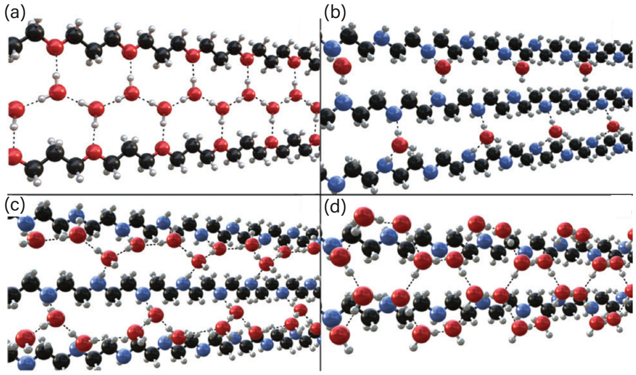
Investigating Polymer Crystal Hydrates

More than 50 years ago, a research group in Japan began characterizing polymers in the presence of water under different conditions. They discovered that two different polymers, polyoxocyclobutane (POCB) and polyethyleneimine (PEI), can bind to water and form crystalline hydrate structures upon cooling. The unit cells of these hydrates were altogether different from those of the pure polymers, and this was not a case of a homopolymer crystal absorbing water into interstitial spaces. Instead, the water and polymer were synergistically combining into entirely new ordered structures.

Co-crystallization of two distinct species is relatively common among metal alloys, and numerous intermetallic compounds are known. Co-crystallization is less common among organic compounds. In fact, water can itself crystallize with small molecules such as methane, carbon dioxide, and cyclopentane to form clathrate hydrates. Even a relatively large molecule like t-butyl ammonium bromide (TBAB) can form a hydrate. However, polymer co-crystallization with any kind of small molecule is unusual, whereas co-crystallization of a polymer with water is exceptionally rare.

Since the original research from the 1970s, only a total of four polymer crystal hydrates (PCHs) of POCB or PEI have been discovered, and these PCH compounds have properties that have gone unnoticed by the larger research community. In the *AIChE Journal* Perspective article, "The Fascinating World of Polymer Crystal Hydrates: An Overview," Dominick Filonowich, Sachin Velankar, and John A. Keith (Univ. of Pittsburgh) revisit the past literature of these compounds with modern context to pique the curiosity and interest about PCHs as a class of materials that may find broad and deep applications as smart materials.



▲ **Figure 1.** Atomic-scale depictions of structural features in different polymer crystal hydrates (PCHs) are shown here. These include: (a) polyoxocyclobutane (POCB) hydrate with a water chain; (b) polyethyleneimine (PEI) hemihydrate with isolated water molecules; (c) PEI sesquihydrate with water ribbons; and (d) PEI dihydrate with water layers. Figure created by Dominick Filonowich.

A notably striking aspect of PCHs is how water is structurally arranged within them (Figure 1). In POCB crystal hydrates, water is aligned into (a) well-defined one-dimensional "wires" that run parallel to each other. In PEI crystal hydrates, individual water molecules may be positioned to be (b) isolated away from other water molecules, (c) in pseudo one-dimensional ribbons formed from pentagons of water, or (d) in hexagonal ice-like two-dimensional layers, all depending on the polymer-to-water ratio. Such fundamentally distinct atomic-scale arrangements of water are not usually observed in self-assembling materials. Other PCHs, if they can be discovered, may provide a scaffold to understand fundamental water structures.

In terms of thermodynamics, the enthalpic driving force of hydrogen bonding between the polymer and water clearly is strong enough to compensate for the entropic driving force that would be expected to bring greater disorder in both compounds. Peculiarly, medium molecular weight POCB is a liquid at room temperature, but its hydrate melting temperature is over 35°C. That means that when liquid POCB is mixed with liquid water at room temperature, it spontaneously crystallizes into the solid hydrate.

Room temperature crystallization of water might be better recognized as the key plot point in Kurt Vonnegut's 1963 science fiction novel, Cat's Cradle, where the infamous "Ice Nine" crystals bring about unintentionally catastrophic consequences for humanity. Fortunately, the actual room temperature crystallization process requires both POCB and water (as well as long time scales of hours for crystallization), and hence poses no danger to freezing the world's oceans. Nevertheless, PCHs present an opportunity for exploring new and creative solutions for challenges to society.

The Perspective article mentions several ways that PCHs might be found useful while also highlighting potential challenges that would need to be overcome. For example, the well-ordered water structures observed in PCHs may be uniquely well-suited as a proton conduction membranes in energy storage and conversion devices, but high macroscopic alignment would also likely need to be introduced. Alternatively, PCHs may become a way to create "smart materials" that stiffen in response to humidity and soften upon drying. Other possible applications from thermal desalination to the stabilization of gas hydrates are mentioned as well.

Time will tell if more PCHs will be discovered, but there are likely many opportunities to investigate different aspects of the known PCHs with modern computational and experimental methods. The Perspective provides a launch point to become more familiar with these fascinating materials and their possible uses. CEP