Coarse-Grained Molecular Dynamics Simulations of Thermal Annealing of P3HT:PCBM Bulk Heterojunctions for Organic Photovoltaic Applications

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Bulk Heterojunction Architecture (BHJ)

Design criteria:
1. Domain size \~ 10 nm
2. High interfacial area
3. Percolated interpenetrating networks
Coarse-Grained Model


Harmonic Bond Potential

\[ U_{\text{bond}} = \frac{1}{2} k_b (r_{ij} - r_0)^2 \]

Harmonic Angle Potential

\[ U_{\text{angle}} = \frac{1}{2} k_\theta (\theta_{ijk} - \theta_0)^2 \]

OPLS Dihedral Potential

\[ U_{\text{dihedral}} = \frac{1}{2} V_1 (1 + \cos \phi) + \frac{1}{2} V_2 (1 - \cos 2\phi) + \frac{1}{2} V_3 (1 + \cos 3\phi) \]

LJ Pairwise Potential

\[ U_{\text{vdw}} = 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right] \]
# System Sizes

<table>
<thead>
<tr>
<th>$\phi_m$</th>
<th>m</th>
<th>N</th>
<th>L (nm)</th>
<th>$N_{P3HT}$</th>
<th>$N_{PCBM}$</th>
<th>$N_{TOTAL}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>32,400</td>
<td>100</td>
<td>127</td>
<td>3,240,000</td>
<td>1,776,150</td>
<td>5,016,150</td>
</tr>
<tr>
<td>0.33</td>
<td>32,400</td>
<td>100</td>
<td>115</td>
<td>3,240,000</td>
<td>1,182,916</td>
<td>4,422,916</td>
</tr>
<tr>
<td>0.50</td>
<td>32,400</td>
<td>100</td>
<td>100</td>
<td>3,240,000</td>
<td>591,458</td>
<td>3,831,458</td>
</tr>
<tr>
<td>0.67</td>
<td>32,400</td>
<td>100</td>
<td>90</td>
<td>3,240,000</td>
<td>295,729</td>
<td>3,535,729</td>
</tr>
</tbody>
</table>

N: Length of the degree of polymerization of the conductive polymer, P3HT.

m: Number of P3HT chains.

$\phi_m$: Weight fraction of P3HT in the P3HT:PCBM system.

L: Dimensions of the simulation box where the volume of the box is L x L x L.

$N_{P3HT}$: Number of P3HT beads.

$N_{PCBM}$: Number of PCBM beads.

$N_{TOTAL}$: Total number of beads.

- 11% Capacity of Titan
- Ran up to 400 ns
- Box size ~ 100 nm
  - The same order as experiments
Simulation Protocol

fix langevin
fix deform
fix nve

fix npt (1 atm and 423 K)
package gpu
400 ns
3456 cpu-cores
216 gpu’s or nodes

*Images were created using dump image*
Simulation Results

Interface area to volume ratio

\[ T = 423 \pm 0.71 \text{ K} \]
\[ P = 1.06 \pm 2.21 \text{ atm} \]

*movie created from dump image and ffmpeg*
Simulation Results

\[ \phi_m = 0.25 \]

\[ \phi_m = 0.33 \]

\[ \phi_m = 0.50 \]

\[ \phi_m = 0.67 \]

\[ N = 10 \]

\[ N = 25 \]

\[ N = 50 \]

\[ N = 100 \]

\[ N = 150 \]
Data Analysis

• Structure factor, $S(q,t)$
• Average local packing fraction, $\eta$
• Interface area to volume ratio, $\gamma$

Run MD simulation and dump trajectory to a file

dump 2 all custom pdump coord/dump.*.txt id type x y z

GPU speedup is $\sim$2x

Use read_data, read_dump and run 0 to perform data analysis

read_dump ${\text{dumpFile}}$ ${\text{dumpTime}}$ x y z box yes Run 0

Post process using dump file

GPU speedup is $\sim$2x
Domain Size

fix ave/spatial to form a 3D density grid of the P3HT beads
Take the FFT of the 3D grid to get $S(q_l, q_m, q_n)$

$S(q,t)$

$10^{-2}$

$10^{-3}$

$10^{-4}$

$10^{-5}$

$10^{-6}$

$10^{-7}$

$q [\text{Å}^{-1}]$

$10^{-2}$

$10^{-1}$

$q [\text{Å}^{-1}]$

$10^{-1}$

$10^0$

$t [\text{ns}]$

$10^{-9}$

$10^{-8}$

$10^{-7}$

$10^{-6}$

$10^{-5}$

$10^{-4}$

$10^{-3}$

$10^{-2}$

$10^{-1}$

$10^0$

$N = 50$

$N = 100$

$N = 150$

RED : neat P3HT
GREEN : neat PCBM
BLUE : P3HT:PCBM
Miscibility of PCBM in P3HT

Persistence Length of P3HT polymer

\[ b_K = \frac{b}{\cos(\theta_0 / 2)} \left( 1 + \cos(\theta_0) \right) \left( 1 + \langle \cos(\phi) \rangle \right) = 75.7 \text{Å} \]

\[ l_p = \frac{b_K}{2} = 37.8 \text{Å} \sim 10 \text{ P3HT beads} \]

Evolution of N=10

Rod-Like
\[ N = 10 \]

Coil-Like
\[ N = 150 \]

Packing fraction, \( \eta \)

Flory \( \chi \) parameter

\[ \Delta U_{\text{mix}} = \chi \phi_v (1 - \phi_v) kT \]

\[ \chi = 0.92 \pm 0.1 \]
Interface Area to Volume Ratio, $\gamma$

Radical Voronoi Tessellation using Voro++

$N = 10$

$N = 150$
Summary

1. It is important to choose the correct time scale and length scale in the simulation of donor and acceptor blends in OPV’s.

2. At constant P3HT weight percent, we observed different morphologies at different P3HT chain lengths.

3. These different morphologies are stabilized by the different conformational entropies of rod-like vs. coil-like chains and short chains vs. long chain.

4. With all the Titan nodes already available, future work includes systems with substrates or addition of compatibilizers.

*This work is currently under review at PCCP.*
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