Supporting Information

Robust Chain Aggregation of Low-Entropy Rigid

Ladder Polymer in Solution

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1. Simulation details

All molecular dynamics simulations were carried out with GROMACS 2018 software suite[1, 2] using a highly parameterized version of the OPLS-AA (optimized potentials for liquid simulations – all atom) force field[3, 4] for all intra- and intermolecular interaction parameters. Atom-centered partial charges were calculated using density functional theory (DFT) at the B3LYP/6-31G(d,p) level of theory within the Charge Model 5 (CM5) framework using the Gaussian 16 software suite[5] on each of the repeat unit and extended to the whole polymer chain.
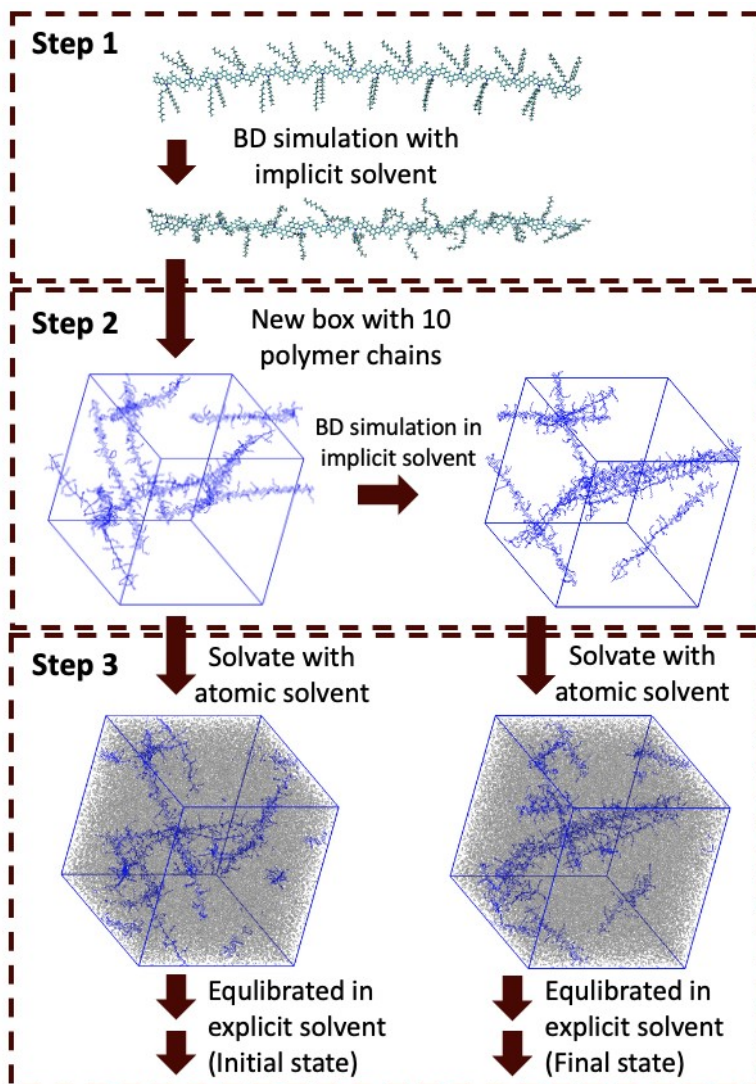
A schematic workflow of the simulation process is shown in the Figure S7. The workflow can be separated into 3 steps.

In **Step 1**, a single polymer chain of CP (16 repeat units) or LP (8 repeat units) was constructed and placed in the center of a $20 \ nm \times 20 \ nm \times 20 \ nm$ box. The relative dielectric constant was specified as 9.93 for the 1,2-dichlorobenzene solvent. The Brownian Dynamics (BD) friction coefficient for each atom was specified as the GROMACS default value (mass/$^{\tau}t$). The BD simulations were carried out at NVT (constant number, N, volume, V, and temperature, T) ensemble with a velocity rescaling thermostat and a temperature coupling time of 0.1 ps for 5 ns. The final conformation was saved for the next step.

