Nacre is a Liquid-Crystal Thermometer of the Oceans

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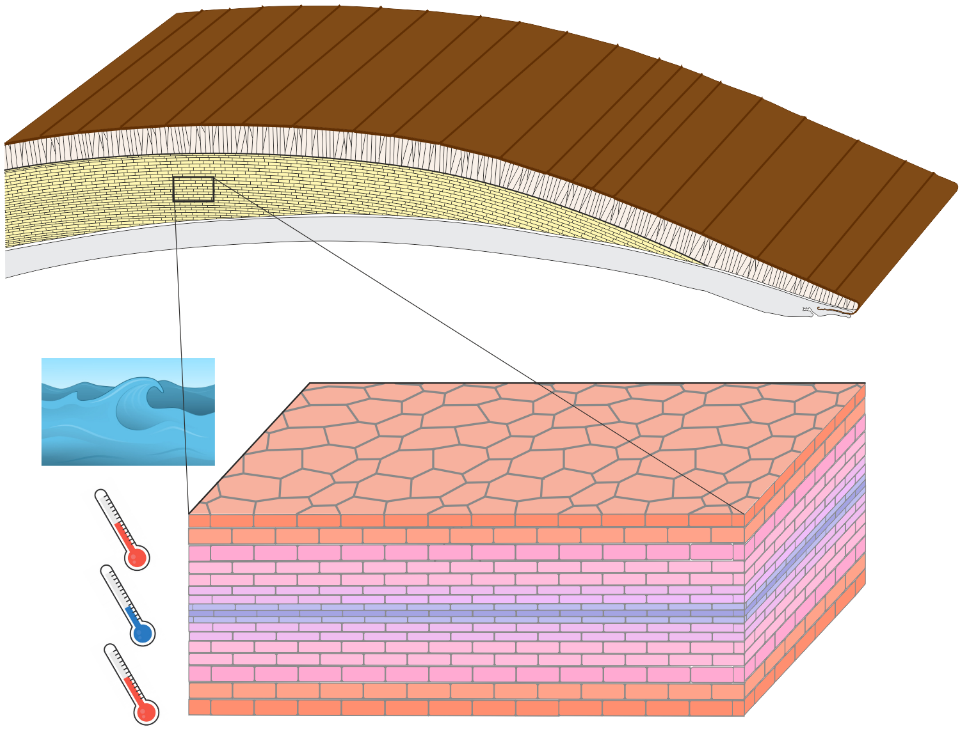
Abstract

Nacre, or mother of pearl, is a biomaterial with a layered structure. In a recent geological study, researchers found that the width of the nacre layers depends on the formation temperature, which is determined by the ocean water temperature. A linear dependence of layer width with respect to temperature is understandable within the transient liquid-crystalline nature of incipient nacre. Thus, developing nacre is a liquid-crystal thermometer recording its formation temperature. A more complete understanding of nacre formation is of interest not just for biology and geology, in terms of biomineralization and paleoclimatology, but also for materials science: for reproducing nacre or fabricating synthetic analogs, and also potentially for developing new

classes of layered materials with layer spacing tuneable by pH and temperature.



Nacre, mother of pearl, is the queen of biomaterials. Prized for thousands of years, it is a biomineral that forms the inner layer of many sea shells and the coating of pearls. It is over 95% calcium carbonate, and only 5% organic proteins and polysaccharides but the organic component increases the strength of the material by a factor of 3000.[1] A dream of modern materials science is to find a philosopher’s stone to turn calcium carbonate to nacre, something the humble mollusk has been doing for hundreds of millions of years.[2] Self-organization of nanostructures into the layered nacre-like assemblies is the key in accomplishing this goal[3] and attaining the mechanical properties many current technologies require.[4]However, there is more to self-assembly of the inorganic plates in this biomaterial. One of the means that nature uses to self-organize material, including in nacre formation, is the liquid crystal with a twist between each layer. Liquid crystals, ubiquitous as they are in modern technology including gas membranes, optical devices, and ultrastrong composites, are also found across biology, including in the initial stage of nacre formation.[5,6] The properties of liquid crystals undergo physical alterations due to temperature changes; an example is liquid crystal thermometers, which are used in refrigerators. Researchers found that the layer spacing in nacre reflects its formation temperature,[7,8] as measured in a geological survey employing a geochemical proxy for temperature: carbonate clumped isotope thermometry. In this Perspective, we discuss how increases in temperature lead to increases of the layer spacing in nacre; as a result, nacre is a liquid-crystal thermometer of the oceans.

