ESRF	**Experiment title:** **Nanometric Emulsions Through Phase Inversion**	**Experiment number**: SC2974
Beamline: ID02	**Date of experiment**: from: 25/11/2010 to: 29/11/2010	**Date of report**: 10/02/2013
Shifts: 12	**Local contact(s)**: J. Gummel	*Received at ESRF:*

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Report: Populations of droplets or particles dispersed in a liquid may evolve through Brownian collisions, aggregation and coalescence. We have found a set of conditions under which these populations evolve spontaneously toward a narrow size distribution. The experimental system consists of poly (methylmethacrylate) (PMMA) nanodroplets dispersed in a solvent (acetone) + non-solvent (water) mixture. The droplets carry a low surface charge, from ionic endgroups of the macromolecules. We used time-resolved Small Angle X-ray Scattering with a stopped flow device at the sample position of ID02. We used an inversion procedure that relies on deviations from Porod's law to determine the size distribution of droplets. We find that the droplets grow through coalescence events: the average radius $<R>$ increases only logarithmically with time while the relative width σ_R / $<R>$ of the distribution decreases as the inverse square root of $<R>$. We interpret this evolution as resulting from coalescence events that are hindered by ionic repulsions between droplets. We generalize this evolution through a simulation of the Smoluchowski kinetic equation, with a kernel that takes into account the interactions between droplets. In the case of vanishing or attractive interactions, all droplet encounters lead to coalescence. The corresponding kernel leads to the well-known "self-preserving" particle distribution of the coalescence process, where $\sigma_R/<R>$ increases to a plateau value. However, for droplets that interact through ionic repulsions, "large + small" droplet encounters are more successful at coalescence than "large + large" encounters. We show that the corresponding kernel leads to a particular scaling of the droplet-size distribution - known as the "second-scaling law" in the theory of critical phenomena -, where $\sigma_R/<R>$ decreases as $<R>^{1/2}$ and becomes independent of the initial distribution. We argue that this scaling explains the narrow size distributions of colloidal dispersions that have been synthesized through aggregation processes. Furthermore, the Smoluchowski approach can be used for quantitative predictions of the outcome of aggregation or coalescence processes that are hindered by repulsions.

Reference [1]. Botet, R. ; Cabane, B. *J. Appl. Cryst.* **2012**, *45*, 406–416

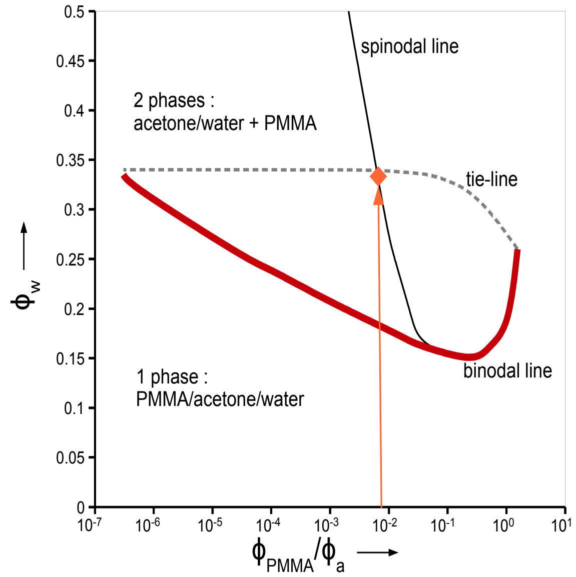

Figure 1: Phase diagram of the PMMA/acetone/water system. Horizontal axis : ratio of PMMA volume fraction to acetone volume fraction, $\phi PMMA/\phi a$, in log scale. Vertical axis : water volume fraction, ϕw. The solvent-shifting path is the ascendant vertical line. When the system crosses the binodal line, phase separation takes place, high values of the supersaturation are quickly reached.