In **Step 2**, 10 single polymer chains from the previous step were inserted into a $20 \ nm \times 20 \ nm \times 20 \ nm$ box and equilibrated under the same condition for another 10 ns. The boxes before and after this equilibrium step were labeled as 'Initial' and 'Final' state. In **Step 3**, a pre-equilibrated 1,2 dichlorobenzene solvent was used to solvate both the 'Initial' and 'Final' boxes to make all-atomic

systems. Then, MD simulations were carried out for both NVT and NPT ensembles. For NPT (constant number, N, pressure, P, and temperature, T) simulations, a Parrinello-Rahman barostat with 2.0 ps pressure coupling constant and velocity rescaling thermostat with 0.1 temperature coupling constant were used. An isotropic compressibility of 4.5×10^{-5} bar was applied. Periodic boundary conditions were applied to all simulations with a spherical cutoff of 1.4 nm for short-range van der Waals (vdW) interactions while long-range electrostatic interactions are treated via particle-mesh Ewald (PME) with 1.4 nm cutoff. The LINCS (LINear Constraint Solver) algorithm was used to constrain intramolecular bonds, angles, and dihedrals in an effort to reduce computation time without sacrificing accuracy. All the simulations were carried out at 384 K and repeated 8 times for statistics.

The entropies of these systems were calculated with the two-phase thermodynamics (2PT) model introduced by Lin and co-workers, detailed description of the method can be found in their original papers.[6] For the 2PT evaluations, a 20 ps MD runs were run at 384 K in the NVT ensemble. Here, we made use of the DoSPT code developed by Caro and co-workers, which can be found at http://dospt.org.[7, 8] with minor modifications to the code as distributed to accommodate the large system sizes used here. These modifications include vectorization of the position and volume data arrays and parallelization via OpenMP of the Voronoi cell calculations for each atom. The modified code is available at https://github. com/sryno/DoSPT.

Figure S1 Schematic depiction of the key workflow of the simulation method. Step 1 and Step 2 were performed with implicit solvent with dielectric constant setup to 9.93. The Step 3 was performed with all-atomic simulations in 1,2-dichlorobenzene.

2. Experimental results
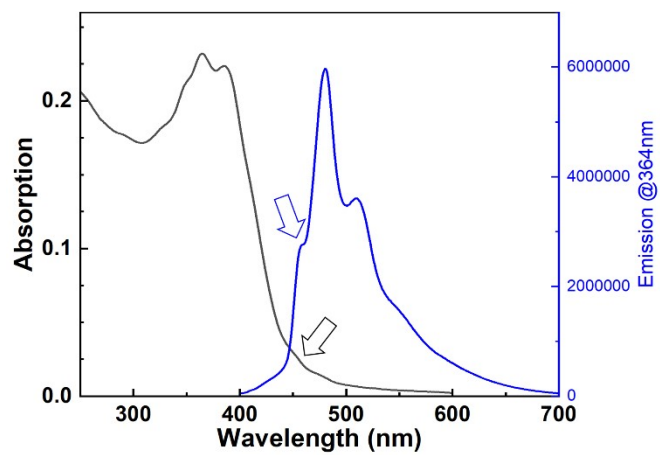
Figure S2 The absorption and emission spectra of LP. The true Stokes shift is quite small and the difference of absorption and emission of the same electronic transition are labeled.
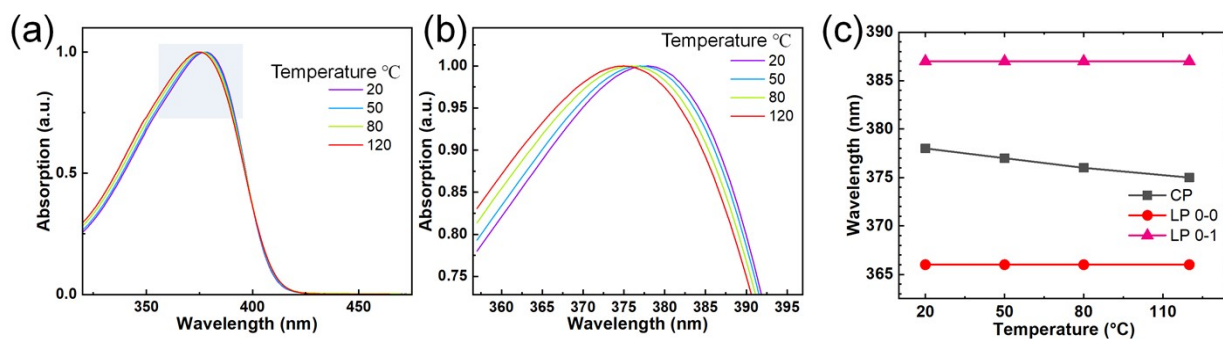
Figure S3 (a) UV-Vis of CP solutions in CB at different temperatures and (b) enlarged plot of gray region.

