

PERSPECTIVE

Thermodynamics and Molecular-Scale Phenomena

The fascinating world of polymer crystal hydrates: An overview

Dominick Filonowich | Sachin Velankar | John A. Keith 

Department of Chemical Engineering,
University of Pittsburgh, Pittsburgh,
Pennsylvania, USA

Correspondence

John A. Keith, Department of Chemical
Engineering, University of Pittsburgh,
Pittsburgh, PA, USA.

Email: jakeith@pitt.edu

Abstract

Polymer crystal hydrates (PCHs) are crystalline solids that form between a polymer and water. To date, only four distinct PCHs have been discovered—one of polyoxacyclobutane (POCB) and water, and three different polymorphs of polyethyleneimine (PEI) and water. These PCHs were first reported decades ago and have fascinating structures and peculiar properties that make them potentially useful for a wide range of applications including refrigeration, proton conduction membranes, and desalination. This perspective revisits what is known about these compounds, categorizes their similarities and differences with other known compounds, and offers a perspective into future efforts to discover new PCHs to address technological needs for society.

KEYWORDS

crystallization, hydrates, polymer properties

1 | INTRODUCTION

In 1967, Tadokoro et al. reported that a crystal hydrate formed when high molecular weight polyoxacyclobutane (POCB) and water were combined,¹ while several crystal hydrates were reported between polyethyleneimine (PEI) and water in the early 1980s.^{2,3} Apart from a relatively small number of studies,^{4–9} polymer crystalline hydrates have received little attention in subsequent decades. We propose that these compounds be classified as “polymer crystal hydrates” (PCHs), which exhibit some similarities and some differences from traditional gas clathrate hydrates. This perspective aims to rekindle interest in PCHs that possess fascinating properties that would be potentially useful in a variety of applications.

We first distinguish PCHs from other highly studied materials such as gas clathrate hydrates, polymer clathrates, and hydrogels. Gas clathrate hydrates consist of ice-like cages

formed from water molecules that encapsulate guest molecules such as methane. Gas hydrate structures are naturally found in low temperature permafrost environments (e.g. temperatures below 2 °C) and high pressure marine environments (at 500–2000 m underwater),¹⁰ and interest in their potential applications in refrigeration,¹¹ desalination,^{12,13} and as organic solvents for pharmaceuticals¹⁴ has made them the subject of extensive research for several decades.^{15–17} Gas clathrate hydrates are classified as Type-I, Type-II, or Type-H clathrates depending on their water-cage structures.^{18,19} These cages are not present in PCHs, but water structures form in both. PCHs instead contain other nanoscale structures such as planes or ribbons of water, so the polymer solutes are not fully enclosed as in the solutes in traditional gas clathrate hydrates. While most gas clathrate hydrates only form under high pressures, some small molecules (e.g., cyclopentane, tetrahydrofuran, and tetra-n-butylammonium) can form hydrates at atmospheric pressure above 0 °C.^{20–23} For additional reading on gas clathrate hydrates, we suggest articles by Chatti et al., Khurana et al., Buffet, and Hester et al.^{17,18,24,25}

Abbreviations: EDA, energy decomposition analyses; PCH, polymer crystal hydrate; PEI, polyethyleneimine; PO CB, polyoxacyclobutane.

This is an open access article under the terms of the [Creative Commons Attribution](https://creativecommons.org/licenses/by/4.0/) License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

© 2024 The Author(s). *AIChE Journal* published by Wiley Periodicals LLC on behalf of American Institute of Chemical Engineers.

Polymer clathrates that form with solvents besides water are also known. The δ -form of syndiotactic polystyrene (s-PS) can assemble into a crystalline lattice that contains vacant spaces in which a second guest species can occupy,²⁶ for example, toluene or iodine.²⁷ Poly(ethylene oxide) (PEO) also forms a clathrate with urea;^{28,29} urea will assemble into a crystalline complex whereby linear PEO molecules occupy channels in the urea adduct. Polymer scientists use the term ‘modification’ to refer to different crystalline forms that result from different crystallization procedures, and these complexes can have two modifications: (a) a trigonal crystal structure and (b) a hexagonal crystal structure formed upon melting and recrystallization.³⁰ Several other polymer-solvent molecular compounds have also been reported.³¹

Lastly, hydrogels assemble from a polymer and water similar to PCHs, but unlike PCHs, hydrogels assemble from one or more hydrophilic polymers and water. Hydrogels are often categorized as either (a) chemical hydrogels (permanent hydrogels) that are crosslinked via covalent bonds, resulting in strong, permanent junctions within the network or (b) physical hydrogels (reversible hydrogels) that are crosslinked via noncovalent interactions such as hydrogen bonding, hydrophobic interactions, crystallization of the polymer, and chain entanglement.³² Hydrogel networks can be amorphous, semi-crystalline, crystalline, or hydrocolloid aggregates. Regardless of their structure, hydrogels can absorb solvating water molecules that reside in the amorphous regions of the network, and this uptake is not restricted to a well-defined ratio. Under equilibrium swelling conditions, the mass fraction of water may far exceed that of the polymer.³³ Depending on the components of the hydrogel, the absorbed solvent can be released into the environment via changes in factors such as temperature³⁴ and pH.³⁵

To summarize, PCHs, gas hydrates, polymer clathrates, and hydrogels all share a similar characteristic in that a polymer species assembles into another structure with a smaller molecular species. PCHs are distinct because:

1. unlike gas hydrates, the water takes other forms than a cage structure to accommodate the polymer guest, and the water fraction is usually much lower than in a gas hydrate;
2. unlike polymer clathrates, the solvent in a PCH is always water; and
3. unlike hydrogels, PCHs involve water molecules co-crystallizing with the polymer chains at precise compositions to allow water to form highly ordered and intriguing nanostructures.

For these reasons, PCHs have promise for a variety of useful applications, and they may someday be useful scaffolds for nanoscale water structures that have already been identified.^{36,37} We will now discuss the properties of polymers that have so far been discovered to form PCHs.

2 | POLYOXACYCLOBUTANE

2.1 | POCB as a polymer

POCB was first discovered in 1958 by Bunn and Holmes³⁸ and later characterized in 1967 by Tadokoro. The POCB

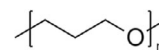


FIGURE 1 Chemical structure of a linear polyoxacyclobutane monomer unit.

homopolymer has the lowest melting point, the lowest heat of fusion, and the most compact chain dimensions among all the polyalkylene oxides having a repeat unit of $[(CH_2)_n-O]$.¹ Its monomer unit is shown in Figure 1.

Tadokoro et al.³⁹ first discovered that POCB exhibits three crystal modifications with distinct characteristics that are summarized in Figure 2. In 1981, a fourth modification of POCB was discovered.⁴⁰

Modification I exhibits a planar zigzag conformation over a fiber identity period of 0.48 nm. Each unit cell modification contains four monomers and four water molecules and forms a PCH structure. Figure 3A shows the crystal structure of Modification I, which will be further discussed in the following subsection.

