

## Zippering Backwards the Other Way – Yet Another Unique Aspect of Cellulose

Martin A. Hubbe

Readers of this journal may be keenly aware of cellulose's remarkable attributes, such as high stiffness, insolubility in just about everything, resistance to enzymatic attack, dimensional stability in the lengthwise direction, and toughness associated with the alternating crystalline zones and less organized regions. But if you dissolve cellulose and then allow it to recrystallize, the resulting crystals are at the same time radically different, and yet remarkably similar in most respects to the native form. Exactly half of the macromolecules in regenerated cellulose have been reversed 180 degrees in their direction. The behavior of dropped pencils can help explain why this happens.

*Keywords: Cellulose; Crystallization details; Regeneration; Hydrogen bonding*

*Contact information: North Carolina State University, College of Natural Resources, Department of Forest Biomaterials, Campus Box 8005, Raleigh, NC 27695-8005, USA, E-mail: hubbe@ncsu.edu*

### Cellulose's Odd Crystallization Behavior

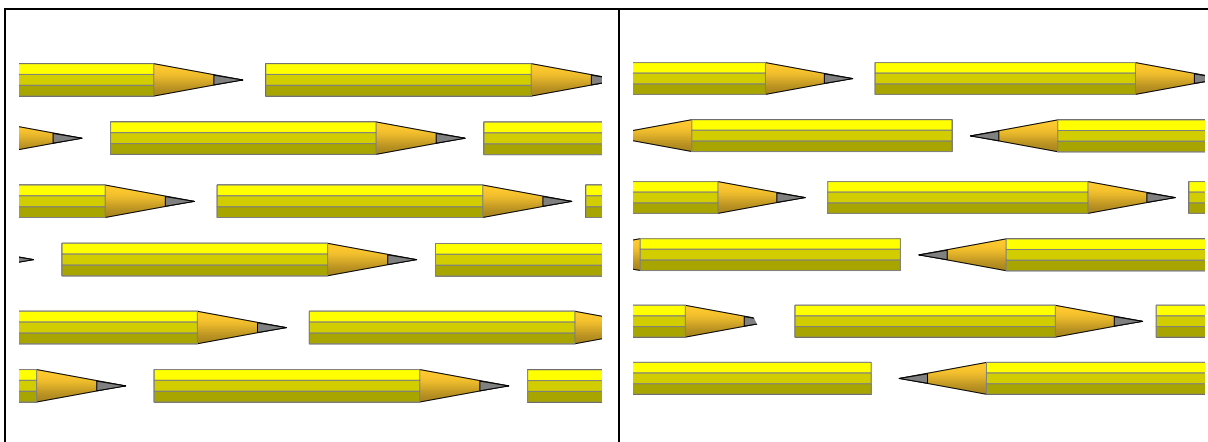
Did it ever occur to you how odd cellulose seems to be with respect to its preferred mode of recrystallization? When cellulose is biosynthesized in a plant, the adjacent macromolecular chains are all facing in the same direction. In other words, we say that the chains are all “in parallel” with each other, and the form of crystal is called “cellulose I”. This is why, in a cellulose nanocrystal prepared from native cellulose, only one end of the crystal is populated by 100% of “reducing ends” of the macromolecules. Thus, it is possible to carry out a grafting reaction such that gold nanoparticles are attached just on one end, and not the other (Lokanathan *et al.* 2013, *Biomacromolecules* 14, 2807). But when you dissolve the cellulose, either with a specialized solvent or by making a chemical derivative of it, and then you regenerate it, something very unique happens. Instead of forming cellulose I again, the molecules arrange themselves in an “antiparallel” fashion. In other words, half of the macromolecules have their reducing ends pointed in one direction and half of them are facing in the opposite direction. Instead of crystallizing as cellulose I, one obtains cellulose II.

Why does cellulose do that? First of all, let's consider the possibility that the heat of formation of the cellulose II crystal is greater than that of cellulose I, making it more energetically favorable. It's a nice theory, but there are a couple of problems. The biggest problem is that the quantities of bonds in cellulose I and II are essentially identical. The covalent bonds are the same, with only minor differences in configurational strain, *i.e.* bond angles close, but not exactly equal to those providing the most favorable enthalpy in each case. And the hydrogen bonds acting within and between adjacent cellulose chains are likewise numerically the same in each case. There may be some minor differences in terms of the orientations and lengths of the hydrogen bonds in cellulose I *vs.* II, but hardly enough to explain why regeneration of cellulose never yields cellulose I, the parallel type of cellulose.

## A Sack Full of Pencils

Take a sack full of pencils and spill them randomly into a big box. Each pencil represents a cellulose macromolecule. Now shake the box gently, while holding it at an angle so that all of the pencils line up. Look carefully at the pencils and verify for yourself that half are pointed in one way and the other half in the other.

Just for fun, the following two figures are offered as a rudimentary form of “molecular diagram” to contrast the crystalline forms of cellulose I and II. Purists can argue over whether the sharpened end ought to represent the reducing end or the non-reducing end of the chain. I have no preference. And maybe nature does not have much preference either: The parallel crystalline form naturally arises during biosynthesis, since the macromolecules are being produced linearly from a set of specialized enzymatic structures within the plant cell. Regenerated cellulose is being prepared from molecular chains having an equilibrated random distribution of orientations. And in general terms most properties of cellulose I and II are quite similar to each other.



Fanciful molecular diagrams of (left) cellulose I crystal and (right) cellulose II crystal

Maybe one does not need to look any further for a reason for the formation of cellulose II, the antiparallel crystal, when cellulose recrystallizes from a random mixture. Statisticians and students of thermodynamics would say that cellulose II is preferred due to entropy. But I say that it is just the law of spilled pencils.

## An Experiment with Real Zippers

In my closet I have a pair of wind-pants that can be zipped apart completely along each side. The purpose is to allow you to put them on or take them off without having to take off your boots, snowshoes, or whatever else happens to be on your feet. Just for fun, as I was in the midst of writing this essay, I attempted to zip the pants back together starting at the “wrong end”. No luck. Only one end of the zipper was provided with the little tip that fits into the pull tab to get the zipping started. My wind-pants are pretty adaptable and useful for hiking in the winter. But they were a complete failure when I attempted to replicate what cellulose molecules do all of the time as a matter of preference.