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Characterization of Fluorescence-tagged Polymeric Particles using Confocal Laser Scanning Microscopy and Three Dimensional Structured Illumination Microscopy

Xuejun Wang[1] and Mingli Wei[2]

[1.] Research Analytical, Nalco Water, an Ecolab Company, Naperville, IL, USA
[2.] Polymer Research – Enterprise, Nalco Water, an Ecolab Company, Naperville, IL, USA

Polymeric particles with both permanent and labile crosslinks are used for increased oil recovery from sandstone reservoirs. The original particle size is around 100nm. It's believed that on heating to reservoir temperature and/or at a predetermined pH, the reversible (labile) internal crosslinks start to break allowing the particles to expand by absorbing the injection fluid (normally water). However, it is very challenging to prove this hypothesis and to measure the size of expanded particles experimentally because the expanded particles consist of ~99% water and they coexist with oil droplets, surfactants and air bubbles, which makes SEM/TEM, optical microscopy and dynamic light scattering measurements difficult. In order to address these issues, fluorescently labeled polymeric particles were synthesized and their expansion upon heating or pH adjustment was studied using confocal laser scanning microscopy (CLSM) and three-dimensional structured illumination microscopy (3D-SIM).

Approximately 150 fluorophores were labeled on each particle by adding small amount of fluorescein derivatized monomer during the polymerization process. Time-series heating at 70^{o}C was used to simulate the slow hydrolysis; high pH was applied to simulate the fast hydrolysis. A series of slow hydrolysis samples were embedded inside Agarose to preserve their original shapes by adapting a literature reported method.[1] Fluorescence images of the particles were acquired with a 100x N.A. oil immersion lens using a DeltaVision OMXTM 3D-SIM^{TM} microscope at University of Illinois, Urbana-Champaign (UIUC). The excitation wavelength was 488 nm, and band pass emission filter (500-550) was used for fluorescence collection. The z-slice distance is 125nm. For comparison, fluorescence images of many polymeric particle samples were also acquired with a 63x N.A. oil immersion lens using a Zeiss LSM 5 inverted confocal laser scanning microscope. The excitation wavelength was 488 nm, and long path filter (LP505) was used for fluorescence collection. The z- slice distance is 200nm.

Figure 1 shows the CLSM image versus 3D-SIM image of the polymeric particles before expansion. Clearly the 3D-SIM image is much better than the CLSM image due to higher resolution and higher contrast. The lateral resolution of 3D-SIM is around 100nm, whereas the lateral resolution of CLSM is around 250 nm. The larger particles on the CLSM image turn out to be aggregates of smaller particles.

Figure 2 exhibits 3D-SIM images after 4 hours (left) and 3 days (right) of the slow hydrolysis expansion. The expanded particles exhibit obvious alternate bright/dark features and appear to be porous. This phenomenon is caused by not enough tagging on the polymer. Based on theoretical calculation, there are about 150 tagged monomers for each particle. The tagged monomers would be randomly distributed inside the particle. Assuming the expanded particle became 1 micron, the average distance between two tagged monomers would be 152 nm, which is larger than 100nm lateral resolution and 40nm pixel size. Thus, the region with one or more tagged monomers would be brighter than the region without tagged monomer.

The results suggest that the particles can expand 5~10 times and still maintain their shape for 2 to 5 days at pH = 8.2 and 70°C. The polymeric particles have mostly hydrolyzed and no clear boundary exists after 7 days at pH = 8.2 and 70°C. Under fast hydrolysis condition (pH 11.5, room temperature), the polymeric particles can expand 10 times in 30 minutes.

References:

[1] Ríos, G. *et al*, Journal of Dispersion Science and Technology **23** (2002), p. 721.