Apart from Modification I, which is a hydrate, the other modifications are all pure crystals of POCB. Modification II (see Figure 3B) features a trigonal lattice with a space group of $R_3c-C_{3v}^6$, a unit cell of $a=1.413$ nm and $c=0.841$ nm, and a fiber identity period of 0.841 nm. It consists of nine molecular chains that adopt a more helical conformation, with some chains forming a screw to the right and others to the left.³⁹

Modification III (see Figure 3C) features an orthorhombic unit cell with dimensions of $a=0.923$ nm, $b=0.482$ nm, and $c=0.721$ nm. It adopts a helical conformation, and four monomers are present within the cell. This modification is the most stable of the four under dry conditions due to the strong dipole moments of the COC groups, which are arranged anti-parallel to each other. The $C_{2221}-D_2^5$ space group permits two unit cell orientations, only one of which is displayed in Figure 3C. The second orientation features the same molecular axis, but the helical axis is rotated by approximately 90° from the first orientation, making it unclear which unit cell is more chemically accurate.³⁹

Modification IV features a planar zigzag conformation similar to Modification I. However, Modification IV could only be synthesized in the presence of a large amount of Modification III.⁴⁰ Additionally, Modification IV has a disordered structure, and methyl groups and oxygen atoms are randomly substituted for each other.

2.2 | POCB as a PCH

Modification I is one of the few known PCHs. Its melting point is $37-41^\circ\text{C}$, depending on the molecular weight of the polymer.⁷ Even at low molecular weights, the POCB hydrate melts at a temperature that is higher than that of either the polymer and water. Its structure was analyzed using infrared adsorption spectroscopy and x-ray diffraction measurements with Ni-filtered $\text{Cu K}\alpha$ radiation.⁴¹ The x-ray

FIGURE 2 Methods of treatment of the polymer to form the three different modifications of polyoxacyclobutane. Adapted from Reference 39.

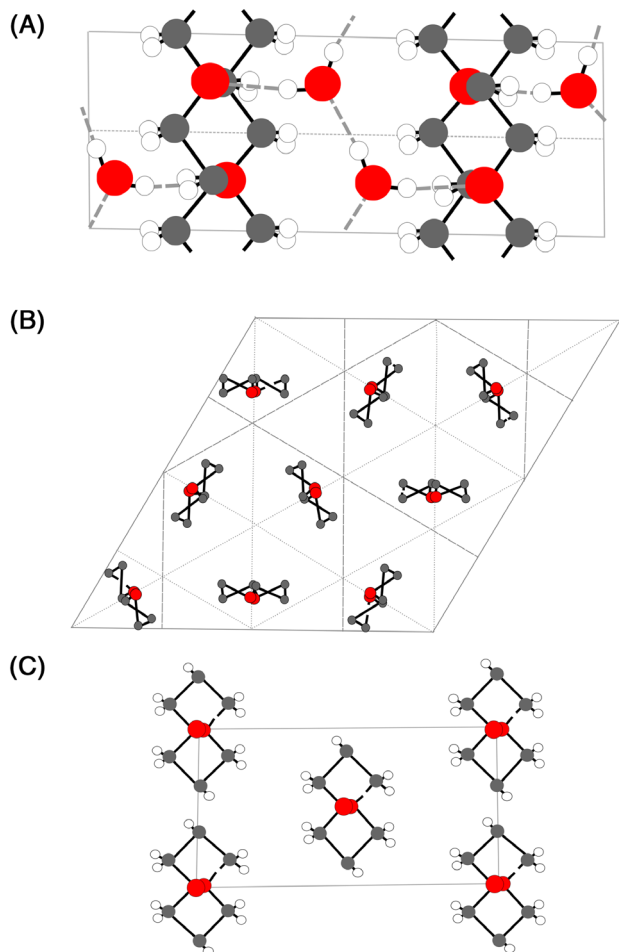
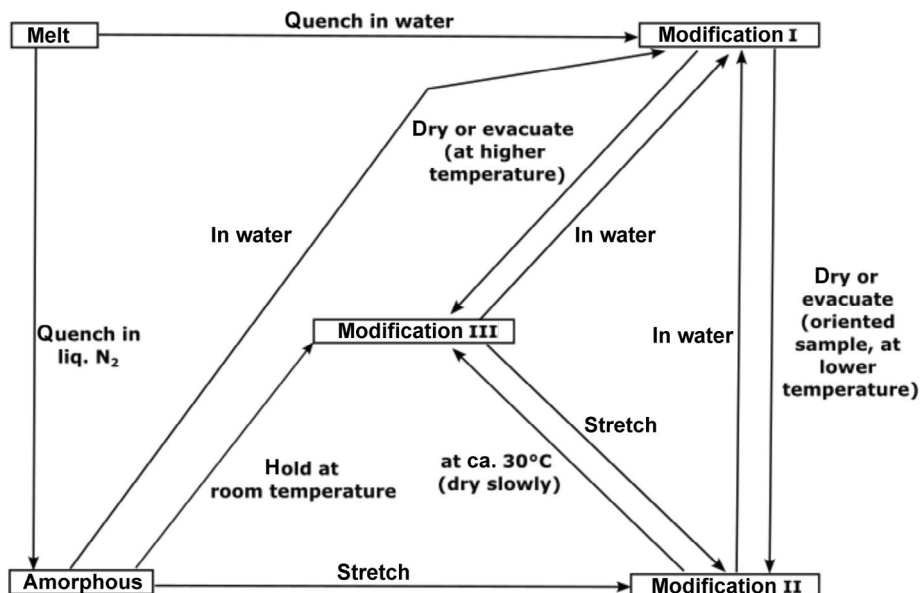


FIGURE 3 (A) Crystal structure of Modification I of the polyoxacyclobutane (POCB)-water hydrate, (B) Crystal structure of Modification II of the POCB crystal, (C) Crystal structure of Modification III of the POCB crystal.³⁹ Red spheres: oxygen atoms, grey spheres: carbon atoms, white spheres: hydrogen atoms, solid black-lines: covalent bonds, dashed-lines: hydrogen bonds.

diffraction results revealed that the distances between oxygen atoms (water-water: 0.268 nm, water-polymer: 0.27 nm) were shorter than twice the van der Waals radius of an oxygen atom (0.28 nm), indicating hydrogen bonding between water molecules and POCB chains. The infrared analysis showed a dichroism in the OH stretching at 3480–3200 cm⁻¹, and HOH bending vibrations are at around 1660 cm⁻¹, which are similar to other species with hydrogen-bonded water molecules, such as ice VII and oxalic acid dihydrate. Additionally, the presence of translational or vibrational modes of water was detected, which indicated that the water was bound within a crystal structure.⁴¹

POCB assembles into its hydrate when water molecules and POCB chains form hydrogen bonds in a zigzag conformation.³⁹ Without water, the zigzag conformation is unfavorable, and Modifications II and III form helices. The POCB hydrate was subjected to isothermal dissociation pressure measurements at temperatures ranging from -25°C to 20°C. The results confirmed that the water molecules were present in the crystal in the same molar ratio as the monomer. Additionally, the dissociation heat was determined to be 3.25×10^3 J/mol.⁴²

Banerjee et al.⁷ reported that crystallization was slow at room temperature with low water content, and it slowed further as the melting temperature was approached. Crystallization was also slowed as the POCB:water ratio increased far above the 1:1 molar ratio needed for the hydrate. At high water content and/or high molecular weight, POCB is immiscible with water, indicating that it is intrinsically hydrophobic. Accordingly, crystallization occurs from a two-phase LLE state, and it is significantly influenced by mixing conditions.⁹ While co-crystallization of water is already unusual, it is especially remarkable considering that POCB is a hydrophobic polymer. This appears to be the only known example of a polymer co-crystallizing with a small molecule with which it is immiscible.