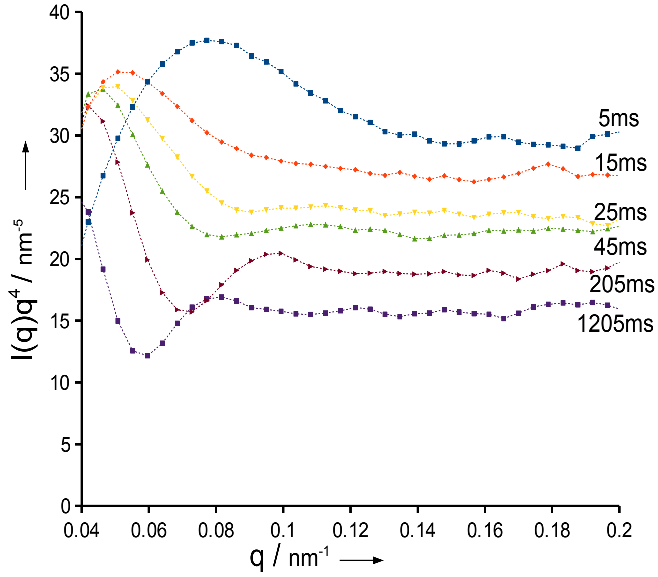

Figure 2: Temporal evolution of the scattering curves in a Porod plot $I(q).q^4$ versus the magnitude of the scattering vector, q . The decrease of the asymptotic value at the large q-values corresponds to an interfacial area decrease, whereas growth of oscillations in the intermediate q range corresponds to a decrease of the polydispersity with time. For clarity reason not all the data are displayed.

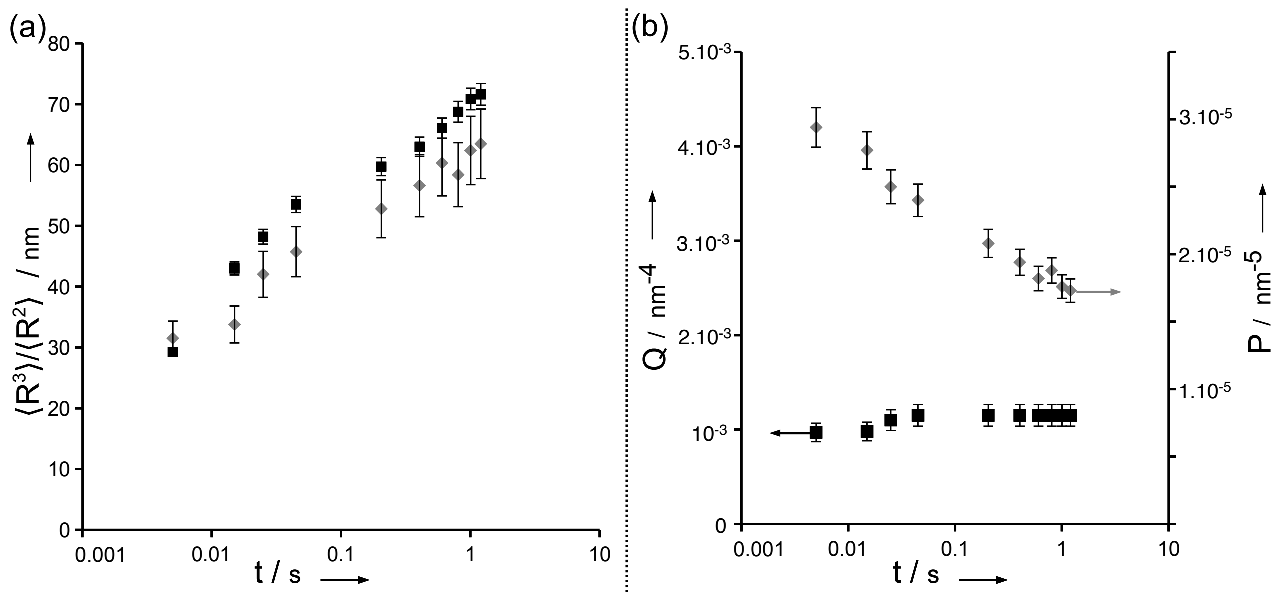

Figure 3: (a) Particle growth law as a function of time, t in semi-logarithmic scale. Grey diamonds : radius extracted from model-independent analysis of the scattering curves displayed in Figure 2 ; black squares : mean radius obtained through inversion of the scattering curves. (b) The invariant Q remains constant over time, hence the amount of scattering matter is constant. The Porod limit P decreases with time, hence the total interfacial area decreases. The system thus evolves through a coalescence process.