Long-chain polyamines from diatom algae: structure, functions and synthetic analogues

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Diatom algae (diatoms) are a diverse group of single-celled photosynthesizing microorganisms (2-2000 mm in length) that generate ~20% of global primary production. As such, they play a key role at the base of aquatic food webs and atmospheric oxygen production over the past 100-200 million years. Diatom cells are contained within a siliceous exoskeleton (frustule) - built from several parts (valves, girdle bands), which contain unprecedented detail and diversity at the nanoscale and are organized in species-specific patterns.

Study of the siliceous frustules resulted in discovery [Kröger N et al. Science 286: 1129] of long-chain polyamines (LCPAs) – spermidine derivatives with a long poly(propylamine) chain (up to 20 nitrogen atoms). Depending on diatom species, some or all of the nitrogens are methylated. Physiological functions of the LCPAs and LCPAs-containing proteins (silaffines) are not clear, hypothesis about their pre-pattern role in condensation of silicic acid contradicts with low LCPAs content in biosilica (< 0.3%).

We have elaborated step-wise approaches to synthetic LCPAs, including long oligomers and substances with other than methyl substituents. LCPAs bearing one terminal NH-group are interesting building blocks for new polymers and dies including models of biopolymers and bio-analytical tools. Interaction between LCPAs and carboxyl- or silanol-containing polymeric acids proceeds as cooperative reaction. Critical length of LCPAs chain for irreversible aggregation with poly(acrylic acid) and poly(silicic acid) is 9 and 5 units correspondingly at pH 5.5 (pH value in Silica Deposition Vesicles, SDVs of diatoms).

We found that condensation of silicic acid in the presence of synthetic polymers having side amine groups often results in stable composite nanoparticles having siliceous core and organic shell. We suppose these particles as models of Silicon Transport Vesicles which are responsible for cytoplasmic storage and transport of silicon in the form of poly(silicic acid). According to our viewpoint, LCPAs and silaffines play an important role in the capture of silicic acid from the environment and in its transport to SDVs but do not participate actively in silica deposition.

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