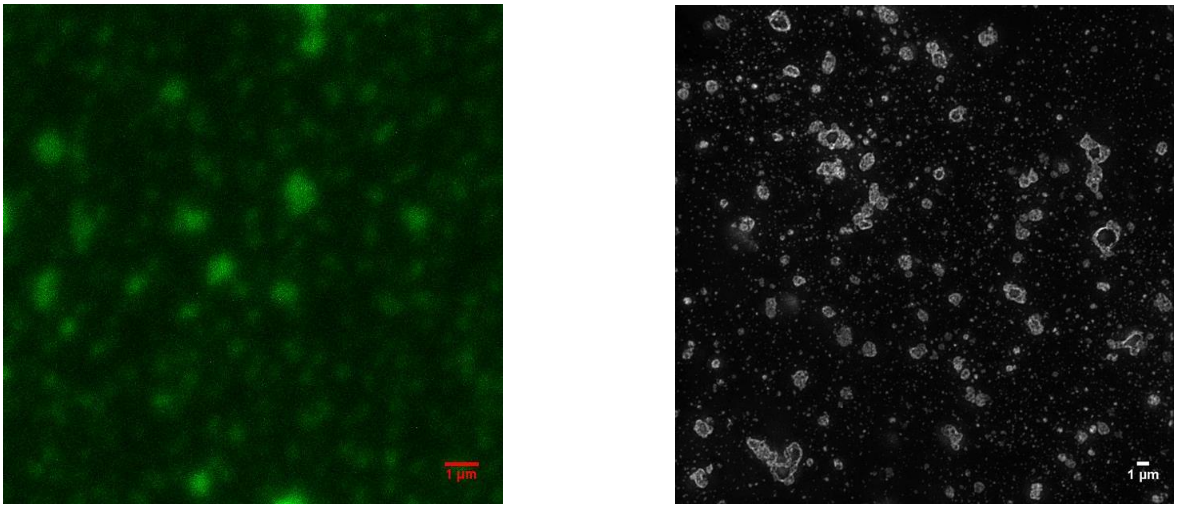

Figure 1. CLSM image (left) versus 3D-SIM image (right) of the polymeric particles before expansion

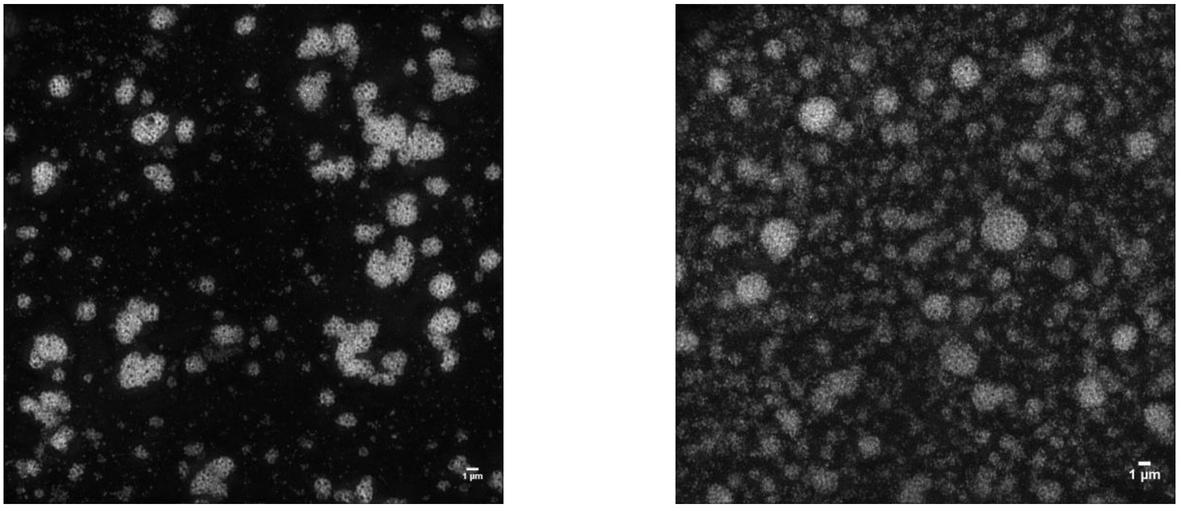

Figure 2. 3D-SIM image after 4 hours (left) and 3 days (right) of the slow hydrolysis expansion