Coarse-Grained Model

In the coarse-grained (CG) model, each thiophene ring is represented by a single spherical bead,[1] and the aliphatic segments are mapped by a three-to-one and a four-to-one scheme based on the specific chemistry.[2] For the specific molecule studied here, four heavy atoms in the end of the aliphatic segment are represented by a single bead (type EO1), and the rest of the segment follows a three-to-one scheme (type EO2).

Non-bonded interactions in this CG model are described by the Mie potential[3]

$$U^{Mie} = C\varepsilon \left[\left(\frac{\sigma}{r}\right)^{\lambda_r} - \left(\frac{\sigma}{r}\right)^{\lambda_a} \right] \quad (1)$$

with

$$C = \frac{\lambda_r}{\lambda_r - \lambda_a} \left(\frac{\lambda_r}{\lambda_a}\right)^{\lambda_a/(\lambda_r - \lambda_a)} \quad (2)$$

where ε and σ are the well depth and the segment diameter, respectively, and λ_r and λ_a are the repulsive and attractive exponents. A cutoff of 20 Å was implemented, and the Mie potential was shifted to zero at the cutoff. For the EO1 and EO2 beads, we adopted a SAFT model for the PEO bead by Lobanova et al.[4]. For the thiophene bead, we parameterized the Mie potential to match the experimental saturated liquid densities over a wide range of temperature.[5] (ref) Figure S4 shows the good agreement attained between our CG model predictions and experimental data.[5] All cross-interaction terms were determined by the usual combining rules shown below.[3] The Mie interactions used in this model are summarized in Table S7.

$$\sigma_{AB} = \frac{\sigma_{AA} - \sigma_{BB}}{2} \quad (3)$$

$$\varepsilon_{AB} = \sqrt{\varepsilon_{AA}\varepsilon_{BB}} \quad (4)$$

$$(\lambda_{r,AB} - 3) = \sqrt{(\lambda_{r,AA} - 3)(\lambda_{r,BB} - 3)} \quad (5)$$

Bonded interactions in this CG model are described by harmonic bond and angle potentials:

$$U_{bond} = K_b(r - r_0)^2 \quad (6)$$

where K_b is the bond force constant, r is the separation distance between the bonded beads, r_0 is the equilibrium separation;

$$U_{angle} = K_\theta(\theta - \theta_0)^2 \quad (7)$$

where K_θ is the bond force constant, θ is the bond angle between successive bonds, and θ_0 is the equilibrium angle. The Mie interaction between the bonded nearest neighbors are excluded. We parameterized bonded potentials to match the bond and angle distribution from all-atom (AA) simulations of 4T-PEO4 using a relative entropy framework.[6] Figure S5 and S6 shows the good agreement attained between our CG model and AA simulations. The bonded parameters of the CG model are given in Table S8 and S9.
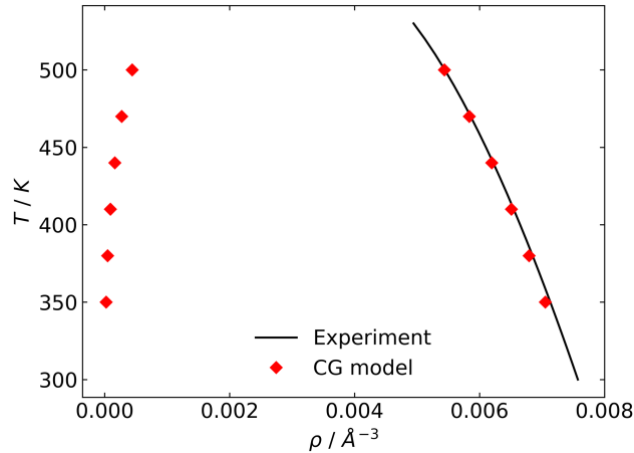