The formation of nacre begins with the extrusion of rod-shaped crystallites of the polysaccharide chitin from cells of the mollusk into a confined, liquid-filled compartment, the extrapallial space, that exists between the cellular tissue of the mollusk and its shell. Within this thin, confined layer of liquid these chitin rods self-organize into a single layer above the already deposited earlier layers of shell material, when their concentration reaches a threshold. These layers become the interlamellar membranes between mineral (aragonite) tablets when the incipient nacre is mineralized, as summarized and depicted in Figure 1. Such self-organization is of rod-shaped units into twisted layers unlike molecular liquid crystals used in optical devices and thermometers, these organic-inorganic materials are supramolecular or colloidal ones where the units are rod-shaped nanoparticles rather than rod-shaped molecules.[9] The layer spacing between them is much greater than in molecular liquid crystals, which strongly affects the material properties in sometimes surprising ways.

Nacre is arranged into layers, but owing to the slow kinetics of phase separation, the order within each layer does not have time to form itself into an arrangement with a single direction, but is jumbled.[5] It is presumably arrested in this state by the solidification process it undergoes in order to end up as a nanocomposite material, which can serve as a permanent record of the geological epoch. In a geological survey, researchers found that the layer spacing of nacre in both modern and fossil shells records the temperature at formation, as determined by carbonate clumped isotope thermometry (Figure 2).[7,8] This work measured the (mineral) nacre tablet thickness, rather than the organic membrane spacing, but the tablet thickness is determined by the position of the interlamellar membranes that have been laid down previously, as we have described and as Figure 1b shows. The observation that the spacing tracks formation temperature is of interest not only to biology, but also to geology because it enables one to chart the paleoclimate, the evolution of temperature in the ocean over geological time. But what is its physical basis?Chitin rods form cholesteric liquid crystals (Figure 3) in laboratory experiments,[12] with layer spacing of the order of a few nm and pitch 40–100 μm. At the first moment when the self-organization of a layer of chitin crystallites is perceptible in the extrapallial space of the mollusk (Figure 1a), the spacing between layers is ~100 nm, but this spacing widens to ~500 nm within 20 μm of the growth front. This widening of the layer spacing has been hypothesized to be owing to the addition of proteins to the chitin layer, which bind to the chitin rods as the first step in a process of solidification and mineralization of the initial liquid crystal.[5] In a molecular cholesteric liquid crystal, the more important physical quantity is often its pitch the distance over which the direction in which the units point, the so-called director, rotates a complete turn, 2π radians.

It is often the case that the pitch of a molecular cholesteric liquid crystal decreases with increasing temperature. This observation is explained by anharmonic torsional molecular vibrations.[13,6] As temperature increases, the angle of torsional vibration in an anharmonic potential becomes larger; that is, each layer of rods rotates a little more relative to the layer next to it. Thus, there is a shorter distance between layers of parallel rods: the pitch of a cholesteric liquid crystal generally becomes shorter. This decrease in pitch does not occur in every case: it is possible, but less common, to have a positive pitch dependence with temperature,[17] for example in cellulose (supramolecular) liquid crystals,[18] or a divergent behavior showing the two opposite effects as a sense inversion in different temperature ranges.[19,20]

Pitch is chosen as an indicator of cholesteric behavior in molecular liquid crystals, where cholesteric layers are not a mathematical reality. In this supramolecular liquid crystal, however, the director within a layer is disordered and it is the individual layer spacing that is the more relevant quantity. Cholesteric layers are seen in mesophases formed by long-chain polymers,[21,22] as well as in mesophases formed by crystallites, as is the case here. The pitch and the layer spacing often have opposite behaviors with temperature: generally, the cholesteric pitch decreases with increasing temperature whereas the layer spacing increases with thermal expansion (Figure 4).[22]

