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Water-in-water mesophases for templating inorganics†

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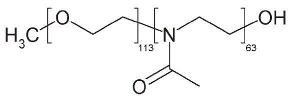
A water-in-water mesophase that contains only hydrophilic domains is reported for the first time; the mesophase templates highly porous calcium phosphate.

Polymeric additives enable the synthesis of complex inorganic or organic–inorganic materials[1,2] and many groups have investigated the effect of double-hydrophilic block copolymers (DHBCs)—polymers with only hydrophilic blocks—on the precipitation of inorganics from aqueous solution. These studies have yielded a variety of inorganic structures, some of which are interesting for *e.g.* catalysis or sensing. Interestingly, all studies have focused on the low polymer concentration regime where typical polymer concentrations range from a few ppm to approximately 1 mg mL^{-1}, see *e.g.* refs. 3–7. For an excellent review see also ref. 1. Unlike amphiphilic block copolymers, where the solution behavior is well studied, there are no data on concentrated DHBC solutions; consequently there are no studies on the precipitation of inorganics in such solutions.

This paper is the first report on a DHBC, poly(ethylene oxide-*block*-2-methyl oxazoline) (PEO-*b*-PMOXA, Scheme 1, M_n = 10 400 g mol^{-1} from ^{1}H NMR),‡ at high concentrations in aqueous solution. We demonstrate that DHBCs do not only, as reported, control the crystallization of inorganics but they also form unique lyotropic mesophases (LMs) in water. LM formation is intriguing because the polymer used here only contains hydrophilic and no hydrophobic moieties. Microphase separation is therefore not predominantly driven by hydrophilic–hydrophobic repulsion but rather by the incompatibility of the two polymer blocks; this leads to microphase separation on a nanometer scale and hence to ordered water-in-water (W/W) mesophases.

Fig. 1(a) is an optical polarization micrograph (Leica DM-RP) of a 70 wt% solution of **1** in water. The mixture is birefringent and hence has a long-range order. Fig. 1(b) is an optical polarization micrograph of an LM in a 1 M K_3PO_4 solution. Similar results were obtained with $CaCl_2$, Na_2SO_4, Na_2CO_3 and Na oxalate; the LMs thus remain intact and are not destroyed by salt addition up to a concentration of 1 mol L^{-1}. The stability is likely to be due to the non-ionic nature of the polymer as interactions with ions are much less pronounced here than in polyelectrolytes.

Fig. 1(c) is the phase diagram of **1** in water. It exhibits two major regions: above approximately 60 wt% polymer, a lamellar LM forms, L_α. At elevated temperatures, a phase transition to the isotropic phase L1 occurs. At lower concentrations we sometimes observe another (presumably hexagonal) mesophase, H1; below 55 wt% polymer the solutions are isotropic.§



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Scheme 1

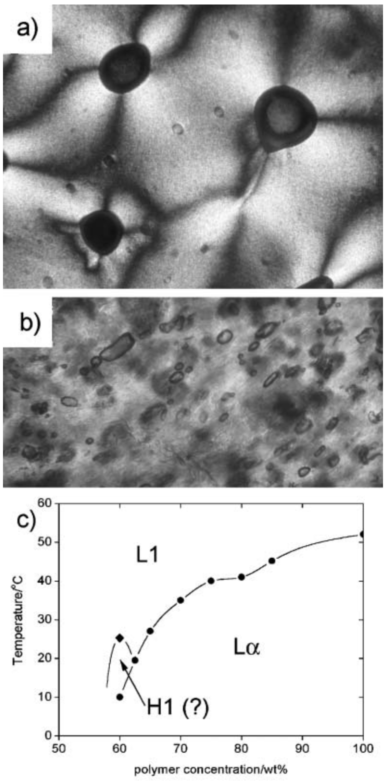

Fig. 1 (a) OPM image of a 70 wt% LM of **1**. (b) OPM image of an 85 wt% LM of **1** in a 1 M K_3PO_4 solution. (c) Phase diagram of **1** in water.

These results have several implications. (1) This, to the best knowledge of the authors, is the first report of an LM with only hydrophilic domains. (2) The absence of both hydrophobic moieties in the polymer and organic solvent suggests an intriguing structure within this particular LM, Fig. 2: in conventional LMs, hydrophilic and hydrophobic domains alternate in some periodic fashion. In contrast, our L_α LM consists of *layers of water stacked on top of one another without a hydrophobic interlayer*. The only "separation" between water-rich domains is provided by the DHBC.

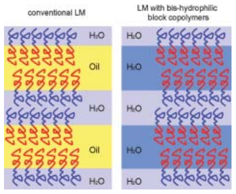

Fig. 2 Schematic comparison of a conventional LM with our W/W LM; in a conventional LM, water domains are separated by either a layer of pure hydrophobic polymer or by a layer of hydrophobic polymer and an organic solvent. In a W/W LM, the separation between water layers is provided only by the DHBC. The different blues of the water layers are used for clarity and do not imply differences between them.