3 | POLYETHYLENEIMINE

3.1 | PEI as a polymer

PEI has a long history of industrial use, dating back to 1938, when it was primarily used for water-repellent finishing of paper and textiles, manufacturing reactive dyes, and enhancing the dyeability of said materials.⁴³ PEI is a highly branched polymer that exhibits an increase in branching as the temperature and concentration of the acid catalyst increase. The branched form of PEI is synthesized via the ring-opening polymerization of the aziridine monomer.⁴⁴ In contrast, linear PEI is obtained through the ring-opening of polymerization of N-substituted aziridine,^{45,46} and ring-opening polymerization of 2-phenyl-2-oxazoline,⁴⁷ and 2-ethyl-2-oxazoline are followed by hydrolysis.⁴⁸ The linear PEI crystals have a melting point of approximately 60 °C and can achieve a maximum molecular weight of 10⁵ g/mol^{47,49} with a monomer unit, as shown in Figure 4.

The PEI crystal consists of double-stranded helical polymer chains. Each chain is a 5/1 helix with an identity period of 0.958 nm. Two chains form a double strand with a relative rotation of 180° about the helical axis. The closest inter-chain atomic distances in the double strand are 0.396 and 0.417 nm for C–C pairs and 0.310 and 0.316 nm for N–N pairs.⁵⁰ These are comparable to twice the van der Waals radius, and thus the double strand is considered to be very tight. This crystallization is strongly correlated with hydrogen bonding between NH groups on each chain. All of the NH hydrogen atoms can participate in hydrogen bonding, making PEI an example of a double-stranded helical polymer that is stabilized by interchain hydrogen bonds,⁵⁰ as seen in Figure 5B. These strands are packed into a large *Fddd* unit cell. In the structure, a right-handed strand is surrounded by two right-handed strands and four left-handed strands, and vice versa as seen in Figure 5B.⁵⁰

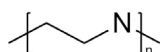


FIGURE 4 Chemical structure of a linear polyethyleneimine monomer unit.

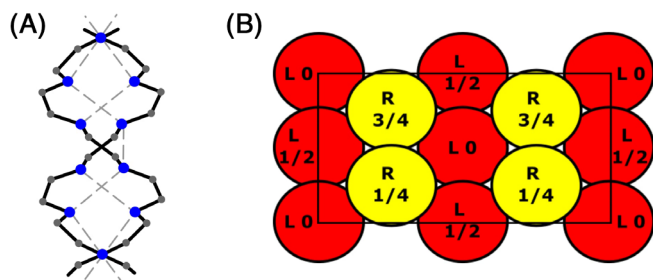


FIGURE 5 (A) Double-stranded helical chain of polyethyleneimine (PEI). Broken lines indicate N–H...N hydrogen bonds, blue spheres: nitrogen atoms, grey spheres: carbon atoms, black-lines: covalent bonds, dashed-lines: hydrogen bonds. (B) Packing of double strands viewed along the chain axis. R and L indicate right/left handed strands, and numbers indicate the fractional height of the strands.

3.2 | PEI as PCHs

Compared to POCB, PEI and its hydrates have a much larger body of work exploring their chemistry and possible applications.^{51–65} It would be outside the scope of this perspective to discuss all of these studies, but we reference them for further reading. In the next sections, we summarize the three different crystalline hydrates of PEI.

3.2.1 | Hemihydrate

The hemihydrate (see Figure 6A) has a PEI:water molar ratio of 1:0.5, and a unit cell with dimensions of $a = 1.089$ nm, $b = 0.952$ nm, $c = 0.731$ nm, $\beta = 127.6^\circ$, and a density of 1.14 g/cm³.³ The PEI chains align as planar zigzags that are parallel to the *bc* plane, while the water molecules are on a twofold rotation axis parallel to the *b* axis. The water molecules are tetrahedrally coordinated by their oxygen atoms and the nitrogen atoms of the PEI. The N–H...O hydrogen bonds have a bond length of 0.287 nm and N...H–O hydrogen bonds have a bond length of 0.305 nm. The hemihydrate structure is unique for a PCH in that water molecules appear to be too distant from each other to form hydrogen bonds with other water molecules.

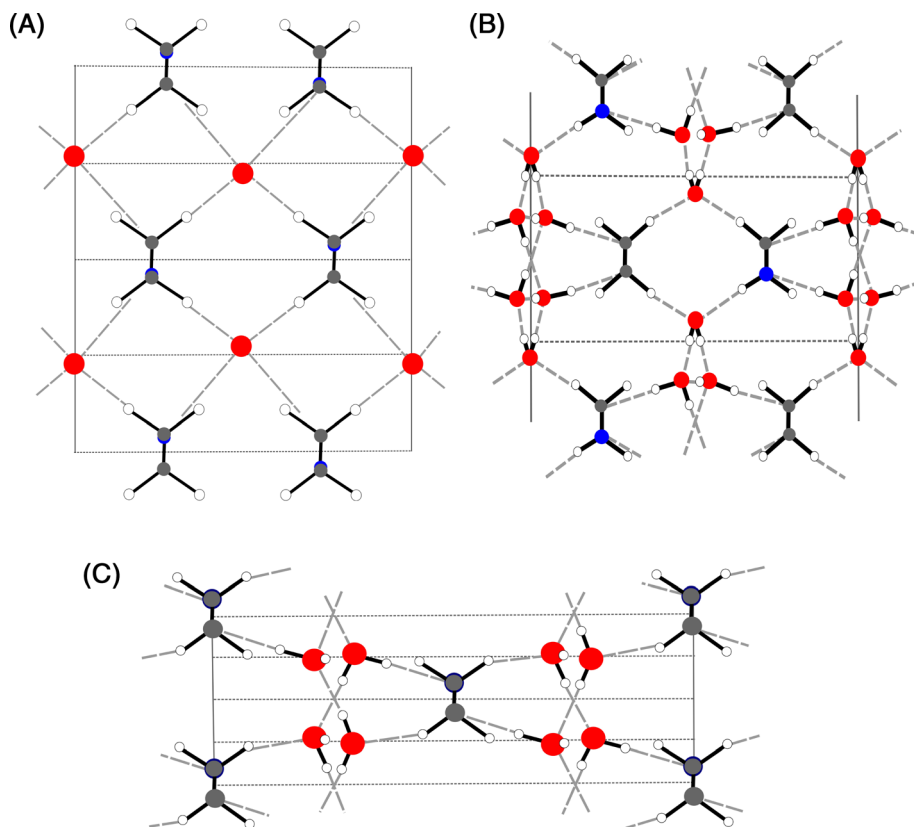
3.2.2 | Sesquihydrate

The sesquihydrate (see Figure 6B) has a PEI monomer:water molar ratio of 2:3. The PEI chains again adopt a planar zigzag conformation (as in the hemihydrate) and are parallel to the *bc* plane. Eight monomer units of PEI are accompanied by twelve water molecules, which form a more complex network in the crystal. The monoclinic unit cell for this structure is $a = 1.155$ nm, $b = 0.993$ nm, $c = 0.736$ nm, and $\beta = 104.5^\circ$, with a *C2/c* space group. In the water network, each water molecule forms two hydrogen bonds either to other water molecules or NH groups in the PEI polymer. Here, the water structures are staggered pentagonal rings aligned anisotropically as ribbons. The pentagonal configurations of water are similar found in clathrate and semiclathrate gas hydrates in 3D structures, but in the sesquihydrate of PEI, the oxygen atoms are approximately coplanar (see Figure 7).