A linear relationship between temperature and the thickness of the nacre tablet being laid down is seen in Figure 2. The increase of nacre layer spacing with increasing temperature strongly suggests that this factor is under physical rather than biological control, because if this layer spacing were under direct biological control, there is no reason why the alteration of a physical variable in the environment, such as temperature, should alter the structure. In other words, Figure 2 suggests that nacre layer spacing is one of the factors that the overall biological control of growth delegates to a self-organized physical mechanism, that of a liquid crystal.

The principle of the nacre thermometer is based on the fact that the layer spacing in a supramolecular liquid crystal varies with temperature. Consider a colloidal rod-shaped element buffeted by molecules of water and, thus, undergoing Brownian motion. We can write for it an equation of motion as an anharmonic oscillator

$$\ddot{x} + \omega_0^2 x - \frac{1}{2} A x^2 = 0 \tag{1}$$

where x is the distance of the center of mass from its equilibrium position in the liquid crystal and the cubic anharmonicity represents the fact that repulsion will be stronger than the long-range forces as the elements are squeezed closer together. This has a solution to lowest order in *A*

$$x = x_o \cos \omega_0 t - \frac{A x_0^2}{12 \omega_o^2} \cos 2\omega_0 t + \frac{A x_0^2}{4 \omega_0^2}, \tag{2}$$

