Atomistic Model

For atomistic simulations, we use all-atom (AA) force field potential developed by Marcon and Raos (MR) as our base potential.[1,2] The non-bonded interactions in MR model are defined by a combination of Lennard-Jones (LJ) and Coulombic interactions truncated at a cut-off of 12Å. The LJ parameters in the MR model were obtained from Optimized potentials for liquid simulations−all atom force field (OPLS-AA),[3,4] while the partial charges on the atoms for Coulombic interactions were obtained from ab initio density functional theory (DFT) calculations. The MR model also introduces the definition of heteronuclear non-bonded interactions and scaling of non-bonded interaction for bonded atoms from OPLS-AA. Due to the inherent similarity to OPLS-AA, we use it to define the missing potential parameters for PEO4. However, the charges on the terminal carbon attached to 4T on PEO4 unit was modified to maintain charge neutrality. We further refine the model by calculating the equilibrium distances and angles, and torsional parameters by fitting to the difference in energy between the force field and BLYP 6-31G*. To make the torsion potential fit all configurations satisfactorily, it was necessary to modify the atomic partial charges suggested by MR. These were set to match Mulliken charges scaled down by a factor of 1.8 and are shown in Figure S3(b).

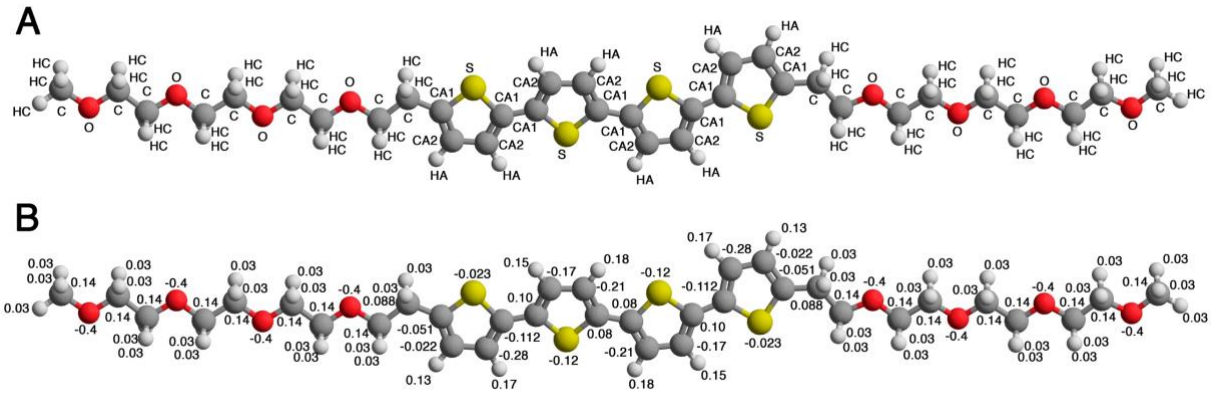

Figure S3. Chemical structure of 4T/PEO4. (a) Atom types and (b) charges are labeled with different numerical suffixes.

Table S3 Non-boned parameters used in the AA model. The atom types are defined in Fig S5.

Atom type	ε / (kcal/mol)[1,2,4,5]	σ / Å[1,2,4,5]
C	0.066	3.50
CA1	0.07	3.55
CA2	0.07	3.55
HA	0.03	2.42
HC	0.03	2.5
O	0.17	3.07
S	0.355	3.6

Table S4 Harmonic bond parameters,[1,2,4,5] where the potential is defined by harmonic potential; $U_{bond} = k_b(r - r_0)^2$

Type	k_b / (kcal / (mol·Å^2))	r_0 / Å
C-C	268	1.541
C-CA1*	300	1.502
C-HC	340	1.095
C-O	320	1.410
CA1-CA1	392.29	1.450
CA1-CA2	514.27	1.373
CA1-S	291.25	1.082

CA2-CA2	453.1	1.432
CA2-HA	370.63	1.082

*This Work

Table S5 Harmonic angle parameters,[1,2,4,5] where the potential is defined by harmonic potential; $U_{angle} = k_\theta(\theta - \theta_0)^2$

Type	k_θ / (kcal / (mol·radian^2))	θ_0 / degree
C-C-CA1	120.140	115.44
C-C-HC	37.500	110.70
C-C-O	50.00	109.50
C-CA1-CA2*	166.320	126.329
C-CA1-S*	41.740	123.671
C-O-C	60.00	109.50
CA1-C-HC	74.060	109.19
CA1-CA1-CA2	54.694	130.14
CA1-CA1-S	41.740	119.57
CA1-CA2-CA2	39.582	113.33
CA1-S-CA1	86.360	92.77
CA2-CA1-S	86.360	110.29
CA2-CA2-HA	35.263	113.32
HC-C-HC	33.000	107.80
HC-C-O	35.000	109.50

*This Work

Table S6 Multi-Harmonic torsional parameters,[1,2,4,5] where the potential is defined by harmonic potential; $U_{dihedral} = \sum_{n=0}^{4} V_n \cos^n \phi$

Type	V_0(kcal/mol)	V_1(kcal/mol)	V_2(kcal/mol)	V_3(kcal/mol)	V_4(kcal/mol)
C-C-CA1-CA2	0.318	1.127	14.143	-22.297	6.672
C-C-O-C	-1.831	-4.661	0.390	15.981	-0.191
C-C-CA1-S	0.318	1.127	14.143	-22.297	6.672
C-CA1-CA2-CA2	75.595	116.000	42.679	-1.528	-3.814
C-CA1-S-CA1	158.700	418.340	521.330	376.730	115.120
CA1-C-C-HC	-5.545	-16.345	2.437	47.610	-0.569
CA1-C-C-O*	3.010	-8.846	22.599	34.835	10.524
CA1-CA1-CA2-CA2	75.595	116.000	42.679	-1.528	-3.814
CA1-CA1-S-CA1	158.700	418.340	521.330	376.730	115.120
CA1-CA2-CA2-CA1	126.320	-109.810	-19.738	-25.303	28.530
CA2-CA1-CA1-CA2	2.953	0.157	-4.233	0.398	1.886
CA2-CA1-CA1-S	2.953	-0.157	-4.233	-0.398	1.886
CA2-CA1-S-CA1	126.320	-109.810	-19.738	-25.303	28.530
HC-C-C-HC	-0.305	-2.378	0.063	7.156	-0.086
HC-C-C-O	-0.476	-3.710	0.098	11.163	-0.133
HC-C-O-C	-5.545	-16.345	2.437	47.610	-0.569
O-C-C-O	0.550	-0.550	0.000	0.000	0.000

S-CA1-CA1-S	2.953	0.157	-4.233	0.398	1.886
S-CA1-CA2-CA2	126.320	-109.810	-19.738	-25.303	28.530

*This Work

Reference

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