 Lennard-Jones (LJ) potential were taken from OPLS-AA[1] using a geometry mixing rule:

$$E_{LJ} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right] \qquad r < r_c \tag{1}$$

where ϵ is the depth of the potential and σ the distance at which the potential energy is zero and r_c the cutoff distance which was set to 12 Å. Electrostatic interaction are computed between point charges centred on each atom. The atomic point charges of the alkyl side chains were directly taken from OPLS-AA, while they were explicitly computed for the backbone atoms. A chain of three repeating units of each of the systems was optimised using the DFT method at B3LYP/6-311G** level via CHelpG (charges from electrostatic potentials using a grid-based method),[2] however, the point charges of the middle monomer were extracted for the backbone atoms. Charge-neutrality of the oligomer chain was obtained by distributing the remaining charges evenly between the sulphur atoms of the system. Different methods of electrostatic summations were used to compute the long-range electrostatic energies in k-space where Ewald[3] summation was used during the simulated annealing and pppm[4]

(particle-particle particle-mesh) was used for the production simulations. Harmonic bond and angle potentials were assumed and calculated as:

$$E_{bond} = K(r - r_0)^2 \tag{2}$$

where r_0 is the equilibrium bond distance and K the force constant.

$$E_{angle} = K(\theta - \theta_0)^2 \tag{3}$$

where θ_0 is equilibrium angle value and K is the force constant. The force constants for all bonds and angles were directly taken from OPLS-AA FF, however, the equilibrium values were taken of the DFT optimised geometry at the same level used for the charges. OPLS-AA parameters were used for the torsion of alkyl side chains calculated as:

$$E = \frac{1}{2}K_1[1 + \cos(\phi)] + \frac{1}{2}K_2[1 - \cos(2\phi)] + \frac{1}{2}K_3[1 + \cos(3\phi)] + \frac{1}{2}K_4[1 - \cos(4\phi)] \tag{4}$$

where ϕ is the torsional angle defined by the quadruplet of atoms and all four parameters of K_1, K_2, K_3 and K_4. A tabulated potential was constructed instead for the torsions between backbone rings for which the potential energy was calculated at every 10 degrees of rotation using MP2/6-311G**[5,6] level of theory. The tabulated potential was obtained by a spline interpolation of the numerical potential containing 1000 values. The aromatic rings in the backbones were kept planar with a potential $\frac{1}{2}K_2[1 - cos(2\phi)]$ with K_2=30 $kcal/mol$.
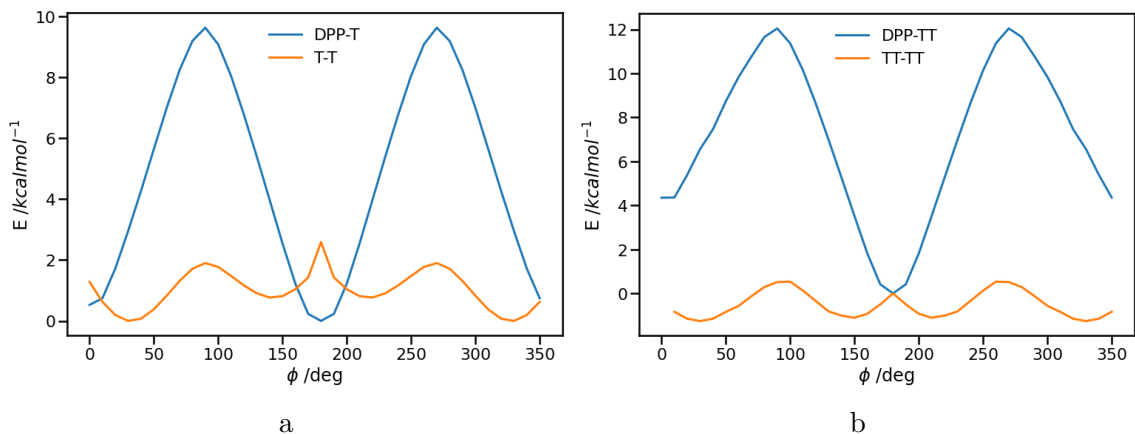
Figure 2: Plots of torsional potential energies for the torsions between backbone rings.

All simulations were performed using an NPT ensemble using Nóse-Hoover thermostat and barostat. Integration time of 1 fs was used for the simulated annealings, however, for the production simulations shake and rattle algorithms were used to constrain X-H bonds to enable increasing the integration time to 2 fs.