(c) Peak positions of LP and CP as a function of temperatures. The sampling rate of UV-Vis is 1 pt/nm.
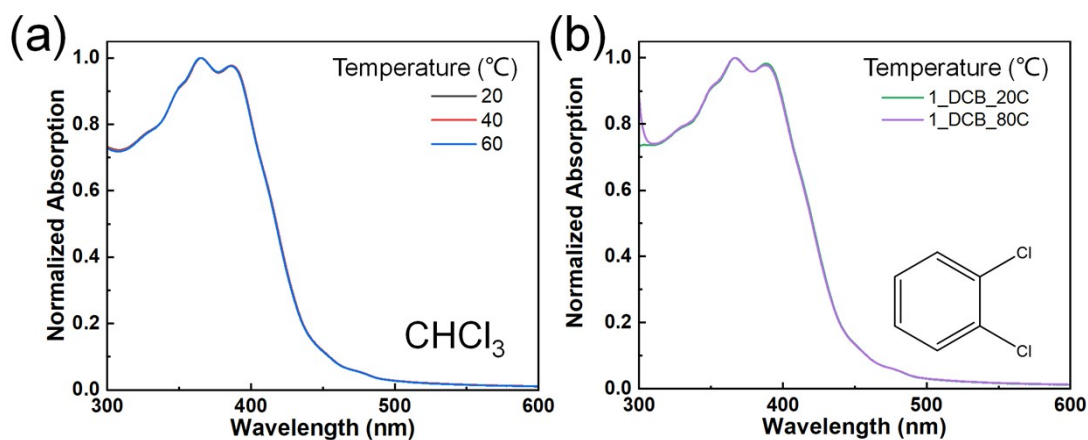
Figure S4 UV-Vis of LP solutions at different temperatures. The solvent is shown in the insert.