3.2.3 | Dihydrate

The dihydrate (see Figure 6C) has a PEI monomer:water molar ratio of 1:2. Again, the PEI chains in this structure adopt a planar zigzag conformation arranged in parallel to the *bc* plane, and the monoclinic unit cell has dimensions $a = 1.326$ nm, $b = 0.461$ nm, $c = 0.736$ nm, and $\beta = 101.0^\circ$, and a *C2/c* space group. As with the sesquihydrate, each water molecule forms at least two hydrogen bonds with other water molecules and/or PEI groups (see Figure 7), and the net result is a water network that resembles thin two-dimensional (2D) sheets similar akin to hexagonal monolayers of ice I_h.

FIGURE 6 Crystal structures of the (A) the polyethyleneimine (PEI) hemihydrate; (B) PEI sesquihydrate; and (C) PEI dihydrate. Red spheres: oxygen atoms, blue spheres: nitrogen atoms, white spheres: hydrogen atoms, grey spheres: carbon atoms, black-lines: covalent bonds, dashed-lines: hydrogen bonds. Structure obtained from Reference 3.



3.2.4 | Melting behaviors

Hashida et al. have reported melting behaviors of PEI hydrates and compiled a phase diagram to map melting behaviors,⁶⁶ and the melting points of each hydrate depend on the amount of water present (see Figure 8). Dried PEI polymer (anhydrate) will melt at approximately 60°C, but when a small amount of water was introduced, the anhydrate can transition into a mixture of the hemihydrate and sesquihydrate at approximately 40°C. A pure hemihydrate will transition into the sesquihydrate at 60°C, which then melts at 80°C. Starting at a system with substantially more water, the dihydrate is usually dominant, but with water content held at approximately 1.0, the dihydrate can transition into a sesquihydrate at about 65°C, while the dihydrate melts at temperatures between 90 and 110°C depending on available water content.

All tabulatable properties for PCHs are summarized in Table 1.

4 | COMPUTATIONAL PATHS FOR INVESTIGATIONS OF PCHS

Modern computational algorithms have recently been developed that would be especially helpful to study PCHs. Quantum mechanics calculations suitable for intermolecular energy decomposition analyses (EDA) such as local energy decomposition (LED)^{67,68} or symmetry adapted perturbation theory (SAPT)⁶⁹ methods would identify and quantify electrostatic and other non-bonding interactions. There are

also novel developments in intramolecular energy decompositions⁷⁰ that would be useful to understand how chemical design would lead to new and presently undiscovered PCHs.

Efficient computational methods for high-throughput screening have already been developed for polymers^{71–73} and hydrates^{74–76} but to our knowledge they have not yet been used for polymer hydrates or PCHs. This screening has helped develop different design principles based on the desired application of the screened material. For example, polymers designed specifically for interaction with the cyanobacterial toxin microcystin-LR is discussed in detail by Chianella et al.⁷⁷ In the article, the authors discuss the design process, which included screening 20 commonly used monomers to test interactions with a molecular model of the toxin, and were scored according to binding. Similar processes may be used for the screening of PCHs, including testing common polymers for possible interactions with water complexes.

Further methods for exploring the dynamics of configurations that dictate nucleation events include WESTPA,⁷⁸ a computational approach to efficiently sample large simulation data sets for rare events. Nucleation is also an active field of study,⁷⁹ and it plays a fundamental role of the formation of traditional clathrate hydrates.^{80–82} Therefore, computational efforts that to date have focused on exploring nucleation⁸³ could be extended into PCHs to bring useful insights into how and why nanoconfined water structures are formed. For example, microsecond simulations of the formation of PCHs, similar to that done by Walsh et al. for methane hydrates⁸⁴ would likely be useful to elucidate design principles for environmental conditions that enable PCH crystal growth. The computational effort needed to

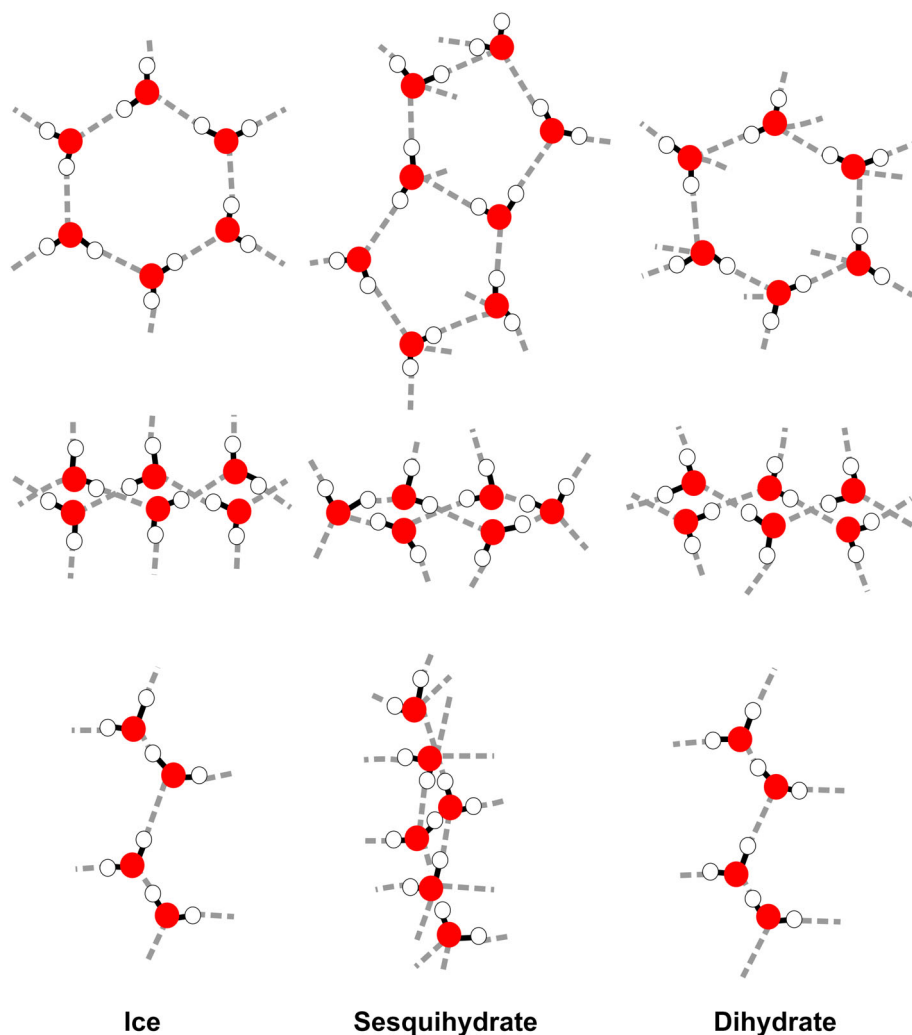


FIGURE 7 Three different perspectives (top, middle, and bottom rows) of water networks for ice Ih, the PEI sesquihydrate, and the PEI dihydrate. Red spheres: oxygen atoms, white spheres: hydrogen atoms, Black-lines: covalent bonds, dotted-lines: hydrogen bonds. Structures from Ref. 2.