from which we obtain the nonzero time average

$$\langle x \rangle = \frac{A x_0^2}{4 \omega_0^2}. \tag{3}$$

Now, the virial theorem gives

$$\frac{1}{2} I \omega_0^2 x_0^2 = kT \tag{4}$$

where *I* is the moment of inertia, so

$$\langle x \rangle = \frac{AkT}{2 I \omega_0^4}. \tag{5}$$

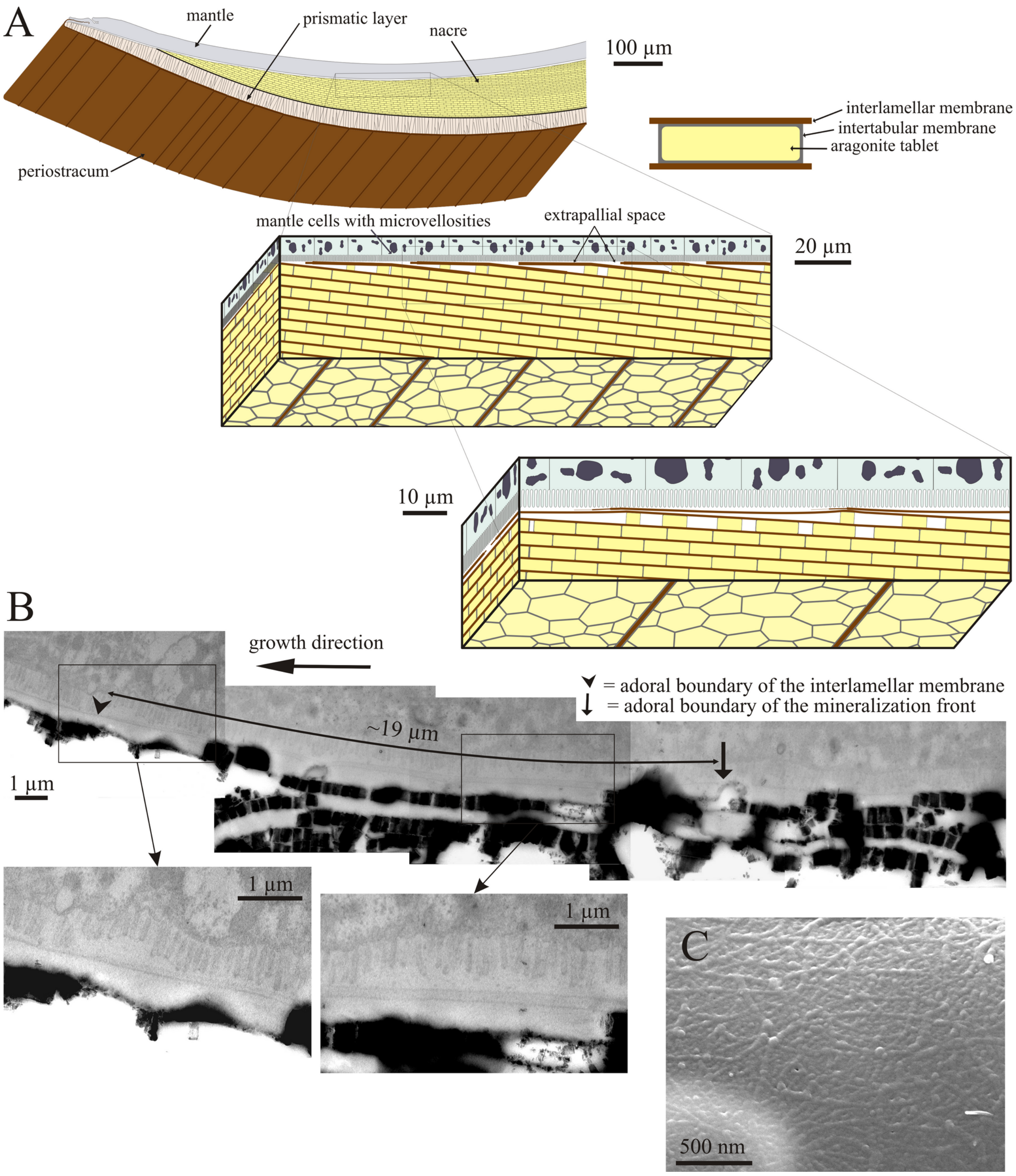
There is a linear expansion with temperature in this model if the coefficients are approximately constant. We may compare this result with the slope of Figure 2, the degree of increase in layer spacing with *T*: the coefficient of linear expansion is $\Delta L / L \times 1 / \Delta T \approx (0.75 - 0.25) / 0.5 \times 1/30 = 0.03\ \mathrm{K}^{-1}$ *i.e.*, there is threefold linear thermal expansion over a range of 30 K.

A relevant observation of such large expansion of layer spacing is of a lyotropic liquid-crystalline lamellar phase comprising an aqueous dispersion of planar solid-like sheets in which all the atoms involved in a layer are covalently bonded. The spacing of these layers can be increased 100-fold, resulting in one-dimensional structures whose periodicity can be tuned from 1.5 to 225 nanometers.[23] Another example of such extreme swelling of a layered material is the protonated oxide $H_{0.8}[Ti_{1.2}Fe_{0.8}]O_4 \cdot H_2O$, which shows a reversible hundredfold swelling induced by polar amines.[24] Both of these instances utilize pH rather than temperature changes for extreme linear expansion. In addition, liquid crystalline inorganic nanosheet colloids derived from layered materials show a linear swelling law $d = L/\phi$ for a lamellar phase.[25]

Such tuned layering can be compared to that seen in incipient nacre. We hypothesize that the extreme thermal expansion of incipient nacre over a small temperature range may be owing to the addition of proteins to the chitin nanocrystals. As we discussed above, a large change of layer spacing is perceptible from initial formation of a chitin layer to when mineralization of the structure is initiated, and proteins bond chitin rods together to form what becomes a cohesive layer, the interlamellar membranes between sheets of nacre tablets. This process can be seen in Figure 1a, where the initial spacing is ~100 nm, but widens to ~500 nm within 20 μm of the growth front. Small temperature variations may induce large changes in the equilibrium layer spacing in this process.

