

**Task ID:** 425.031

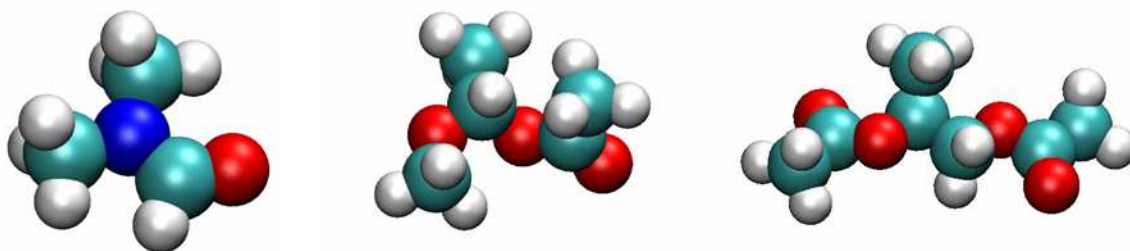
**Task Title:** Supercritical Carbon Dioxide Compatible Additives: Design, Synthesis, and Application of an Environmentally Friendly Development Process to Next Generation Lithography: Resists and Additives

**Deliverable Title:** Report on the simulation and molecular-level evaluation of new resist systems and processes for scCO<sub>2</sub> development

## **Results**

### **Computational Simulations:**

Consistent with our goal to promote environmentally-friendly processes, we have screened several new, non-fluorinated additives to use with scCO<sub>2</sub>. PGMEA and Diace were chosen to test the possibility that oxygen-containing functions groups could interact sufficiently with scCO<sub>2</sub> to solubilize photoresist, while the additive (CH<sub>3</sub>)<sub>2</sub>NCOH was selected as a slight variation from the acetate structures in the other two. These additives were tested against our PHOST, ESCAP, and 193nm resists.



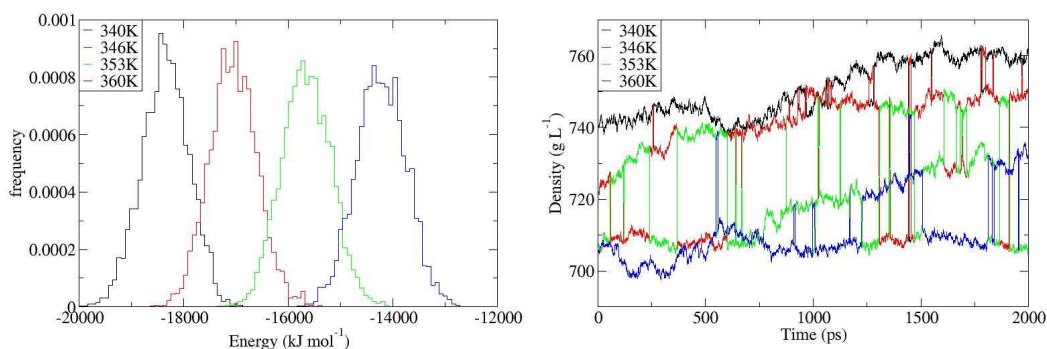
Non-fluorinated additives; from left to right: (CH<sub>3</sub>)<sub>2</sub>NCOH, PGMEA, Diace

As before, model parameters for bonds, angles, and torsions were used from the Optimized Potential for Liquid Simulation (OPLS) force field. A charge model for each species was derived through quantum calculations, as well as any parameters not available in the standard OPLS force field. Using this model, thin films of the model photoresists were prepared and then equilibrated in the presence of scCO<sub>2</sub> and the chosen additive. Integration of average force on each chain as a function of position then provides a description of the free energy associated with being on the surface versus the center of the film. Systems in which chains prefer to reside deeper in the film are stable, while those with a thermodynamic driving force towards dissolution are unstable and hence dissolve.

Whereas previous fluorinated additives have provided clear, significant shifts in the free energy curves that are plainly visible and easily interpreted, the free energy changes associated with oxygen-based additives have been relatively muted. For the ESCAP resist, only (CH<sub>3</sub>)<sub>2</sub>NCOH is clearly capable of dissolving the protected photoresist. Free energy changes for PGMEA are within the noise of the measurement, but the best current estimate is that it is effective. For the 193-nm photoresist, all oxygen-based additive results are again within the error of the measurement, but tend towards dissolution. PHOST is not soluble in (CH<sub>3</sub>)<sub>2</sub>NCOH.