Figure S4. Temperature-density vapor-liquid coexistence curve for thiophene. The experimental data is obtained from Ref 6.
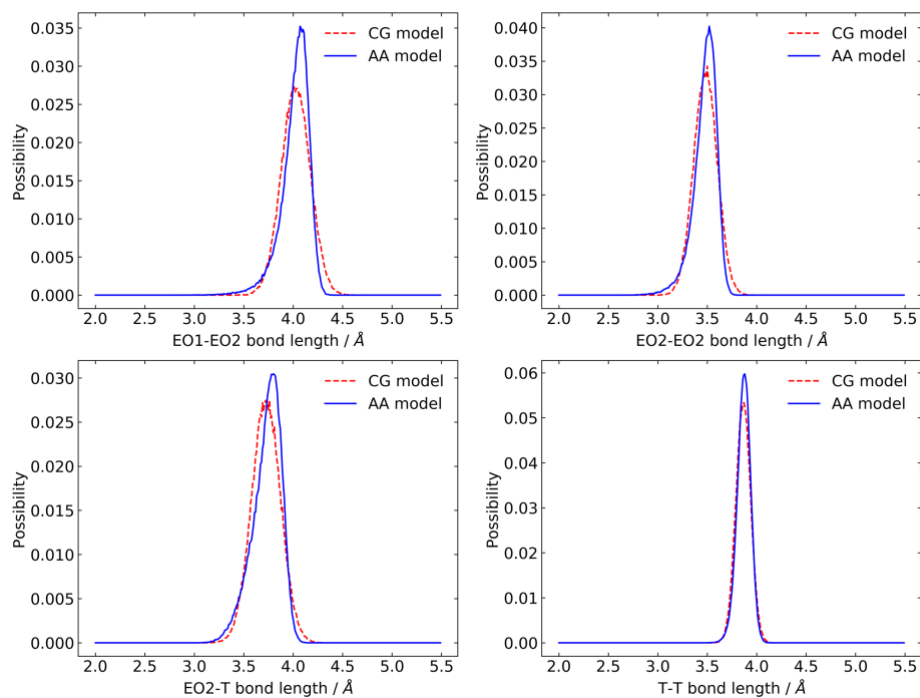
Figure S5. Probability distribution of bond lengths of different types between our CG model and
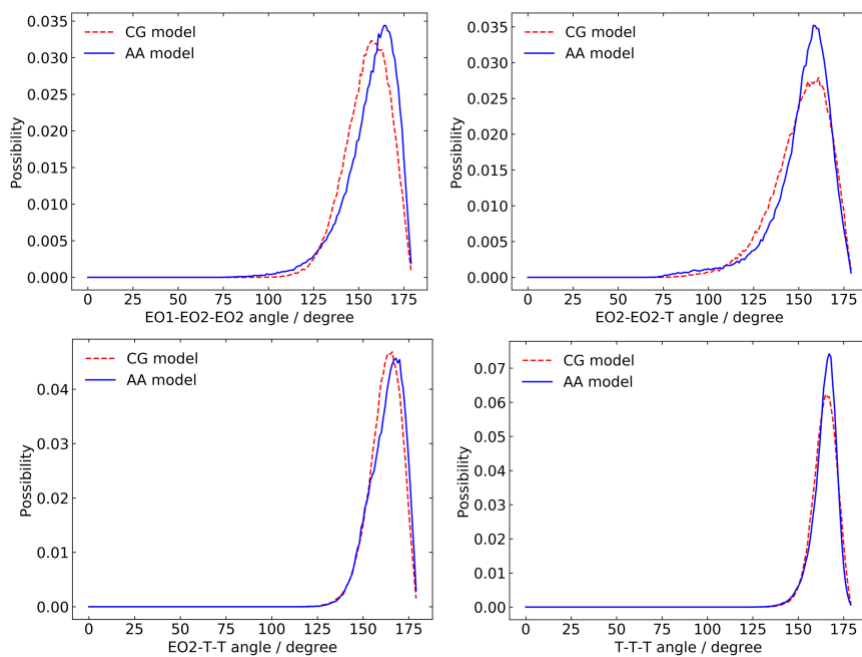
corresponding AA model.

Figure S6. Probability distribution of angles of different types between our CG model and

corresponding AA model.

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Table S7 Non-boned parameters used in the CG model

Atom 1	Atom 2	ε / (kcal/mol)	σ / Å	λ_r	λ_a
EO1	EO1	0.805	4.15	19	6
EO2	EO2	0.805	4.15	19	6
T	T	1.420	5.09	40	6
EO1	EO2	0.805	4.15	19	6
EO1	T	1.069	4.62	27.33	6
EO2	T	1.069	4.62	27.33	6

Table S8 Harmonic bond parameters used in the CG model

Type	k_b / (kcal / (mol·Å^2))	r_0 / Å
EO1-EO2	18.628	4.04
EO2-EO2	27.676	3.50
EO2-T	18.898	3.76
T-T	70.835	3.88

Table S9 Harmonic angle parameters used in the CG model

Type	k_θ / (kcal / (mol·radian^2))	θ_0 / degree

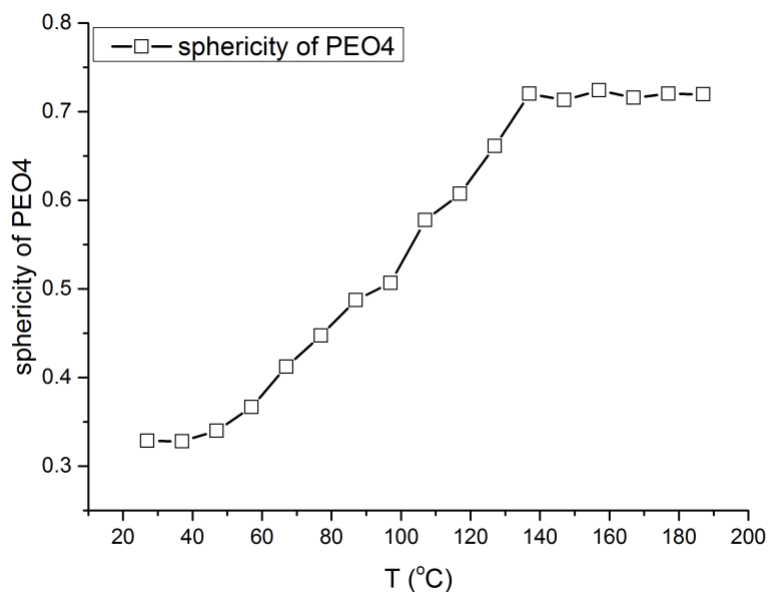|		
EO1-EO2-EO2	4.184	168
EO2-EO2-T	1.858	164
EO2-T-T	6.417	167
T-T-T	13.407	162

Figure S3. Sphericity of PEO4 chains at different temperatures run from AA simulations.

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