Looking forward, might it be possible to go beyond nacre, to make an artificial nacre in a similar way to how the mollusk makes nacre, but using high-performance materials? A crucial element that the mollusk uses to make nacre is controlled liquid crystallization. We humans use many liquid crystals in technology today, but in a globally controlled fashion. We place together elements of a liquid crystal and then alter a global variable, such as electrical potential, or temperature, to cause a liquid crystal to form throughout the space. In contrast, the mollusk takes care to control locally the space in which liquid crystallization takes place. It controls the width of the chamber filled with liquid -the extrapallial space- so that only one fresh layer of liquid crystal is laid down at a time. It grows a liquid crystal layer by layer in this locally controlled manner, and it subsequently solidifies it by growing mineral tablets within the space between the liquid-crystal layers. Supernacre would be a material composed, like nacre, of small tablets, together with a mortar between them. However, supernacre would not need to be calcium carbonate, proteins and polysaccharides. Like nacre, it would be thousands of times as strong as its component elements, but these elements would already be -unlike in the mollusk- strong materials, so that supernacre would be a true supermaterial.

Synthetic materials do not yet appear to have reproduced the temperature-controlled swelling seen in nacre. However, within the last decade a thriving field has emerged studying cellulose nanocrystals and chitin nanocrystals, or chitin whiskers, for technological applications.[26,27] Although nacre, which grows layer by layer within the exquisitely biologically controlled nanoenvironment of the extrapallial space, is a far more precisely controlled natural nanocomposite material than any that can be artificially synthesized today, it begins to be within technological reach to reproduce the extreme thermal expansion seen in incipient nacre.


A
mantle
prismatic layer
nacre
100 µm
periostracum
interlamellar membrane
intertabular membrane
aragonite tablet
mantle cells with microvellosities
extrapallial space
20 µm
10 µm
B
growth direction
= adoral boundary of the interlamellar membrane
= adoral boundary of the mineralization front
~19 µm
1 µm
1 µm
1 µm
C
500 nm