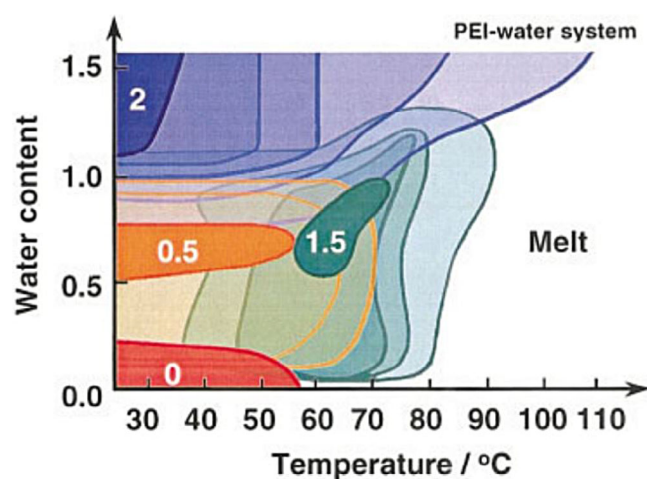


FIGURE 8 A phase diagram of polyethyleneimine (PEI) hydrates as a function of water content and temperature, where the water content is indicated by the relative intensity of the infrared water band reduced by an internal standard band.⁶⁶ Reprinted with permission from Reference 66.

elucidate PCH crystallization (which involves similar hydrogen bonding interactions with the added complexity of conformational disorder of the polymer) will likely require advanced protocols and computational resources as those used to study methane hydrates.

5 | FUTURE OUTLOOK

We have already mentioned how atomic scale structural analyses reveal that several PCH structures have water molecules oriented in anisotropic water structures (e.g., one-dimensional water chains in the POCH hydrate and 2D sheets of water in the PEI dihydrate), and one might envision that such chains and sheets may enable useful properties such as high proton transport rates. Indeed, the POCH hydrate was found to allow trapping and shuttling of charge under applied gate bias by proton migration.⁵ However, for such hydrates to function as a practical proton exchange membrane, the water chains would likely require more macroscopic alignment than are naturally grown during crystallite formation.

TABLE 1 Known physical properties for PCHs.

	POCB	Hemihydrate	Sesquihydrate	Dihydrate
Density (g/mL)	1.17 ^a	1.14 ^b	1.16 ^c	1.18 ^c
Melting temperature (K)	311 ^{d,e}	333 ^{f,g}	353 ^{f,g}	383 ^{f,g}
Weight % of Water	23.6 ^d	17.3	38.6 ^c	45.5 ^c
Monomer: water molar ratio	1:1 ^a	1:0.5 ^b	1:1.5 ^c	1:2 ^c
Space group	C2/m ^a	C2/c ^b	C2/c ^c	C2/c ^c
Infrared adsorption	a	b	c	c
Proton conduction	—	h	h	h
Bulk crystallization kinetics	i	—	—	—

^aReference 41.^bReference 2.^cReference 7.^dReference 3.^eThe molecular weight of PO CB for this measurement was 650 g/mol.^fReference 51^gLinear PEI had a weight-average molecular weight of 500,000 g/mol.^hReference 4.ⁱReference 8.

A second opportunity with PCH formation is based on the observed liquid-to-solid transition. For instance, PO CB of relatively low molecular weight is miscible with water, and simply cooling it changes it into a waxy solid. Similarly, there have been numerous studies on the gelation of PEI-water mixtures induced by simply cooling the initially-liquid mixture to below 80°C. As expected from a phase change, these changes are fully reversible. Moreover, PO CB can form hydrates by absorbing water directly from humid air.⁷ This offers the potential for smart materials to be used, for example, as humidity sensors, or materials that stiffen in response to humidity but soften upon drying. Furthermore, like most polymer crystallization, PEI or PO CB hydrates crystallize via lamellar growth processes, resulting in spherulitic or dendritic morphologies. Such structures have been used for templating the deposition of inorganic materials, for example, silica.^{57,85–90}

A final aspect peculiar to PO CB (but not PEI) is that it is an intrinsically hydrophobic polymer. Upon melting the hydrate, demixing occurs into a PO CB-rich and water-rich state. It is possible that this behavior may be exploited for thermal desalination, that is, by binding water at low temperature (while rejecting salt), and then recovering the water by melting the hydrate to induce demixing of water and PO CB. Similar desalination approaches have been considered using gas hydrates^{12,91} or other small molecules,^{92,93} but PO CB has the advantage of forming hydrates at atmospheric pressure and room temperature and then further releasing the water with little or no PO CB upon modest heating. If desalination approaches based on PO CB hydrates are successful, this would constitute a large scale and potentially high impact application for PCHs. While PCHs are not the only hydrate material that may be exploited for thermal desalination, we believe that they should be considered for further investigation due to their desirable properties found in Table 1.

As a last example of a large-scale potential application, we postulate that PCHs may be used to stabilize gas hydrates. Large amounts of methane trapped in clathrate hydrates has sparked many studies, and some researchers suggest studying the possible impact of these clathrates on global climate change. For instance, in 2017 Ruppel et al.⁹⁴ suggested that if 0.1% of the estimated methane was released due to the clathrates melting, it would raise the amount of methane in the atmosphere by up to 60%, a catastrophic amount according to MacDonald,⁹⁵ Bohannon,⁹⁶ and Whiteman.⁹⁷ To prevent this, some have suggested reinforcing methane sediments by injecting them with chemical promoters to prevent the hydrates from melting as temperatures increase.^{98,99} We postulate that due to the similarities between clathrates and PCHs, PCHs may have a similar damping effect on the melting temperature of these large clusters of clathrates while also being benign since they cannot evaporate, they are nontoxic, and they have no global warming potential.

In the context of feasibility for PCH applications, while only a small number of PCHs from PO CB and PEI have been known for decades, it is intriguing that PCHs may have already found use in a variety of applications already. Medium weight PO CB, once licensed under the name Cerenol, has already been used for automotive coatings, personal care products, thermoplastic elastomers, as a functional heat transfer fluid, and as an impact-resistant engineering plastic.¹⁰⁰ Given the known hygroscopic behavior of PO CB, it is possible that one or more of the useful applications already known for PO CB are due to unique properties of PCHs that might form under hydrating conditions.

