# A Polymer Guest Transforms Clathrate Cages into Channels: The Single-Crystal X-Ray Structure of Tetra-*n*-butylammonium Polyacrylate Hydrate, $n\mathrm{Bu_4NPA\cdot 40\,H_2O}$**

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Furthering the understanding of macromolecular hydration continues to generate a great deal of experimental as well as theoretical interest from the point of view of the organization of water in close contact with biopolymers as well as with synthetic organic polymers.[1–3] Although the structural chemistry of biopolymer hydration is well developed,[4] mainly because of advances in protein crystallography and computer modeling,[5] it has been difficult to find hydrated polymers with sufficient long-range order to give diffraction structures with resolution characteristic of small-molecule structural determinations. Here we report a first structural study on the incorporation of a polymer, in this instance polyacrylic acid (PA), into a crystalline clathrate with tetra-*n*-butylammonium hydroxide as co-guest.

Following the extensive structural work of Jeffrey and coworkers[6] on alkylammonium salt hydrates with various small anionic counterions, Nakayama[7] reported the first hydrates with polymeric anions. He determined the phase diagrams of $n\mathrm{Bu_4NPA-H_2O}$[8] and $i\mathrm{Am_4NPA-H_2O}$, and gave the approximate composition of the hydrates as $n\mathrm{Bu_4NPA\cdot 30\,H_2O}$ and $i\mathrm{Am_4NPA\cdot 42\,H_2O}$. Remarkably, Bogatyrov et. al.[9] found that tetra-*n*-alkylammonium polyhydrates also could be formed inside the grains of cross-linked polyacrylic acid resins. So far, structural information on the solid hydrates of simple organic polymers is not available. A model has been proposed[5, 6] in which the polyacrylate chains are arranged in dodecahedral ($\mathrm{D}$-$5^{12}$)[10] cavities. However, this model must be incorrect as the proposed structure is a tetragonal form of structure I hydrate, and it is impossible to find a chain of connected D cavities as required by the model. Besides, the presence of a polymer in the small cavities should stabilize the polymer hydrate with respect to the $\mathrm{Bu_4NOH}$ hydrate structure where these cavities are known to be empty,[5] but instead the phase diagram of $n\mathrm{Bu_4NPA}$ hydrate shows that it is less stable.

We have investigated the structure of $n\mathrm{Bu_4NPA}$ hydrate with single-crystal X-ray crystallographic methods. The $n\mathrm{Bu_4N}$ ion in $n\mathrm{Bu_4NPA\cdot 40\,H_2O}$ (**1**) is located in a four-sectioned $\mathrm{T_3P}$ (for explanation of notation see ref. [10]) fused cavity[9] (Figure 1), and the polymer molecule is in the channel made up from modified T cavities.[9] Two T cavities sharing a horizontal face form the basic segment of the channel. A vertical stack is formed by stacking the basic segments so that alternate segments are at right angles to each other. The actual channel forms upon removal of two water molecules that are shared by every four T cavities, so that we may designate the channel as a $(\mathrm{T_4})_n$ arrangement. The hydrocarbon chain of the polymeric molecule is disordered over eight possible positions in the channel, and the disordering of the carboxyl groups is yet more complicated. The carbon atom of the carboxyl group is disordered over four possible positions on each hydrocarbon chain and the oxygen atoms also are able to occupy one of two sites. The carbon atoms in the hydrocarbon chain were found on the difference map in the structure refinement. The carbon and oxygen atoms of the carboxyl groups were put in calculated positions and refined isotropically.

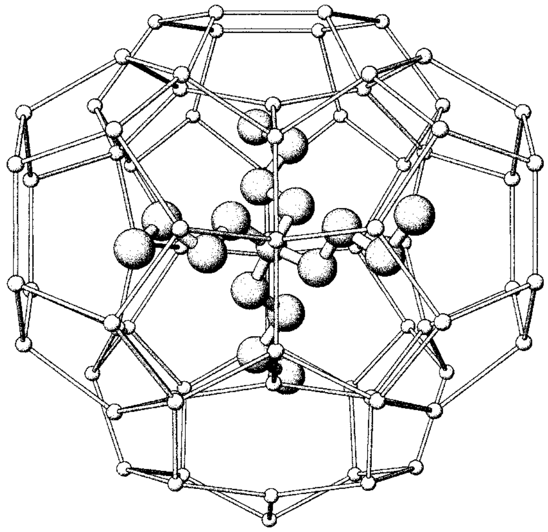

Figure 1. The tetra-*n*-butylammonium cation in the four-sectioned fused $\mathrm{T_3P}$ supercage.

The polymer and the hydrate lattices would normally not be expected to be structurally compatible in the sense that they have quite different periodicities. However, the polymer adapts to the hydrate lattice remarkably well by folding into a complex spiral with the appropriate periodicity. This is accomplished through the presence of two conformations of the carbon skeleton: the first is all *anti*, the second is *gauche-anti-anti-anti*. The polymer chain is located in the channel (Figure 2) in such a way that some of the carboxyl groups displace the water molecules in the clathrate framework. On the other hand, some of the carboxyl groups are included in the cavities in a hydrophobic way, namely, lacking hydrogen bonds with water molecules. According to this model some of the large T cavities forming the channel are filled with only carboxyl groups that interact hydrophobically with the cavity. We note that such bimodal forms of hydration have been observed in the recently reported structure of a complex clathrate hydrate incorporating choline hydroxide.[11]

Approximately 10% of the T cavities are vacant, as are all of the small D cavities. This partial filling of the large cavities by the polymer chain can account for the decrease in the hydrate melting point from 19 °C, which is the incongruent melting point of the $n\mathrm{Bu_4NOH\cdot 32\,H_2O}$, to 14.3 °C. The phenomenon of partial filling of the large T cavities is not