Simulated annealing

Simulated annealings were performed on each of the systems for three rounds during which the temperature of the systems were decreased from 1000 K to 100 K during 45 ns. The first round was started from the last conformation at 1000 K, however, the following rounds were performed by taking the last snapshot at suddenly heating to 1000 K and then annealed to 100 K. Graph showing the insignificant changes in sets of RDFs calculated during three different annealing processes for different classes of material in the three polymers.
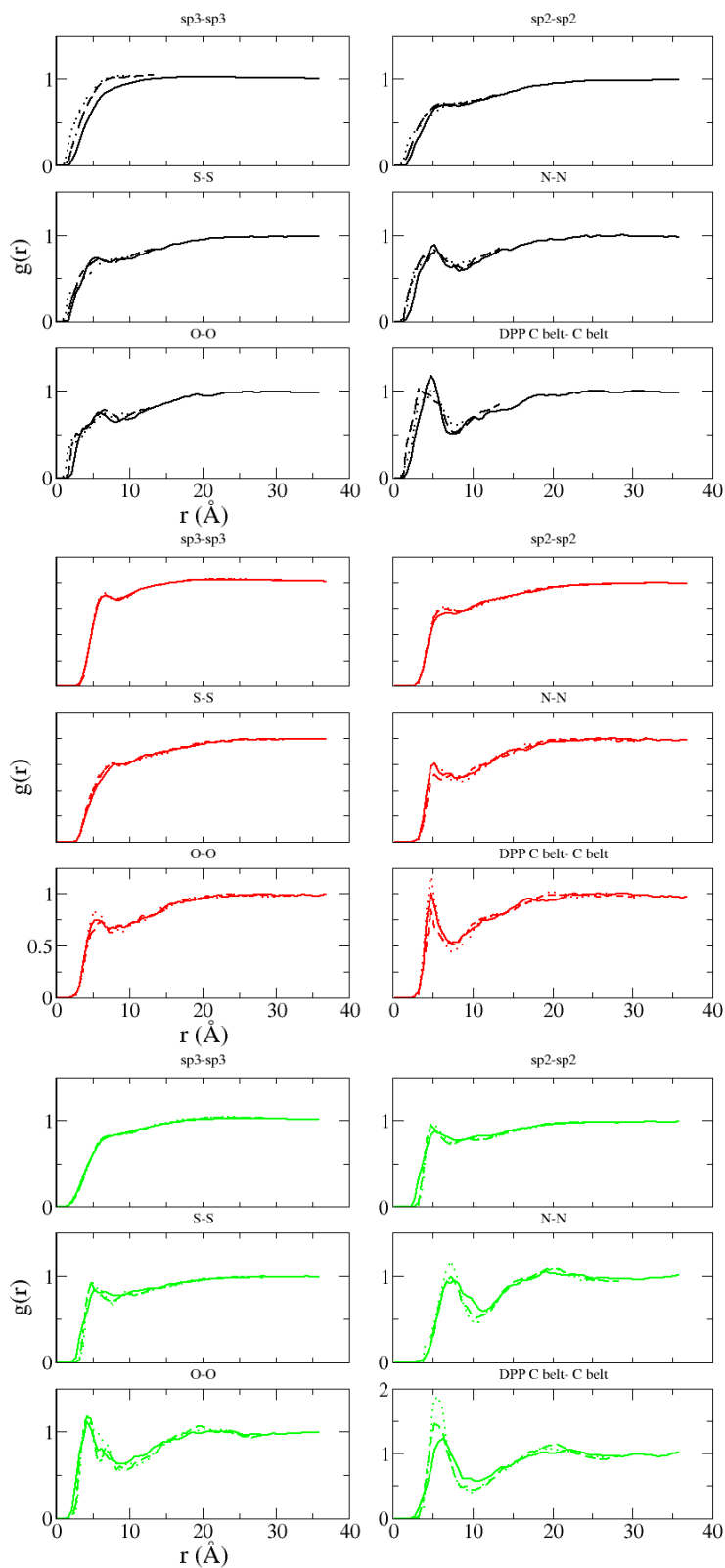
Figure 3: Radial distribution function of each polymer during the three rounds of annealings. No significant difference is being observed between different rounds.

Radius of gyration of simulated annealings

Radii of gyration (R_g) during the simulated annealings are plotted below as a secondary form of studying the dynamics of the systems as well as an indication of glass transition temperature (T_g).
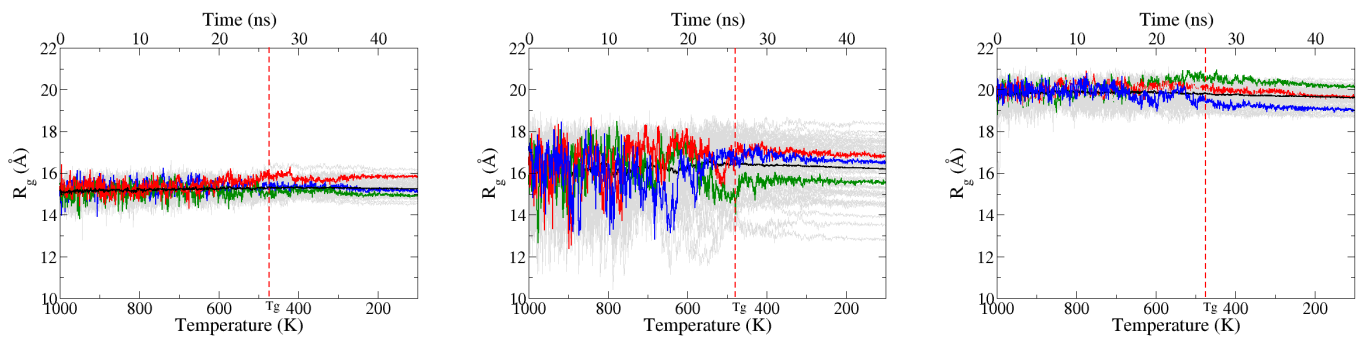

Figure 4: Radii of gyration for individual chains in the systems. A few are highlighted in colours for clarity. The average is shown in black.

References

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