In sum, PCHs are fascinating materials and present a promising avenue for future research in materials science, chemistry, and chemical engineering. Modern high-throughput screening and computational modeling may help advance how more of these materials might be realized for different applications to benefit

society, for example, in proton transport, thermally-driven water desalination, and methane hydrate stabilization make them an exciting field of study. Additionally, while clathrates have been the focus of substantial research in recent decades, their expense and technical limitations have limited their actual applications to date, and PCHs may provide an alternative route for similar applications with the added benefit of hydrates capable of forming under far less extreme conditions.

AUTHOR CONTRIBUTIONS

Dominick Filonowich: Conceptualization (shared); writing—original draft (lead); writing—review and editing (shared). **Sachin Velankar:** Writing—review and editing (shared). **John A. Keith:** Conceptualization (shared); writing—review and editing (shared).

ACKNOWLEDGEMENTS

JAK acknowledges support from the NSF (CBET-1653392) and SV acknowledges support from the NSF (CBET-1933037) and the Mascaro Center for Sustainable Innovation at the University of Pittsburgh.

DATA AVAILABILITY STATEMENT

Data sharing not applicable to this article as no datasets were generated or analyzed during the current study. This is a perspective article that contains no new data.

ORCID

John A. Keith  <https://orcid.org/0000-0002-6583-6322>

REFERENCES

1. Tadokoro H, Takahashi Y, Chatani Y, Kakida H. Structural studies of polyethers, $[(CH_2)mO]_n$. V. Polyoxacyclobutane. *Die Makromol Chem.* 1967;109:96-111.
2. Chatani Y, Tadokoro H, Saegusa T, Ikeda H. Structural studies of poly(ethylenimine). 1. Structures of two hydrates of poly(ethylenimine): sesquihydrate and dihydrate. *Macromolecules.* 1981;14:315-321.
3. Chatani Y, Kobatake T, Tadokoro H. Structural studies of poly(ethylenimine). 3. Structural characterization of anhydrous and hydrous states and crystal structure of the hemihydrate. *Macromolecules.* 1983;16:199-204.
4. Watanabe M, Ikezawa R, Sanui K, Ogata N. Protonic conduction in poly(ethylenimine) hydrates. *Macromolecules.* 1987;20:968-973.
5. Chido MT, Koronaos P, Saravanan K, et al. Oligomer hydrate crystallization improves carbon nanotube memory. *Chem Mater.* 2018;30:3813-3818.
6. Kobayashi M, Sato H. Structure analysis for hydrate models of Ethyleneimine oligomer by quantum chemical calculation. *Pharmacol Pharm.* 2010;01:60.
7. Banerjee J, Koronaos P, Morganstein B, et al. Liquids that freeze when mixed: cocrystallization and liquid-liquid equilibrium in polyoxacyclobutane-water mixtures. *Macromolecules.* 2018;51:3176-3183.
8. Barker EF, Banerjee S, Meyer TY, Velankar S. Liquids that freeze when mixed: homogeneous cocrystallization kinetics of polyoxacyclobutane-water hydrate. *ACS Appl Polym Mater.* 2022;4:703-713.
9. Banerjee S, Gresh-Sill M, Barker EF, Meyer TY, Velankar SS. Polymer co-crystallization from LLE: crystallization kinetics of POCB hydrate from two-phase mixtures of POCB and water. *Polymer.* 2023;282:126087.
10. Boswell R, Collett TS. Current perspectives on gas hydrate resources. *Energy Environ Sci.* 2011;4:1206-1215.
11. Bi Y, Guo T, Zhu T, Zhang L, Chen L. Influences of additives on the gas hydrate cool storage process in a new gas hydrate cool storage system. *Energy Conver Manage.* 2006;47:2974-2982.
12. Khan MN, Peters CJ, Koh CA. Desalination using gas hydrates: the role of crystal nucleation, growth and separation. *Desalination.* 2019;468:114049.
13. Kang KC, Linga P, Park K-N, Choi S-J, Lee JD. Seawater desalination by gas hydrate process and removal characteristics of dissolved ions (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , B^{3+} , Cl^- , SO_4^{2-}). *Desalination.* 2014;353:84-90.
14. Ogienko AG, Myz SA, Nefedov AA, et al. Clathrate hydrates of organic solvents as auxiliary intermediates in pharmaceutical research and development: improving dissolution behaviour of a new anti-tuberculosis drug, Perchlozon. *Pharmaceutics.* 2022;14:495.
15. English NJ, MacElroy JMD. Perspectives on molecular simulation of clathrate hydrates: progress, prospects and challenges. *Chem Eng Sci.* 2015;121:133-156.
16. Ratcliffe CI. The development of clathrate hydrate science. *Energy Fuel.* 2022;36:10412-10429.
17. Khurana M, Yin Z, Linga P. A review of clathrate hydrate nucleation. *ACS Sustainab Chem Eng.* 2017;5:11176-11203.
18. Buffett BA. Clathrate hydrates. *Annu Rev Earth Planet Sci.* 2000;28:477-507.
19. Das S, Tadepalli KM, Roy S, Kumar R. A review of clathrate hydrate nucleation, growth and decomposition studied using molecular dynamics simulation. *J Mol Liq.* 2022;348:118025.
20. Chami N, Bendjenni S, Clain P, et al. Thermodynamic characterization of mixed gas hydrates in the presence of cyclopentane as guest molecule for an application in secondary refrigeration. *Chem Eng Sci.* 2021;244:116790.
21. Conrad H, Lehmkuhler F, Sternemann C, et al. Tetrahydrofuran clathrate hydrate formation. *Phys Rev Lett.* 2009;103:218301.
22. Nakayama H, Saitoh T, Uchida H. The formation of clathrate-like hydrates of tetrabutylammonium halogenated carboxylates. *J Incl Phenom Macrocycl Chem.* 1990;8:177-186.
23. Rodionova TV, Komarov VY, Villevald GV, Karpova TD, Kuratieva NV, Manakov AY. Calorimetric and structural studies of tetrabutylammonium bromide ionic clathrate hydrates. *J Phys Chem B.* 2013;117:10677-10685.
24. Chatti I, Delahaye A, Fournaison L, Petitot J-P. Benefits and drawbacks of clathrate hydrates: a review of their areas of interest. *Energy Conver Manage.* 2005;46:1333-1343.
25. Hester KC, Brewer PG. Clathrate hydrates in nature. *Ann Rev Mar Sci.* 2009;1:303-327.
26. De Rosa C, Rizzo P, de Ballesteros O, Petraccone V, Guerra G. Crystal structure of the clathrate form of syndiotactic polystyrene containing 1,2-dichloroethane. *Polymer.* 1999;40:2103-2110.
27. Chatani Y, Shimane Y, Inagaki T, Ijitsu T, Yukinari T, Shikuma H. Structural study on syndiotactic polystyrene: 2. Crystal structure of molecular compound with toluene. *Polymer.* 1993;34:1620-1624.
28. Tadokoro H, Yoshihara T, Chatani Y, Murahashi S. A preliminary report of structural studies on polyethylene oxide-urea complex. *J Polym Sci Pt B Polym Lett.* 1964;2:363-368.
29. Tadokoro H, Chatani Y, Yoshihara T, Tahara S, Murahashi S. Structural studies on polyethers, $[-(CH_2)m-O-]_n$. II. Molecular structure of polyethylene oxide. *Die Makromol Chem.* 1964;73:109-127.
30. Ye H-M, Peng M, Xu J, et al. Conformation transition and molecular mobility of isolated poly(ethylene oxide) chains confined in urea nanochannels. *Polymer.* 2007;48:7364-7373.