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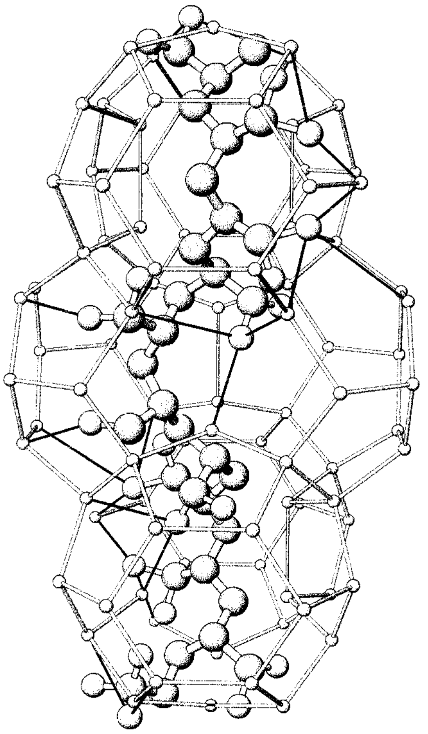

Figure 2. The polyacrylate polymer chain in the channel formed by stacks of T cages. Only one of eight possible disordered chain conformations is shown. Hydrogen-bonded interactions between the "hydrophilic" carboxylate groups and the channel are denoted as thick lines. The remaining carboxylate groups are present as hydrophobic moieties without strong directional interactions with the channel water molecules.

surprising in light of the recent work on a similar tetragonal structure[12] of bromine hydrate with partially filled cavities.

Since on average each carboxyl group displaces one water molecule in the framework (cases where two water molecules are displaced by one carboxylic group are also possible) the calculated composition of the hydrate will be $\mathrm{Bu_4NPA \cdot 40\,H_2O}$, which is quite near to Nakayama's results.[7] Since both $n\mathrm{Bu_4NOH \cdot 32\,H_2O}$ (this compound is isostructural with $n\mathrm{Bu_4NF \cdot 32\,H_2O}$[13]) and $n\mathrm{Bu_4NPA \cdot 40\,H_2O}$ hydrates have the same structure the channel can be filled by combinations of $n\mathrm{Bu_4N}$ cations and polyacrylic acid molecules. The composition of the hydrate, depending on the experimental conditions, can be described by the formula $n\mathrm{Bu_4NOH \cdot 32\,H_2O}$ if the channel is completely filled with $n\mathrm{Bu_4N}$ and $n\mathrm{Bu_4N(PA)_{1.2} \cdot 41.6\,H_2O}$ if the channel is completely filled with polymer molecules.

A feature of note in this structure is the flexible way that the cages aligned along the $c$ axis convert into a channel by the omission of two water molecules for every four adjoining T cavities. In addition, the structure displays a remarkable flexibility in that the carboxylate groups are incorporated either hydrophobically or by replacing one or more water molecules in the cage structure. Whether the polymer contributes significantly to the lattice stability is a moot point. It seems more likely that the presence of the polymer is tolerated at the cost of a small reduction in stability of the lattice. The channel also offers a model for the hydration of the hydrophobic portions of the polymer chain, although it is likely that in solution all carboxylate groups interact with water molecules by hydrogen bonding. The results presented also show that there should be no particular problems forming a hydrate in the cross-linked polymer[9] with incorporation of the anionic polymer chain in the hydrate lattice between the cross-links as long as the polymer resin is sufficiently swollen.

## *Experimental Section*

$n\mathrm{Bu_4NPA \cdot 40\,H_2O}$ (**1**) was crystallized from an aqueous solution of $n\mathrm{Bu_4NOH}$ and polyacrylic acid ($M_\mathrm{W} \approx 1000$) at +10 °C. The crystals were colorless with distinct faces and a melting point of +14.3 °C. A crystal with the morphology of a tetragonal prism was chosen for the diffraction experiment.[15]

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[10] The $x^y$ notation refers to a cage consisting of $y$ polygonal faces with $x$ sides; **1** has dodecahedral ($\mathrm{D} = 5^{12}$), tetrakaidecahedral ($\mathrm{T} = 5^{12}6^2$), and pentakaidecahedral ($\mathrm{P} = 5^{12}6^3$) cages.

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[14] $n\mathrm{Bu_4NPA_{1.2} \cdot 41.6\,H_2O}$ is the hypothetical composition of the hydrate in the case when the channel is completely filled with polymer molecules. This requires 20% of the polymer carboxylate groups to be present as the acid form.

[15] Crystal structure analysis of $n\mathrm{Bu_4NPA \cdot 40\,H_2O}$: Siemens SMART CCD diffractometer, $\mathrm{Mo_{K\alpha}}$ radiation ($\lambda = 0.71073$ Å), crystal size $0.5 \times 0.5 \times 0.5$ mm, tetragonal, space group $P4_2/m$, $a = 23.420(3)$, $c = 12.342(3)$ Å, $V = 6769.5(19)$ Å$^3$, $\rho_\mathrm{calcd} = 1.015$ mg m$^{-3}$; $\mu(\mathrm{Mo_{K\alpha}}) = 0.099$ mm$^{-1}$, $T = 123$ K, scan mode ($3.7 < 2\theta < 46.5$), reflections collected/unique 25576/4856, 989 parameters. The structure was solved with the SHELXTL programs, refined with full matrix least squares on $F^2$, GOF ($F^2$) 1.032; final $R$ indices ($I > 2\sigma(I)$): $R_1 = 0.0593$ $wR_2 = 0.1392$; $R$ indices (all data) $R_1 = 0.0840$, $wR_2 = 0.1606$. Crystallographic data (excluding structural factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-112256. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).