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# Electronic Supplementary Information

# Smectic liquid crystal polymers as a template for ultrathin CaCO3 nanolayers

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## Experimental Section

*Materials*

The hydrogen bridged 4-(6-acryloyloxylhexyloxy)benzoic acid (6OBA) and the liquid crystalline crosslinker, 4-((4-(6-(acryloyloxy)hexyloxy)phenoxy)carbonyl)phenyl 4-(6-(acryloyloxy)hexyloxy) (C6H) were both custom made by Synthon Chemicals, Germany. Initiator 1-hydroxycyclohexylphenylketone (Irgacure 184) was supplied by Ciba Specialty Chemicals. Analytical grade $CaCl_2$, $(NH_4)_2CO_3$, inhibitor p-methoxyphenol and poly-(α,β)-DL-aspartic acid sodium salt (pAsp, mw=2000~11000) were purchased from Aldrich.

*Preparation of smectic liquid crystal membrane*

A LC mixture was made with the hydrogen bridged 6OBA, and the covalently bonded crosslinker C6H in a 90/10 w/w ratio. In order to make the mixture accessible for photopolymerization, 0.5 wt% 1-hydroxycyclohexylphenylketone was added as photoinitiator. For stabilization, 0.1 wt% of p-methoxyphenol was added as thermal polymerization inhibitor. The mixture was dissolved in tetrahydrofuran1, which was subsequently evaporated at 50 °C for approximately 1 hour. Films with a thickness that varied between 15 and 20 μm were made by processing the mixture in the melt at 105 °C by capillary suction between two accurately spaced glass plates. The photo-polymerization in the smectic state of the monomers was performed at 95 °C for 5 min with a mercury lamp (Omnicure s1000) at the intensity of approximately 5 mW $cm^{-2}$ at the sample surface followed by a heat treatment at 135 °C to ensure maximum conversion of the acrylate groups.

*Infiltration of $CaCO_3$ nanolayers*

The as-prepared polymer networks were cut in smaller flakes of approximately 0.5 × 0.5 cm and immersed in 0.05 M KOH solution for 30 min to break up the hydrogen bridges and open the nanogaps. They were quickly washed with a few milliliters of distilled water to remove the residual base and, subsequently, immersed in 10 mM $CaCl_2$ solutions with 25 or 100 mg/l pAsp. The pH value of the solution was adjusted to 9 by 0.1 M KOH solution in order to keep the nanogaps open. The solutions were sealed with parafilm and standstill for 24 h at room-temperature. After that, the solutions were placed into a desiccator, and several needle holes were made on the parafilm cover. A vial of $(NH_4)_2CO_3$ powder with holey cover was placed near the solutions. The $CO_2/NH_3$ mixture gas released by $(NH_4)_2CO_3$ was slowly diffused into the solutions at room-temperature to induce the $CaCO_3$ formation. The pH value is constant at ~10 during the reaction. After growth, the membranes are quickly washed by deionized water and dried by filter paper.

*Characterization*

POM studies were conducted using a Leica CTR 6000 microscope. FTIR spectra were obtained using a FTS 6000 Spectrometer from Bio-Rad equipped with Specac Golden gate diamond ATR and were signal-averaged over 50 scans at a resolution of 4 $cm^{-1}$.

For TEM observations the membranes were embedded in EMS EPO-FIX cold-setting embedding resin and cured at 70 °C. The embedded sample was cross cut using a Reichert-Jung Ultracut-E ultramicrotome with 70 nm setting thickness. The cross sections were transferred on a carbon film on a 200 square mesh copper grid. TEM imaging was performed under slight defocus on a FEI-Titan TEM equipped with a field emission gun (FEG) and operating at 300 kV. Images were recorded using a 2k × 2k Gatan CCD camera equipped with a post column Gatan Energy Filter (GIF).

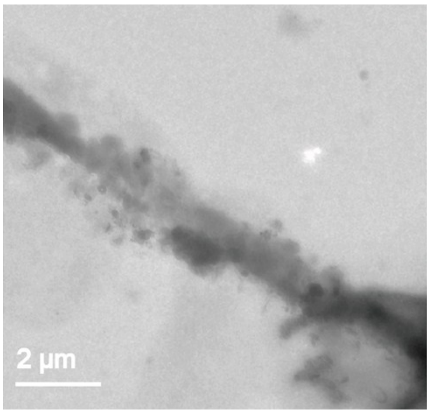

Figure S1. Low magnification TEM images of microtomed thin sections from the sample grown in the presence of 25 mg/l pAsp for 24 h, showing a ~1 μm thick band with increased contrast, which corresponds to the mineralized membrane surface.

