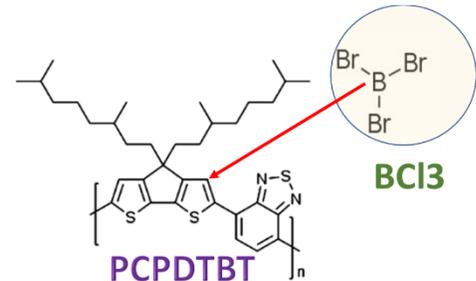


Abstract

Devices utilizing organic semiconductors (OSCs) are attractive for applications such as organic light-emitting diodes, photovoltaics, transistors, etc. due to their solution processability, tunability, and relatively low cost of fabrication compared to their inorganic counterparts. Addition of certain small molecules can result in an increase in the conductivity of these materials via electrical doping. Achieving this has historically involved techniques which were not replicable such as vapor diffusion of dopants into the material of interest or the addition of poorly soluble materials which both place constraints on the processing conditions available for OSCs. Recently, some researchers have focused on Lewis acids as comparatively potent, highly soluble and commercially available dopants.¹ In our own research lab at UCSB, one researcher noticed that batches of a particular OSC with a larger molecular weight required larger amounts of the Lewis acid used in order to exhibit doping. This simulation displays the mean squared distance (MSD) for the Lewis acid BCl_3 and the polymer poly[2,1,3-benzothiadiazole-4,7-diyl[4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2,6-diyl]] (P4).

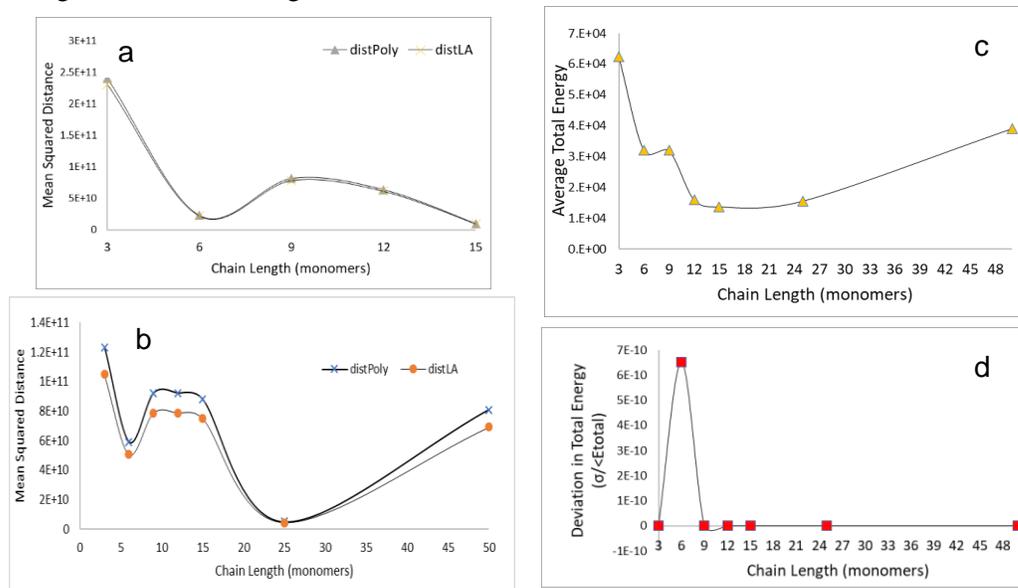
**Methods**

The simulation consisted of Lennard-Jones chains of the polymer, P4, with interspersed LA molecules in which the individual 240 “N atoms” were assigned the LJ parameters of the respective molecules. P4 was allowed to interact with itself through a LJ potential when the two atoms were not bonded and a harmonic potential when bonded. Assuming that the Lewis acid does not bond to itself, these molecules were modeled as only interacting with the polymer through a LJ potential. BCl_3 was set to interact with the polymer through a LJ potential. Parameters used in the calculation of the LJ and harmonic bond potentials were obtained from the literature.^{2,3,4} It is important to note that in OSC devices, the dopant molecules make up a small mol fraction of the film, the polymer which this study is inspired by specifically showed optimal doping with a mol fraction of 2% Lewis acid. This MSD simulation was established with the following parameters: 0.02 and 0.08 LA:P4 molar ratios, P4 chain lengths (3, 6, 9, 12, 15, 25, 50), number density of atoms in simulation box = 0.9 ($\rho = N/L^3$), $N = 240$, Temp = 1, dt = 0.001, Maximum steps = 200000. The non-bonded potential was cut and shifted at the value of $r_c = 2.5$ so that it continuously approached zero as the molecules moved apart. This avoided computation of molecules separated by a distance larger than r_c while preventing discontinuity in the potential which would result from a simple cut.

A conjugate gradient was used to allow the randomly placed molecules to move along the energy landscape until they arrived at a potential energy minimum. After saving the initial trajectory, the velocities of the simulated atoms were rescaled every 100 steps to approach the set temperature. The system was evolved in accordance with Newton’s equations of motion by utilizing the Verlet algorithm for a total of 5000 steps. After equilibrating to the set temperature, this MD simulation was continued for 20000 steps during which the kinetic and potential energy were measured. The kinetic energy at the end of that equilibration period was added to the instantaneous potential energy to determine the average total energy value which was used to rescale the velocities. In order to perform a simulation with NVE dynamics, in which the energy is conserved, this velocity rescaling was not used for the production runs which continued until a total of 200000 MD steps were completed. Since the mean squared distances were being computed in the production runs, the different atom types needed to be identified from the position array. The method chosen for this was one I found particularly clever which I first saw in an old project from a previous student named Ike Risness. In this method, 1 is subtracted from vectors of 1s and 0s representing the Lewis acid and polymer, respectively and the absolute value is taken of the resulting vectors. The dot product of these vectors with the position vectors provides the positions corresponding only to those molecules currently represented by “1”.

Results

This results of this limited simulation did not show a discernable relationship between polymer chain length and mean squared distance of motion. It could be said that it may be interesting to observe that the plots of the mean squared distance and average total energy have similar shapes. The trend hypothesized was that the mean squared distance of the Lewis acid would decrease with increasing chain length. These simulations could be improved, by including the influence of the steric profiles of these materials as well as their relative size. The poor distinction between the properties of these two materials within the simulation is highlighted by the high similarity in the MSD plots. It would also be interesting to incorporate some form of conformational restraint on the polymer chain as the polymers are likely to become more entangled upon increasing the molecular weight.



Figures a and b: MSD results for simulations with varying polymer chain lengths with 8% and 2% molar equivalents of BCl₃. C: Changes in the average total energy with the polymer chain length. D: deviation in total energy as calculated from the standard deviation and average energy.

Lennard-Jones Parameters:

interaction	epsilon eV/particle	sigma nm	r0 [ref. 4] nm	k0 [ref. 4] nm
PCPDTBT-PCPDTBT [ref. 3]	0.20	0.36	0.63	0.35
BCl ₃ -BCl ₃ [ref. 3]	0.05	0.5		
BCl ₃ -PCPDTBT	0.15	0.42		
	*numerical average	*geometric average		

Citations:

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