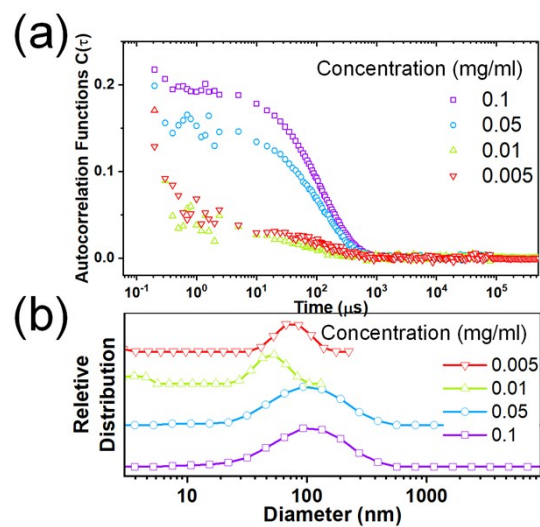
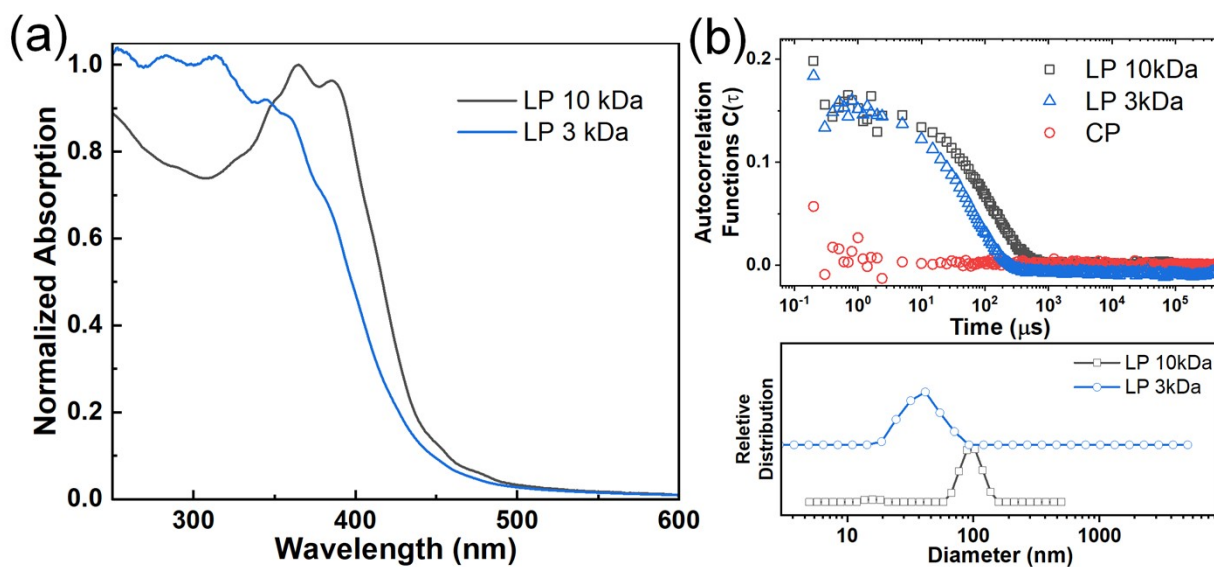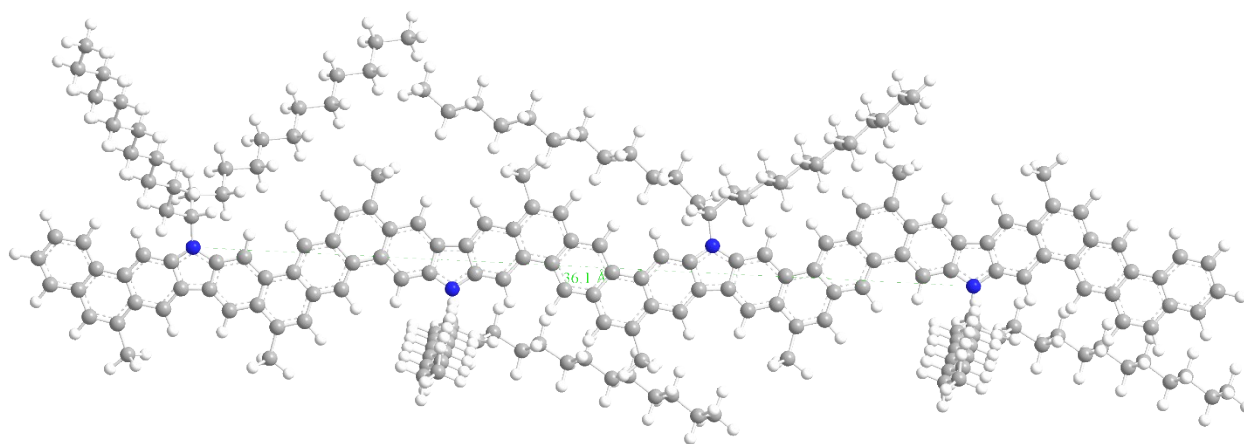**Figure S5** DLS of LP in chloroform at different concentrations.

