doi:10.1017/S1431927616012095
Microsc. Microanal. 22 (Suppl 5), 2016

Studying Polymer Self-Assembly by Combined Cryogenic and Liquid Phase Transmission Electron Microscopy

Joseph P. Patterson,[1,2] Alessandro Ianiro,[2,3] Mark van Rijt,[1,2] Remco Tuinier, [2,3] Catarina Esteves, [2,3] and Nico Sommerdijk[1,2]

[1.] Laboratory of Materials and Interface Chemistry & Center of Multiscale Electron Microscopy, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, PO box 513, Eindhoven, The Netherlands.
[2.] Institute for Complex Molecular Systems, Eindhoven University, Eindhoven, The Netherlands.
[3.] Laboratory of Physical Chemistry, Department of Chemical Engineering and Chemistry & Institute for Complex Molecular Systems, Eindhoven University, Eindhoven, The Netherlands.

The functionality of many materials depends on their hierarchical organization. Although in biology such materials can be formed through the self-organization of preformed building blocks, the bottom-up assembly of synthetic materials with predefined structures and properties is still out of reach. Our long term vision is to enable synthesis of hierarchical materials through multiscale assembly by combining the macromolecular self-assembly of predefined building blocks with their subsequent organization into mesostructured materials. The assembly of block copolymers into defined objects with well-defined structure, and the subsequent organization of these objects using colloidal assembly is one promising approach to this goal. However, to achieve this, we must first develop the capability to monitor structure formation *in situ* and on all relevant length and time scales, from the nanometer to the (multi)micron level. Liquid phase electron microscopy (LP-EM) is extremely suited to study materials formation processes on different length scales and to provide detailed information on the mechanisms involved [1-3].

LP-EM is an emerging analytical technique for the study of materials formation, but has already begun to revolutionize our understanding of nanocrystal formation. Many experiments have been performed by the electron beam reduction of metal precursors, which initiates nanoparticle formation [4]. This convenient method of synthesis, along with the high convenient of the metal nanoparticles has greatly aided the success of LP-EM in this area. However, the synthesis of most materials is typically performed by controlled solution mixing, which is still a challenge in the liquid cells available for LP-EM experiments. Furthermore, to study the aqueous solution self-assembly of polymers it is necessary to ensure the liquid layer thickness is on the order of the particle thickness, as the electron density of the macromolecular materials is not vastly different from water. Therefore, we must create new experimental set ups for LP-EM which allow thin cells to be created and either create structures without controlled solution mixing, or allow controlled solution mixing to occur inside the cell.

In this paper we will discuss our efforts to perform block copolymer self-assembly using a solvent switch inside the liquid cell. The system we have chosen comprises poly(caprolactone)-*b*-poly(ethylene oxide) PCL-*b*-PEO, and a solvent switch from acetone to water, which based on ex-situ cryo-TEM and self-consistent field (SCF) theory should form vesicles upon increasing water content (Figure 1). PCL-*b*-PEO is a well-studied system, however little is currently known about the dynamics of assembly, or how the assembly route can be effected by changing experimental conditions. Adam et. al. studied the formation of PCL-*b*-PEO vesicles by scatting and cryo-TEM [5], showing evidence of the conventionally accepted micelle → cylinder → vesicle formation route. However they also suggested the possibility of a precursor phase, based on turbidity measurements and dynamic light scattering which is characterized as being large and of high dispersity. Here we show direct evidence for the formation of this precursor phase by LP-EM (Figure 2) and cryo-TEM, which we characterize as a polymer-rich dense liquid phase. We discuss the role of this precursor phase in the formation of vesicles, and we link this process to our SCF theory calculations.

References:

[1] JJ De Yoreo and NAJM Sommerdijk, Nature Reviews Materials **1** (2016), p. 16035.
[2] PJ Smeets *et al*, Nature Materials **14** (2015), p. 394.
[3] MWP van de Put *et al*, Small **11** (2015), p. 585.
[4] JP Patterson *et al*, Perspectives in Science **6** (2016), p. 106.
[5] JP Patterson *et al*, Microscopy and Microanalysis **22** (2016) p. 507.
[6] DJ Adams *et al*, Soft Matter **5** (2009), p. 3086.

