Multiscale Modelling of Polycaprolactone Self-Assembly in Water-Acetone Mixtures

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Multiscale Modelling of Polycaprolactone Self-Assembly in Water-Acetone Mixtures

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Nicodemo Di Pasquale[1,2], Paola Carbone[2], Daniele Marchisio[1]

[1] Politecnico di Torino, Italy
[2] University of Manchester, UK

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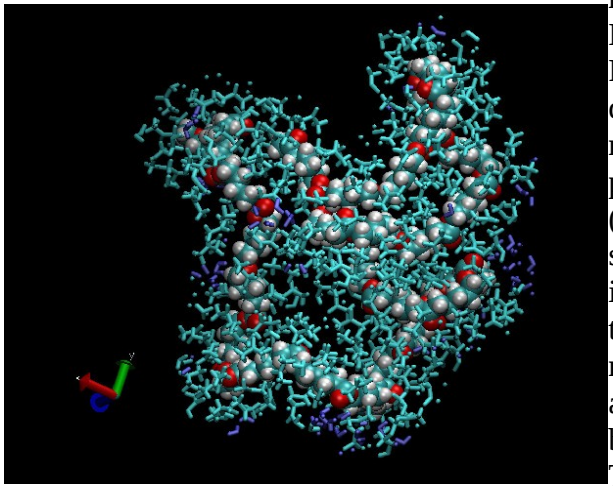
Polycaprolactone (PCL) is an important polymer that finds relevant applications in the pharmaceutical and biomedical fields, often in the form of nanoparticles. These nanoparticles are generally obtained through solvent displacement, namely PCL is dissolved in a "good" solvent (e.g. acetone) and the solution is subsequently mixed with a "bad" solvent (e.g. water). While PCL molecules form in acetone (at moderate concentrations) a stable solution, upon mixing with water (with which PCL exhibits a lower compatibility), PCL molecules self-assemble, via a diffusion-limited aggregation process, into nanoparticles. In this work a multiscale model is developed and validated; the model accounts for all the key factors involved: (1) effect of mixing of water and acetone on the final nanoparticle characteristics, (2) polydispersity of the obtained nanoparticles and (3) complexity of the interactions between water, acetone and PCL molecules. For these three different key factors, three modeling approaches (acting on three different scales) are employed. The acetone-water mixing process is described through computational fluid dynamics, the PCL self-assembly into a polydisperse population of particles is described through a population balance model (directly solved within the computational fluid dynamics code), whereas the PCL molecule aggregation kernel is derived from the radius of gyrations and diffusion coefficients of PCL molecules, calculated in turn from molecular dynamics simulations.
Computational fluid dynamics simulations are carried out in Ansys Fluent 14, in which the population balance model is implemented via the quadrature method of moments with user-defined functions and scalars, while molecular dynamics simulations are carried out with GROMACS 4.6 (by employing the OPLS-AA force field together with the SPC model for PCL, acetone and water molecules).



Molecular dynamics simulations, carried out for PCL molecules of different molecular weights and in different water-acetone mixtures, highlight that PCL molecules behave very differently when they are in pure water or in water-acetone mixtures (notwithstanding the actual composition). In fact, as soon as some acetone is introduced into the system, it clusters around the PCL molecule, as evidenced by the enclosed figure (where acetone molecules are represented in light blue, whereas water molecules are represented in dark blue) drastically changing its behavior.
The values of radius of gyration obtained by

molecular dynamics simulations are well described by the Flory law, whereas the diffusion coefficients obtained are well described by the Stokes-Einstein law. These two pieces of information are then combined together to quantify the PCL molecule aggregation kernel, that is in turn used to predict the final size distribution of PCL nanoparticles obtained by solvent displacement carried out in a confined impinging jets mixer, resulting in satisfactory agreement with experiments.