Figure S6 (a) UV-Vis and (b) DLS result of two LP samples with different molecular weight in chloroform solution (~0.1 mg/ml) at 20℃. The molecular weights are 10 kDa and 3 kDa, respectively.

Figure S7. *3D structure of LP where blue, gray and white balls represent nitrogen, carbon and nitrogen atom, respectively. Each repeating unit is about 12 Å long (e.g. from nitrogen atom from the first repeating unit to another).*
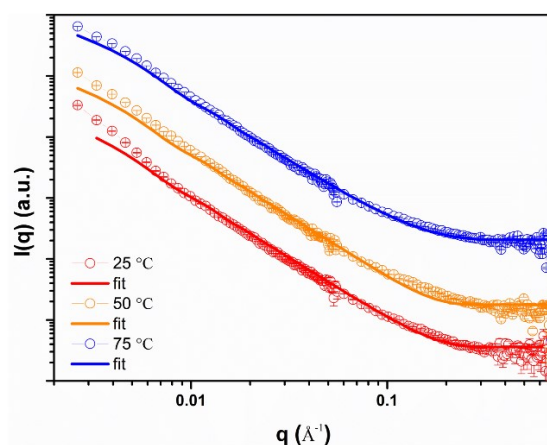
Figure S8 Temperature dependent SANS on LP in deuterated chlorobenzene and fitting curves using parallel parallelepiped model.

Table S1 Fitting parameters for LP at various temperatures from SANS experiment

Parameter	25 °C	50 °C	75 °C
a (Å)	18.8	21.2	16.0
b (Å)	838.3	837.8	727.2
c (Å)	7427.8	3679.5	6033.0
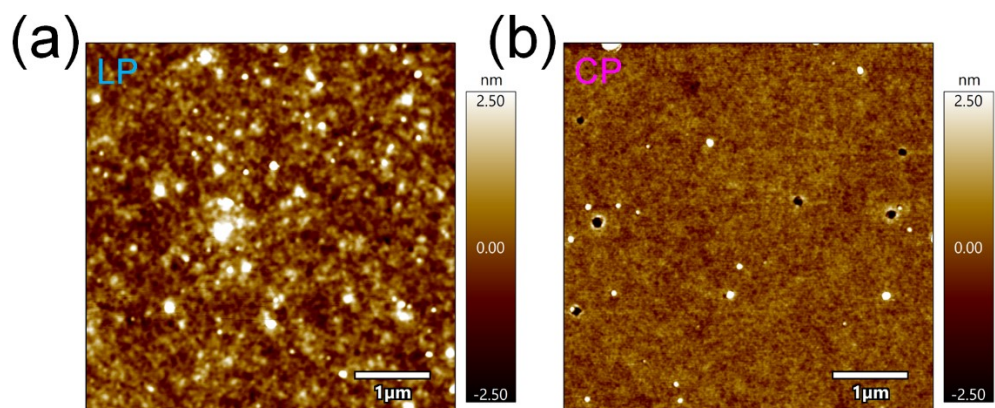
Figure S9 AFM Height image of (a) LP and (b) CP films spun cast on silicon wafer.
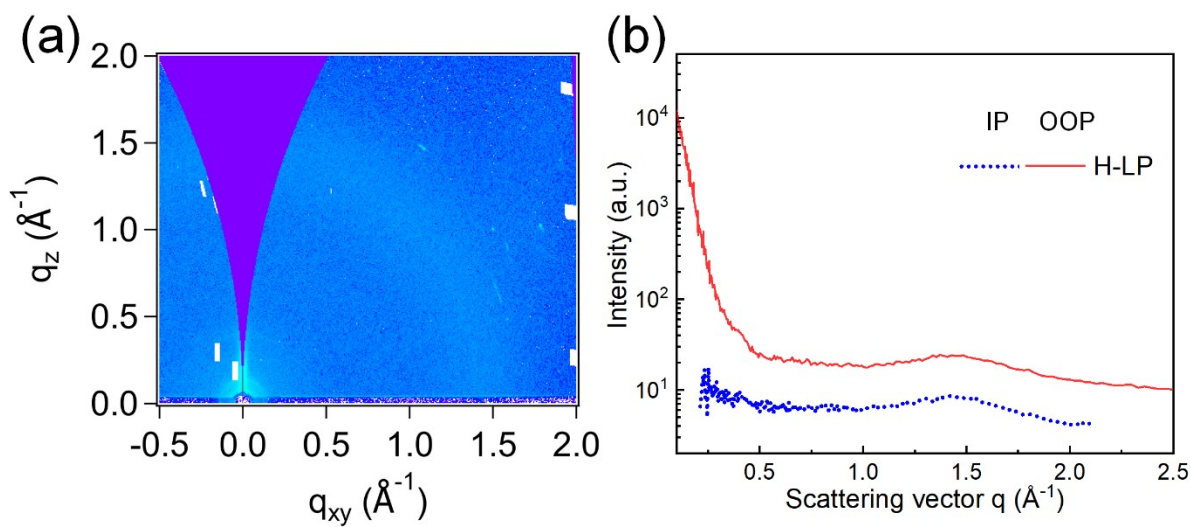
Figure S10 GI-WAXS result of LP thin film. (a) 2D image and (b) intensity curves in the in-plane (IP) and out-of-plane (OOP) directions.