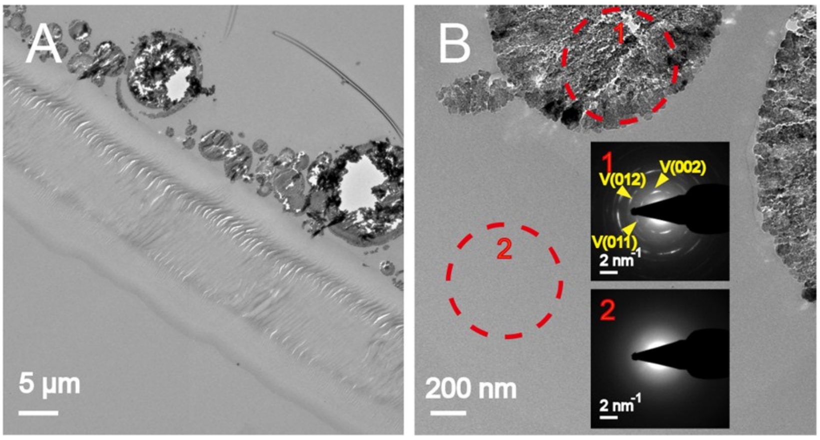

Figure S2. TEM images of microtomed thin sections showing the region covered by large $CaCO_3$ particles in the sample grown in the presence of 25 mg/l pAsp for 24 h. (A) low magnification image. (B) shows a zoom-in image of (A). Two areas at the $CaCO_3$ particle and the membrane are highlighted by red dash line circles 1 and 2, respectively. Insets: SAED patterns corresponding to circle 1 and 2 showing that the diffraction pattern of the $CaCO_3$ particle corresponds to crystalline vaterite (indexed by "V"), while no $CaCO_3$ infiltration could be observed in the membrane below.

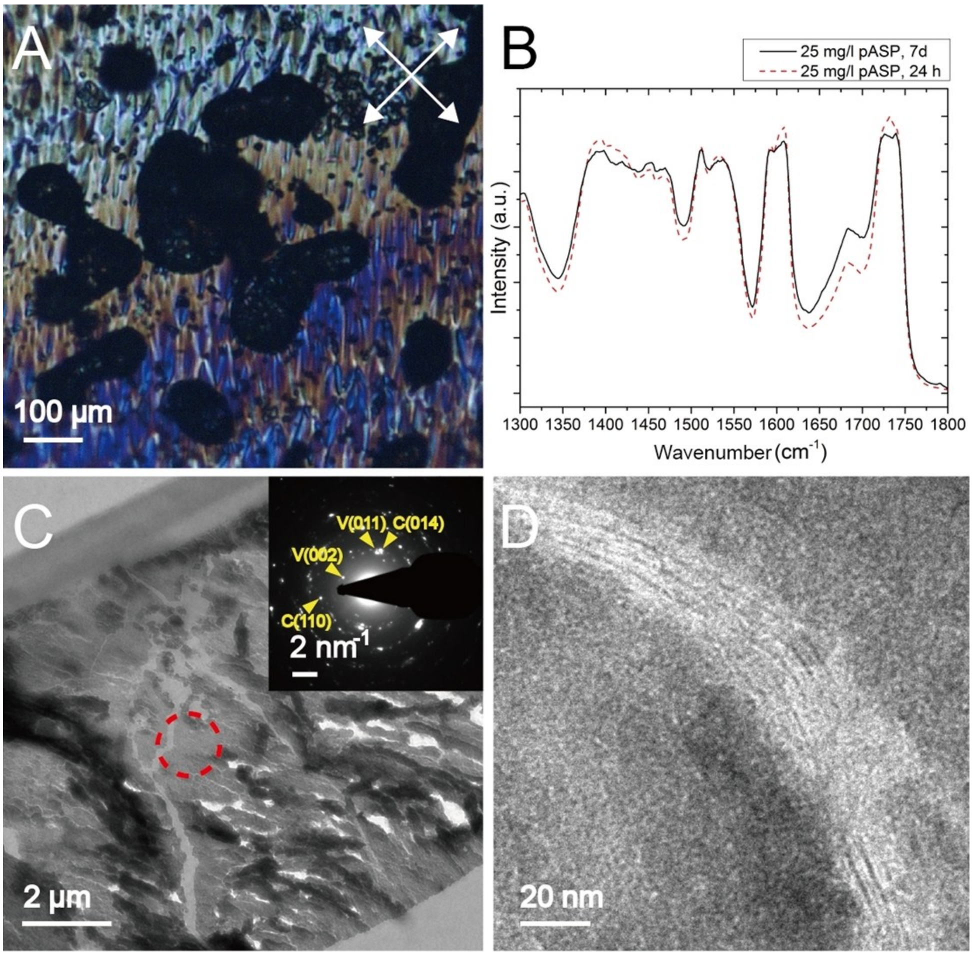

Figure S3. Analysis of the sample grown with 25 mg/l pAsp for 7 d. (A) shows the POM image with polarizer directions indicated by white arrows. The membrane is covered by more and larger $CaCO_3$ particles, and the obvious colourful features indicate enhanced birefringence. (B) shows the FTIR spectrum, with the spectrum of 25 mg/l pASP, 24 h sample as comparison. The enhanced peak at 1675 $cm^{-1}$ indicates that more H-bonds are recovered after 7d. (C, D) TEM images of the mitrotomed thin section. (C) shows the membrane is fully infiltrated by $CaCO_3$. The inset shows the SAED pattern of the area within the red dash line circle, indicating the nanoporous polymer is infiltrated by a mixture calcite and vaterite crystals (index by “C” or “V” spots, respectively) with no preferential alignment. (D) shows a zoom-in image of (C), indicating the nanolayer structures.