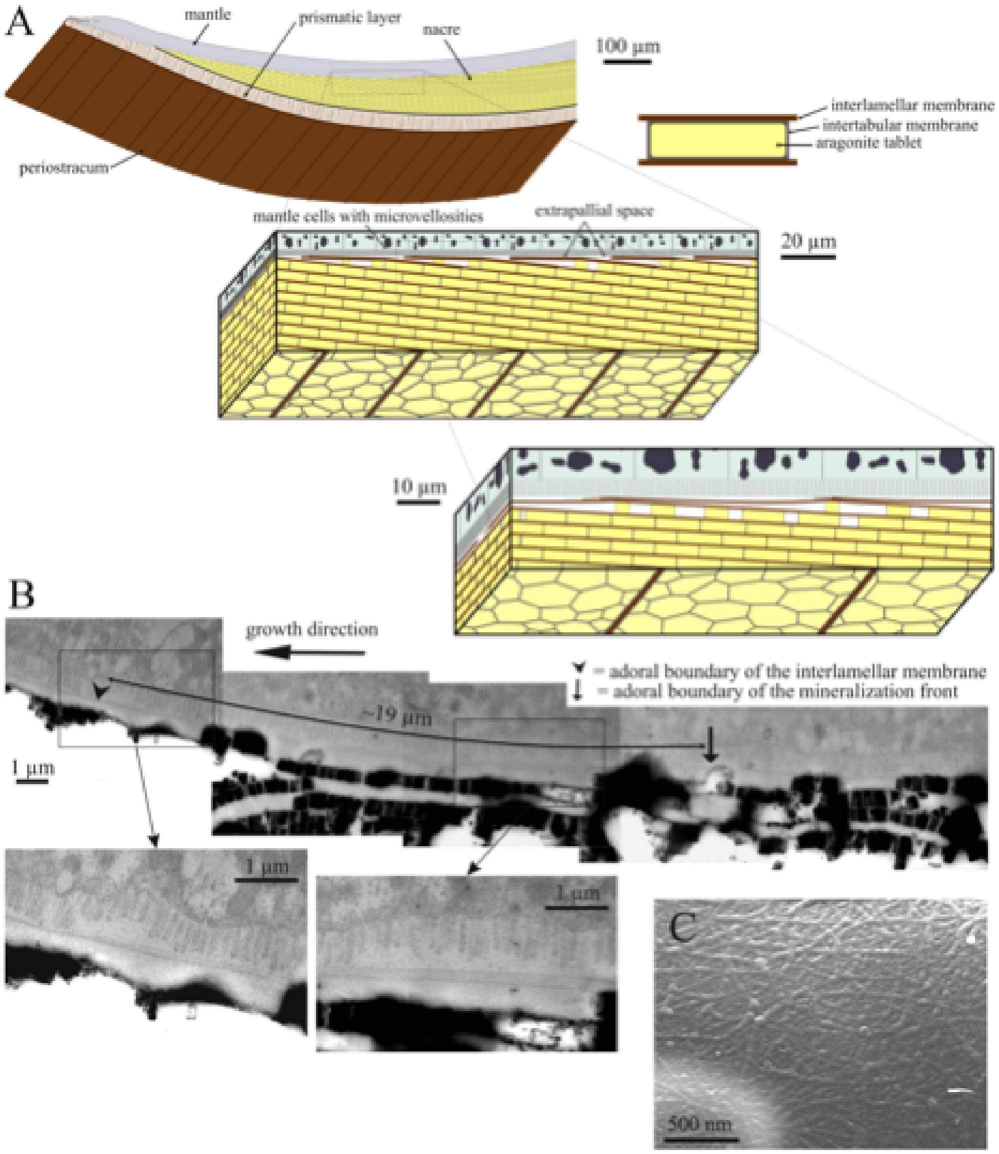


Figure 1. (A) Sketch of bivalve molluscan anatomy indicates the position of the liquid-filled interlamellar space between the mineralized shell and the mantle part of the soft body of the organism, and illustrates with successive amplifications the brick and mortar structure of nacre. (B) Transmission electron micrographs show the interlamellar membranes being laid down prior to mineralization in *Pinctada radiata*; the blowups in the figure provide more detail of the membranes. The orientation of the sample is as in A. (C) Scanning electron micrograph of the interlamellar membrane of *Anodonta cygnea* shows its logjam structure when viewed from above. Reprinted with permission from ref 6. Copyright 2009 Proceedings of the National Academy of Sciences of the United States of America.

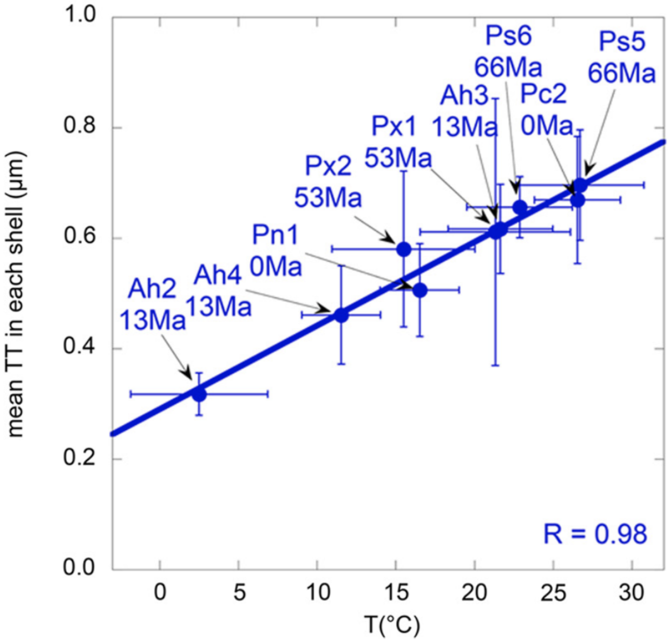


Figure 2. Mean nacre tablet thickness (TT) increases linearly with temperature (T). Reprinted with permission from ref 8. Copyright 2017 Elsevier.

