

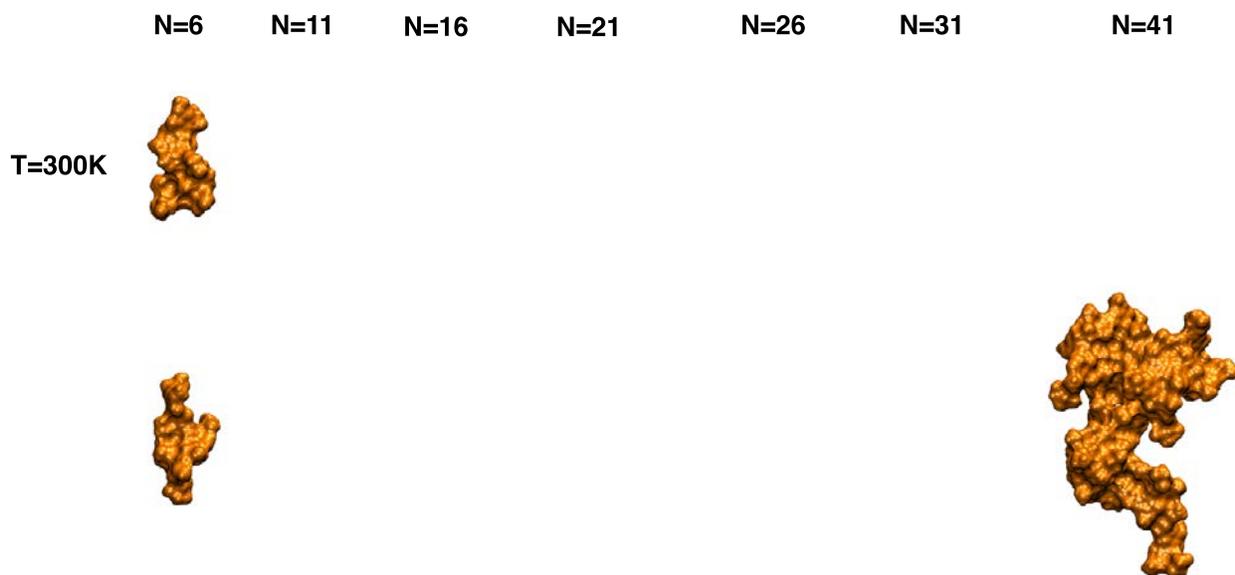
Conformations of Low-Molecular Weight Lignin in Water: Insights on the Chemical Character of Lignin

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<http://cmb.ornl.gov/research/bioenergy/lignocellulose-dynamics>

Project Goals: Lignocellulosic biomass comprises the vast majority of biomass on Earth and has the potential to play a major role in generation of renewable biofuels if cost-effective conversion can be achieved. Largely composed of plant cell walls, it is a complex biological composite material that is recalcitrant to the structural deconstruction and enzymatic hydrolysis into sugars that are necessary for fermentation to bioethanol. The Scientific Focus Area in Biofuels is developing “Dynamic Visualization of Lignocellulose Degradation by Integration of Neutron Scattering Imaging and Computer Simulation” for multiple-length scale, real-time imaging of biomass during pretreatment and enzymatic hydrolysis. This is providing fundamental information about the structure and deconstruction of plant cell walls that is needed to drive improvements in the conversion of renewable lignocellulosic biomass to biofuels.



Representative structures of seven lignin polymers of degree of polymerization N at two temperatures.

Low-molecular weight lignin binds to the cellulose during thermochemical pretreatment of biomass for biofuel production, preventing the efficient hydrolysis of the cellulose to sugars. The binding properties of lignin are strongly influenced by the conformations it adopts. Here we use molecular dynamics simulations in aqueous solution to investigate the dependence on chain length and temperature of the shape of lignin polymers. Lignin is found to adopt collapsed conformations in water at temperatures of 300 K and 500 K. However, at 300 K, a discontinuous transition is found in the shape of the polymer as a function of chain length. Below a critical

degree of polymerization, $N_c = 15$, the polymer adopts less spherical conformations than above N_c . The transition disappears at high temperatures (500 K) at which only spherical shapes are adopted. An implication relevant to cellulosic biofuel production is that lignin will self-aggregate even at high pretreatment temperatures. The above picture is consistent with small-angle neutron scattering experiments showing the building blocks of extracted lignin being oligomeric, with $N \sim 5-12$ and adopting aspherical, rod-like conformations.

The study sheds light on the physico-chemical character of lignin. In general, the conformational properties of polymers in dilute solution are influenced by a balance of interactions between monomers and with the solvent. Block copolymers composed of both hydrophilic and hydrophobic monomers self-assemble in a manner that minimizes unfavorable interfacial areas (hydrophilic-hydrophobic and water-hydrophobic) while maximizing favorable interfaces (hydrophilic-hydrophilic, hydrophobic-hydrophobic and water-hydrophilic), subject to chain connectivity constraints. These polymers are able to do so because their domains consist of multiple monomers that are large enough in number that they can phase separate. However, this phase separation is not possible for "poly-amphiphiles", complex polymers that contain both polar and non-polar groups in their monomers, such as lignin. Lignin monomers themselves contain both hydrophilic and hydrophobic moieties. Although lignin phenylpropanoid monomers are overall hydrophobic due to their dominant aromatic rings, they also contain polar hydroxyl groups that interact favorably with water. The present simulations show that the balance of interactions between lignin and water leads to a chain-length dependent shape of the collapsed polymer in water instead of the microphase separation found in block copolymers.

References

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2. Ratnaweera, D. R.; Saha, D.; Pingali, S. V.; Labbe, N.; Naskar, A. K.; Dadmun, M., The impact of lignin source on its self-assembly in solution. *RSC Adv.* **2015**, *5* (82), 67258-67266.

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