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† Electronic supplementary information (ESI) available: surface tension of **1**, PEO_{113}, and $PMOXA_{85}$. See http://www.rsc.org/suppdata/cc/b4/b405610h/

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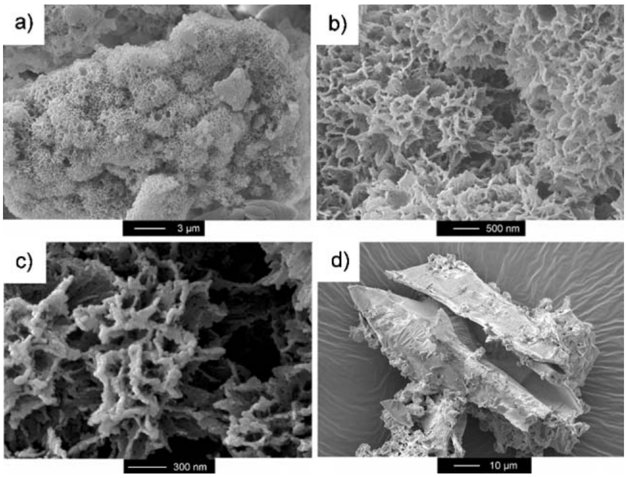

Fig. 3 (a) to (c) SEM images of a calcium phosphate sponge at increasing magnifications; (c) shows the aggregated nanoparticles mentioned in the text. (d) Control sample precipitated from 0.1 M solutions of $CaCl_2$ and K_3PO_4 without polymer.

We explain this peculiar W/W mesophase by microphase separation and block copolymer swelling; both blocks are hydrophilic (with a Flory–Huggins χ parameter <0.5)[8,9] but at the same time the blocks do not mix with one another. Water is thus a nonselective solvent, leading to a structure where both blocks form domains that are swollen with water, but only contain either PEO or PMOXA.¶

The high water content of our LM is attractive for precipitation of inorganics with a well-defined morphology and high inorganic fraction. As Ca minerals have been intensely studied,[2,10] they were chosen as model compounds to determine if and how the W/W mesophases affect their precipitation.‖

Figs. 3(a)–(c) show a highly porous calcium phosphate (CaP) sponge precipitated in an 85 wt% mixture of **1** from 0.1 M $CaCl_2$ and K_3PO_4 solutions.** The pore size distribution is broad and ranges from several tens of nanometers to several hundreds of nanometers; there are no areas with only large or only small pores and all pores are consistently separated by approximately 50 nm thick walls. High magnification SEM shows small spherical subunits of the wall; this suggests that the walls form *via* aggregation of nanometer-sized subunits, similar to aggregation-based growth suggested for TiO_2 and some iron oxides.[11,12]

Fig. 3(d) shows that the control sample, which was also precipitated from 0.1 M solutions but without a polymer template, is not porous but contains large CaP platelets. They have a length of up to several tens of microns and a thickness of about 0.5 to 1 μm. The control sample is by no means comparable to the morphology obtained with the LM template, which demonstrates the importance of the template.

Finally, it is interesting to note that the porous material bears a likeness to bone, even though the high correlation of the calcium phosphate nanoparticles and the hierarchical order of bone are not obtained here. Despite this, the material may be interesting for biomedical applications, in particular because no organic or toxic side products are involved in mineral formation.

In conclusion, we present two intriguing new aspects of materials chemistry: (1) the fabrication of the first LM without hydrophobic domains and (2) the formation of CaP with a new and potentially useful morphology. As the polymeric template is biocompatible and easily modified with respect to its symmetry and its interaction with an inorganic material, we can use W/W mesophases to either fabricate biocompatible organic–inorganic nanocomposites for *e.g.* dental treatments or also purely inorganic materials for *e.g.* catalysis.

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Notes and references

‡ **1** was obtained *via* cationic ring opening polymerization of 2-methyloxazoline with a tosylated PEO 5000 monomethyl ether (Fluka) macroinitiator.

§ The assignments of the LM symmetry are based on OPM data. X-Ray patterns do not show any signal; we interpret this as being due to the weak contrast between domains since all domains predominantly consist of water, C, H and O. Neutron scattering experiments are in preparation. The H1 phase is not consistently observed and it is thus currently not clear how stable it is.

¶ LMs could also form because the blocks are water structure makers or breakers or because of slight hydrophilicity differences between the blocks. We believe that structure making or breaking is not the main cause because neither the structure breakers Ca^{2+} or PO_4^{3-},[13,14] nor (5 wt%) ethanol, a structure maker,[15] measurably alter the phase diagram. For example the L_α-iso transition of a 75 wt% solution of **1** is consistently at 40–41 °C. Surface tension measurements show some effect of the diblock copolymer (see supporting information†). A slight amphiphilicity could thus also contribute to microphase separation. A detailed aggregation study of **1** is under way.

‖ We focus on CaP because here we have observed the most interesting morphologies with the LM. The other results are: $CaSO_4$: no crystallization; $CaCO_3$: particle size reduction from *ca.* 30 μm to *ca.* 3 μm; Ca oxalate: particle size increase from *ca.* 200 nm to over 1 μm.

** Prior to crystallization, the polymer was repeatedly freeze-dried from benzene to minimize the amount of trapped water. 80 mg of dry polymer were mixed with 15 μl of a 0.1 M solution of $CaCl_2{\cdot}2H_2O$ or K_3PO_4 in a Perkin-Elmer vibration mill. Equivalent weights of Ca- and P-containing LM were mixed and reacted for 120 hours at 25 °C in a sealed Eppendorf tube. Control samples were obtained by mixing 100 μl of the polymer-free solutions and reacting at r.t. without stirring. Precipitates were isolated by water, acetone and chloroform washing and centrifugation. Samples were dried at 80 °C for 24 hours. $CaSO_4$, $CaCO_3$ and Ca oxalate were prepared accordingly. Energy dispersive X-ray spectroscopy (data not shown) detected Ca, O and C, S or P, where applicable. No evidence of impurities from the precipitation (K, Na) or the polymer (N) was found.

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