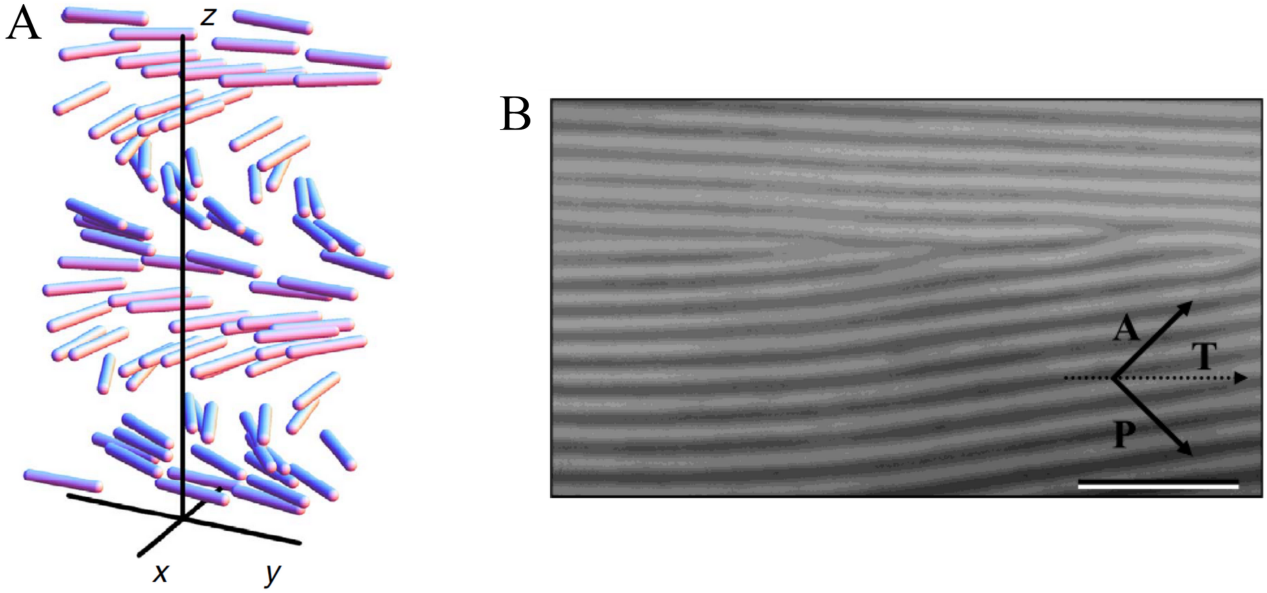


Figure 3. A. Chiral nematic or cholesteric liquid crystal, as found in mollusks in cuttlefish bone[10] and, in a modified form, in nacre.[5,6] Reprinted with permission from ref 11 Copyright 2013 Springer Nature. B. Micrograph of chitin suspension showing the fingerprint pattern characteristic of the cholesteric phase as observed between crossed polaroids. Bar: 100 µm. Reprinted with permission from ref 12.

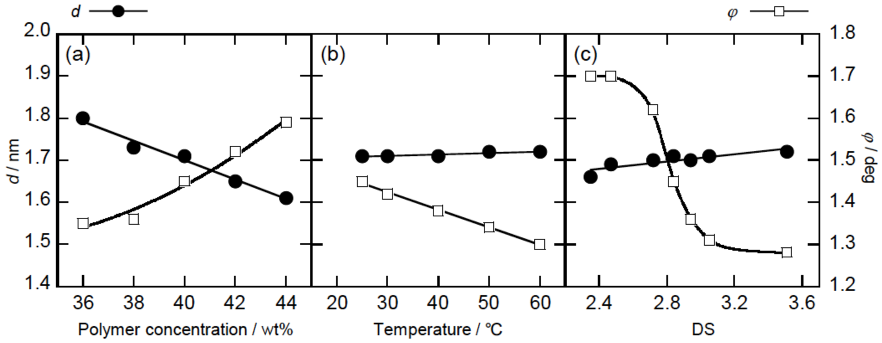


Figure 4: Interlayer distance d (filled circle) and twist angle ϕ (open square) for Ct-sPC/[C$_2$Mim][N(CN)$_2$] lyotropics, constructed as a function of three variables: (a) polymer concentration (at 25 ˚C and DS = 2.84); (b) temperature (at 40 wt % polymer and DS = 2.84); (c) DS of CtsPC (at 25 ˚C and 40 wt % polymer). Reprinted with permission from ref 22. Copyright 2014 Springer Nature.

Acknowledgments

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