31. Guerra G, Daniel C, Rizzo P, Tarallo O. Advanced materials based on polymer cocrystalline forms. *J Polym Sci B*. 2012;50:305-322.
32. Ahmed EM. Hydrogel: preparation, characterization, and applications: a review. *J Adv Res*. 2015;6:105-121.
33. Bahram M, Mohseni N, Moghtader M, Bahram M, Mohseni N, Moghtader M. *An Introduction to Hydrogels and Some Recent Applications*. IntechOpen; 2016.
34. Qiu Y, Park K. Environment-sensitive hydrogels for drug delivery. *Adv Drug Deliv Rev*. 2001;53:321-339.
35. Richter A, Paschew G, Klatt S, Lienig J, Arndt K-F, Adler H-JP. Review on hydrogel-based pH sensors and microsensors. *Sensors*. 2008;8:561-581.
36. Foroutan M, Fatemi SM, Esmaeilian F. A review of the structure and dynamics of nanoconfined water and ionic liquids via molecular dynamics simulation. *Eur Phys J E*. 2017;40:19.
37. Leoni F, Calero C, Franzese G. Nanoconfined fluids: uniqueness of water compared to other liquids. *ACS Nano*. 2021;15:19864-19876.
38. Bunn CW, Holmes DR. Chain configurations in crystals of simple linear polymers. *Discuss Faraday Soc*. 1958;25:95-103.
39. Tadokoro H. Structure of crystalline polyethers. *J Polym Sci Macromol Rev*. 1967;1:119-172.
40. Takahashi Y, Osaki Y, Tadokoro H. Planar zigzag modification of polyoxacyclobutane (modification IV) and its disordered structure1. *J Polym Sci Polym Phys Ed*. 1981;19:1153-1155.
41. Kakida H, Tadokoro H. Structural studies of polyethers $[-(\text{CH}_2)_m\text{O}-]_n$. VIII. 1970;3:10.
42. Yosmna S, Sakiyama M, Seki S. Thermodynamic studies of solid polyethers. I. Poly(Oxacyclobutane), $[-(\text{CH}_2)_3\text{O}]_n$ and its hydrate. *Polym J*. 1970;1:9.
43. Zhuk DS, Gembitskii PA, Kargin VA. Advances in the chemistry of polyethyleneimine (polyaziridine). *Russ Chem Rev*. 1965;34: 515-527.
44. Zhang W, Chen D, Wang X, Xie X. Insight into the synthesis of branched polyethylenimines from 2-haloethylamine via a one-pot two-stage process. *Polymer*. 2022;255:125113.
45. Stewart IC, Lee CC, Bergman RG, Toste FD. Living ring-opening polymerization of N-sulfonylaziridines: synthesis of high molecular weight linear polyamines. *J Am Chem Soc*. 2005;127:17616-17617.
46. Tauhardt L, Kempe K, Knop K, et al. Linear Polyethyleneimine: optimized synthesis and characterization - on the way to "Pharmagrade" batches. *Macromol Chem Phys*. 2011;212:1918-1924.
47. Tanaka R, Ueoka I, Takaki Y, Kataoka K, Saito S. High molecular weight linear polyethylenimine and poly(N-methylethylenimine). *Macromolecules*. 1983;16:849-853.
48. Brissault B, Kichler A, Guis C, Leborgne C, Danos O, Cheradame H. Synthesis of linear polyethylenimine derivatives for DNA transfection. *Bioconjug Chem*. 2003;14:581-587.
49. Gembitskii PA, Chmarin AI, Kleshcheva NA, Zhuk DS. The polymerization of ethylenimine to give linear polyethylenimine. *Polym Sci USSR*. 1978;20:1695-1702.
50. Chatani Y, Kobatake T, Tadokoro H, Tanaka R. Structural studies of poly(ethylenimine). 2. Double-stranded helical chains in the anhydrate. *Macromolecules*. 1982;15:170-176.
51. Hashida T, Tashiro K, Inaki Y. Crystallization of poly(ethylene imine) amorphous sample in water vapor atmosphere. *Polymer*. 2003;44: 1721-1724.
52. Hashida T, Tashiro K, Ito K, Takata M, Sasaki S, Masunaga H. Correlation of structure changes in the water-induced phase transitions of poly(ethylenimine) viewed from molecular, crystal, and higher-order levels As studied by simultaneous WAXD/SAXS/Raman measurements. *Macromolecules*. 2010;43:402-408.
53. Hashida T, Tashiro K. Structural study on water-induced phase transitions of poly(ethylene imine) as viewed from the simultaneous measurements of wide-angle X-ray diffractions and DSC Thermograms. *Macromol Symp*. 2006;242:262-267.
54. Hashida T, Tashiro K. Structural investigation on water-induced phase transitions of poly(ethylene imine), part IV: changes of intra- and intermolecular hydrogen bonds in the hydration processes as revealed by time-resolved Raman spectral measurements. *Polymer*. 2007;48:7614-7622.
55. Kakuda H, Okada T, Hasegawa T. Temperature-induced molecular structural changes of linear poly(ethylene imine) in water studied by mid-infrared and near-infrared spectroscopies. *J Phys Chem B*. 2009; 113:13910-13916.
56. Lott GA, King MD, Hill MW, Scatena LF. Effects of relative humidity on the surface and bulk structures of linear polyethylenimine thin films. *J Phys Chem C*. 2014;118:17686-17698.
57. Yuan J-J, Jin R-H. Fibrous crystalline hydrogels formed from polymers possessing a linear poly(ethylenimine) backbone. *Langmuir*. 2005;21:3136-3145.
58. Buijs W. Molecular modeling study to the relation between structure of LPEI, including water-induced phase transitions and CO₂ capturing reactions. *Ind Eng Chem Res*. 2021;60:11309-11316.
59. Soradach S, Williams AC, Khutoryanskiy VV. Physically cross-linked cryogels of linear polyethylenimine: influence of cooling temperature and solvent composition. *Macromolecules*. 2022;55:9537-9546.
60. Douyère G, Leclercq L, Nardello-Rataj V. From polyethylenimine hydrogels to Pickering-like smart "on/off" emulgels switched by pH and temperature. *J Colloid Interface Sci*. 2022;628:807-819.
61. Lambermont-Thijs HML, van der Woerd FS, Baumgaertel A, et al. Linear poly(ethylene imine)s by acidic hydrolysis of poly(2-oxazoline)s: kinetic screening, thermal properties, and temperature-induced solubility transitions. *Macromolecules*. 2010;43:927-933.
62. Chatani Y, Irie T. Crystal structure of poly(ethylenimine)-hydrogen chloride complex. *Polymer*. 1988;29:2126-2129.
63. Chatani Y, Yakura Y, Ishioka T. Crystal structure of poly(ethylenimine)-acetic acid complex. *Polymer*. 1990;31:208-211.
64. Herlem G, Lakard B. Ab initio study of the electronic and structural properties of the crystalline polyethylenimine polymer. *J Chem Phys*. 2004;120:9376-9382.
65. Herlem G, Gharbi T, Sedrine NB. Analyzing ab initio infrared spectra and electronic properties of polyethylenimine water complexes in the solid state. *J Mol Struct (THEOCHEM)*. 2010;945:27-32.
66. Hashida T, Tashiro K, Inaki Y. Structural investigation of water-induced phase transitions of poly(ethylene imine). III. The thermal behavior of hydrates and the construction of a phase diagram. *J Polym Sci B*. 2003;41:2937-2948.
67. Altun A, Neese F, Bistoni G. Local energy decomposition analysis of hydrogen-bonded dimers within a domain-based pair natural orbital coupled cluster study. *Beilstein J Org Chem*. 2018;14:919-929.
68. Altun A, Saitow M, Neese F, Bistoni G. Local energy decomposition of open-Shell molecular systems in the domain-based local pair natural orbital coupled cluster framework. *J Chem Theory Comput*. 2019;15:1616-1632.
69. Stasyuk OA, Sedlak R, Guerra CF, Hobza P. Comparison of the DFT-SAPT and canonical EDA schemes for the energy decomposition of various types of noncovalent interactions. *J Chem Theory Comput*. 2018;14:3440-3450.
70. Zulueta B, Tulyani SV, Westmoreland PR, et al. A bond-energy/-bond-order and populations relationship. *J Chem Theory Comput*. 2022;18:4774-4794.
71. Lu X, Wu Y, Wu X, Cao Z, Wei X, Cai W. High-throughput computational screening of porous polymer networks for natural gas sweetening based on a neural network. *AIChE J*. 2022;68:e17433.
72. Pilia G, Weis E, Walker EM, Gilbertson RD, Muenchausen RE, Simakov EI. Computational screening of organic polymer dielectrics for novel accelerator technologies. *Sci Rep*. 2018;8:9258.
73. Kanal IY, Owens SG, Bechtel JS, Hutchison GR. Efficient computational screening of organic polymer photovoltaics. *J Phys Chem Lett*. 2013;4:1613-1623.