Due to the difficulty associated with obtaining clear results for oxygen-based additives, we are refining our methods. The apparent limitation is that accurate free-energy curves require long time averaged results, which need to sample a diverse set of minima across the energy landscape. Using brute-force molecular dynamics to explore the landscape has remained satisfactory due to the efficacy of our force averaging technique and the relatively large driving forces that effective fluorinated additives have provided. As we examine additives that are less potent, it becomes necessary to more robustly explore the energy landscape. To that end, we will use parallel tempering.

Parallel tempering consists of running multiple simulations of the same system in parallel, over a range of temperatures. After a set period of time, swap attempts are made between the simulation boxes, which are accepted according to Monte Carlo criteria. These swaps allow each system to sample a range of temperatures, and hence overcome energy barriers. Implementation and optimal allocation of replicas have been addressed in the literature. This provides us with not only a mechanism to more quickly sampling the temperature of interest, but allows for extraction of temperature-dependant properties at a later date.



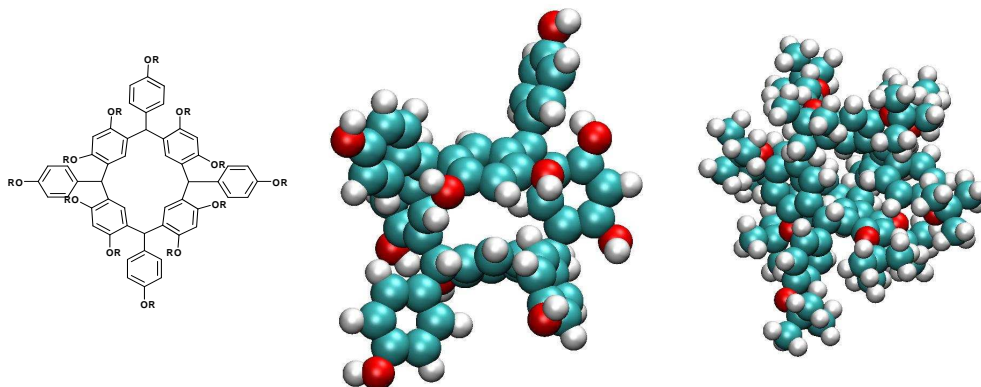
Sample parallel tempering results for bulk ESCAP (no  $\text{scCO}_2$  or additives). Left plot shows histograms of energy across four boxes. Right plot shows density changes in the systems as they sample a range of temperatures. Note: results not final.

Shown above are the results of a 2 ns run of a 4-box parallel tempering scheme for bulk ESCAP. When a swap occurs between two boxes, each configuration retains its potential energy, density, etc., but the velocities of the particles are rescaled to match the new temperature. Effective sampling of the temperature range by each system requires overlapping energy histograms, as shown in the left of the figure. The right figure shows how the density changes. The color denotes the temperature of each configuration. Since density does not change during the swap itself, we can also see the path through temperature-space that an individual configuration explores. For example, the most dense system spends almost the entire 2 ns in the 340 K box, as denoted by the black line. On the other hand, the system that starts in the green box, explores the energy landscape more completely, as denoted by the many color changes. Obviously, 2 ns is insufficient to accurately explore the energy landscape and the conditions used. After we have tuned the temperature distribution and rate of swap attempts to their optimal values for each of

the many systems we are exploring, we will perform longer runs from which to produce free energy curves as a function of position.

### **Future work**

We remain highly interested in finding suitable molecular glass systems for use with  $scCO_2$ . Molecular glasses have inherently low line edge roughness (LER), making them ideal candidates for photoresist testing. We have begun constructing a computational model for both forms of this promising resist.



Molecular glass for future consideration: general formula (left), unprotect form with OH (center), and protected form with t-butyl (right)

### **References**

- Y. Sugita and Y. Okamoto, Chemical Physics Letters, 1999, 314, 141-151  
N. Rathore, M. Chopra, and JJ de Pablo, J. of Chem. Phys., 2005, 122