Figure S11 Statistics of maximum cluster size (a) and number of clusters (b) evolutions for LP and CP during the BD simulations.

Table S2 Calculated change in Entropy values (polymer only) for LP and CP from eight individual simulations

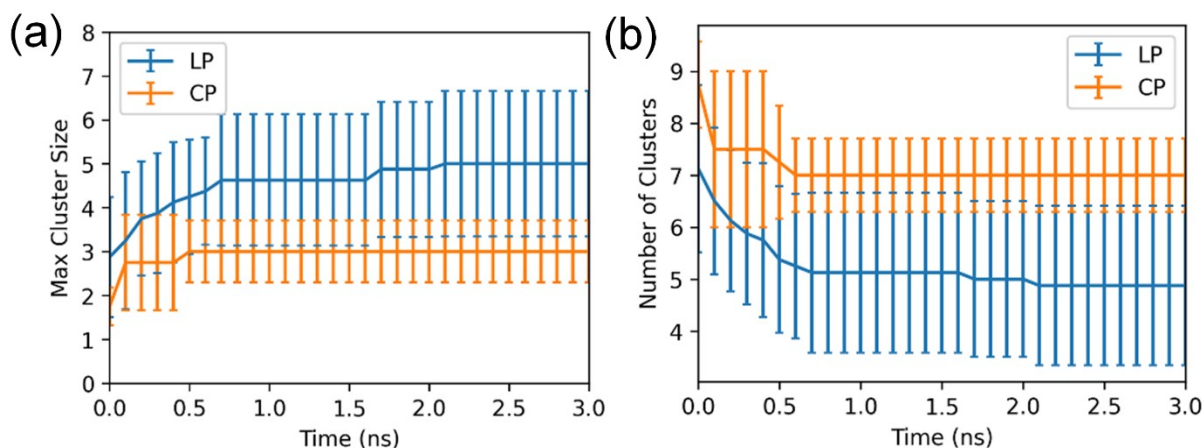| ΔS (J/mol K)	1	2	3	4	5	6	7	8	Average	Std
LP (only)	-93.22	-108.58	-90.31	-79.85	-114.09	-133.79	-34.13	-127.88	-97.73	29.65
CP (only)	-320.68	-215.29	-248.55	-264.78	-240.06	-248.55	-264.78	-240.06	-255.34	28.75

3. References

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