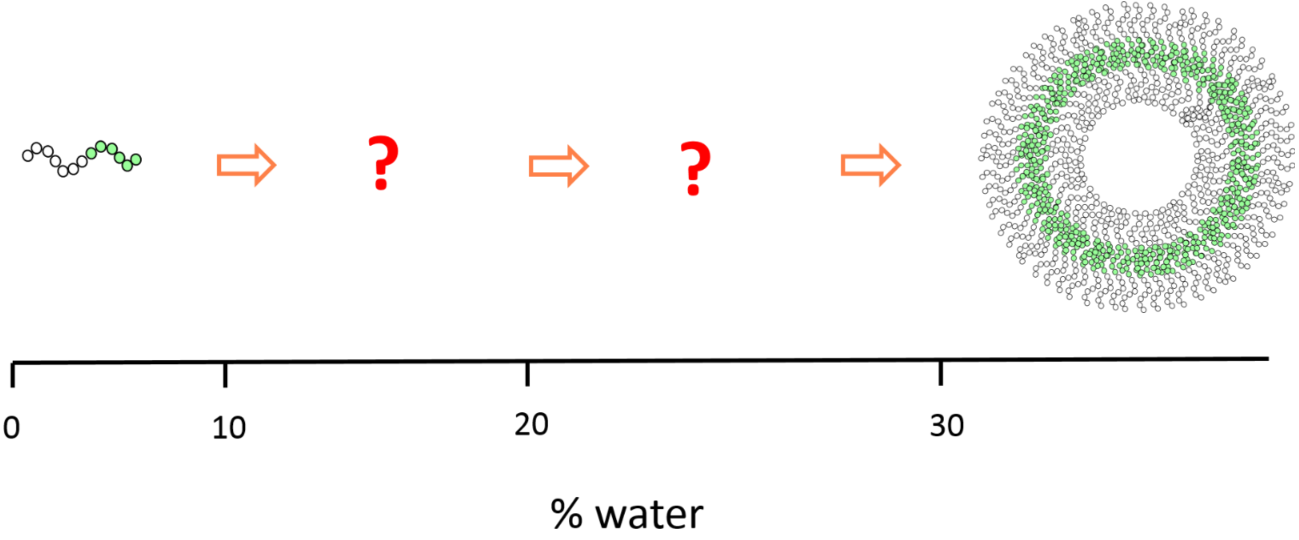

Figure 1. Schematic outlining the assembly of molecular block copolymer PCL-*b*-PEO into vesicles by increasing water content of an acetone solution.

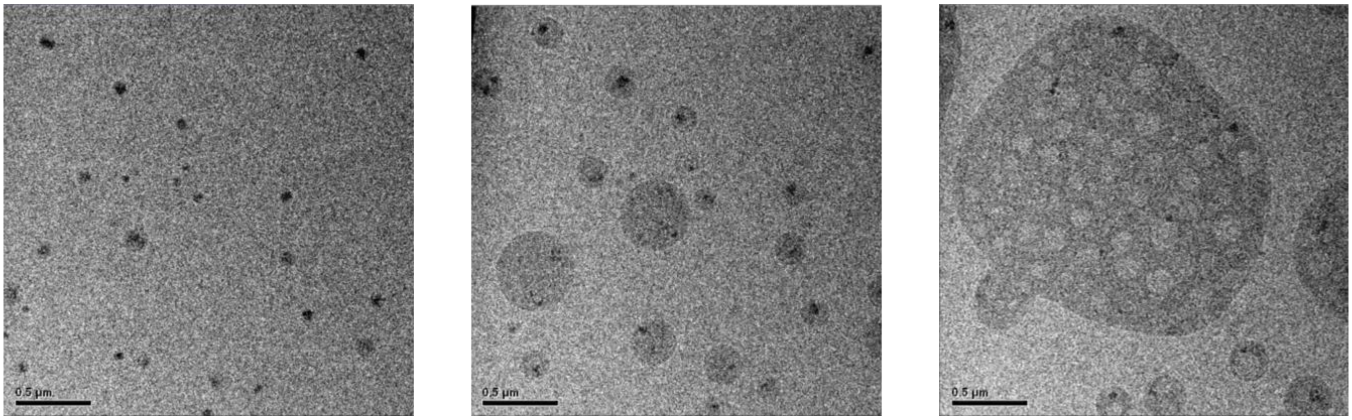

Figure 2. Snapshots from LP-TEM movie showing the formation of a dense liquid precursor phase in the formation of PCL-*b*-PEO vesicles by acetone → water solvent switch.