74. Oluwunmi PA, Finney AR, Rodger PM. Molecular dynamics screening for new kinetic inhibitors of methane hydrate. *Can J Chem*. 2015; 93:1043-1049.
75. Frankcombe J, Kroes G-J. A new method for screening potential sII and sH hydrogen clathrate hydrate promoters with model potentials. *Phys Chem Chem Phys*. 2011;13:13410-13420.
76. Kiyabu S, Lowe JS, Ahmed A, Siegel DJ. Computational screening of hydration reactions for thermal energy storage: new materials and design rules. *Chem Mater*. 2018;30:2006-2017.
77. Chianella I, Lotierzo M, Piletsky SA, et al. Rational design of a polymer specific for microcystin-LR using a computational approach. *Anal Chem*. 2002;74:1288-1293.
78. Russo JD, Zhang S, JMG L, et al. WESTPA 2.0: high-performance upgrades for weighted ensemble simulations and analysis of longer-timescale applications. *J Chem Theory Comput*. 2022;18: 638-649.
79. Peters B. Crystal nucleation: rare made common and captured by Raman. *Proc Natl Acad Sci*. 2022;119:e2204971119.
80. Agarwal V, Peters B. *Advances in Chemical Physics*. Vol 155. John Wiley & Sons, Ltd; 2014:97-160.
81. Factorovich MH, Naullage PM, Molinero V. Can clathrates heterogeneously nucleate ice? *J Chem Phys*. 2019;151:114707.
82. DeFever RS, Sarupria S. Nucleation mechanism of clathrate hydrates of water-soluble guest molecules. *J Chem Phys* 2017;147(20): 204503. doi:10.1063/1.4996132
83. Peters B. Common features of extraordinary rate theories. *J Phys Chem B*. 2015;119:6349-6356.
84. Walsh MR, Koh CA, Sloan ED, Sum AK, Wu DT. Microsecond simulations of spontaneous methane hydrate nucleation and growth. *Science*. 2009;326:1095-1098.
85. Jin R-H, Yuan J-J. Synthesis of poly(ethyleneimine)s-silica hybrid particles with complex shapes and hierarchical structures. *Chem Commun*. 2005;11:1399-1401.
86. Matsukizono H, Jin R-H. Controlled formation of polyamine crystalline layers on glass surfaces and successive fabrication of hierarchically structured silica thin films. *Langmuir*. 2011;27: 6338-6348.
87. Matsukizono H, Zhu P-X, Fukazawa N, Jin R-H. Turbine-like structured silica transcribed simply by pre-structured crystallites of linear poly(ethyleneimine) bounded with metal ions. *CrstEngComm*. 2009; 11:2695-2700.
88. Yao D-D, Jin R-H. Synthesis of comb-like poly(ethyleneimine)s and their application in biomimetic silicification. *Polym Chem*. 2015;6: 2255-2263.
89. Noda D, Arai Y, Souma D, Nagashima H, Jin R-H. Poly(N-cyanoethyl-ethyleneimine): a new nanoscale template for biomimetic silicification. *Chem Commun*. 2014;50:10793-10796.
90. Soma D, Jin R-H. Free-standing disk mold crystalline polyethyleneimine gels: physical properties and chemical function in mineralization. *Colloid Polym Sci*. 2017;295:1585-1594.
91. Montazeri SM, Kolliopoulos G. Hydrate based desalination for sustainable water treatment: a review. *Desalination*. 2022;537:115855.
92. Werber JR, Osuji CO, Elimelech M. Materials for next-generation desalination and water purification membranes. *Nat Rev Mater*. 2016;1:5-15.
93. Ayyar AS-R, Aregawi DT, Petersen AR, et al. Carbon dioxide-mediated desalination. *J Am Chem Soc*. 2023;145:3499-3506.
94. Ruppel CD, Kessler JD. The interaction of climate change and methane hydrates. *Rev Geophys*. 2017;55:126-168.
95. MacDonald GJ. Role of methane clathrates in past and future climates. *Clim Change*. 1990;16:247-281.
96. Bohannon J. Weighing the climate risks of an untapped fossil fuel. *Science*. 2008;319:1753.
97. Whiteman G, Hope C, Wadhams P. Vast costs of Arctic change. *Nature*. 2013;499:401-403.
98. Seo Y-T, Lee H, Yoon J-H. Hydrate phase equilibria of the carbon dioxide, methane, and water system. *J Chem Eng Data*. 2001;46: 381-384.
99. Holder GD, Cugini AV, Warzinski RP. Modeling clathrate hydrate formation during carbon dioxide injection into the ocean. *Environ Sci Technol*. 1995;29:276-278.
100. Sharing insights elevates their impact. <https://www.spglobal.com/commodityinsights/en/ci/products/chemical-technology-pep-reviews-cerenol-dupont-polyether-glycol-2013.html>

How to cite this article: Filonowich D, Velankar S, Keith JA. The fascinating world of polymer crystal hydrates: An overview. *AIChE J*. 2024;e18556. doi:10.1002/aic.18556