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| | Experiment title: <i>Rapid Formation Kinetics of Polymeric Micelles- a Time Resolved SAXS Study</i> | Experiment number: SC2182 |
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Names and affiliations of applicants (* indicates experimentalists):

Dr. Reidar Lund DIPC, San Sebastian, Spain *

Dr. Lutz Willner, Forschungszentrum Jülich, Germany*

Dr. Pierre Panine, ESRF, Grenoble, France*

Prof. Juan Colmenero DIPC, San Sebastian, Spain

Prof. Dieter Richter, Forschungszentrum Jülich, Germany

Report:

The aim of this proposal was to investigate the rapid self-assembly process of block copolymer micelles by interfacial tension jump experiments monitored by time – resolved small angle x-ray scattering (TR-SAXS). The current system of investigation is an amphiphilic poly(ethylene-alt-propylene)-b-poly(ethylene oxide) (PEP-PEO) copolymer in water and dimethylformamide (DMF) as selective solvents for PEO. In pure DMF, PEP-PEO exists as single chains but as soon as the solvent contains water, micelles are formed. This behaviour is triggered by the increase in interfacial tension towards the hydrophobic PEP which is grossly different for water and DMF (46 and 8 mN/m respectively).

A stopped flow apparatus was employed to rapidly mix two reservoirs, one containing the PEP-PEO/DMF unimer solution in pure DMF and the other DMF/water mixtures to induce micellisation. The data acquisition was then triggered after an initial deadtime of 22 ms. A lot of time was spent in order to find the right time conditions for the kinetic measurements which was tuned by varying the final DMF/water content. Also a major portion of the time was spent in order to carefully rinse and refill the stopped-flow apparatus avoiding problems as air bubbles and pollutions. In addition, some time was needed to check for beam damage which was found to be less problematic when the exposure time was cutted to the minimum and system was allowed to relax for about 120 ms between the shots. Beam damage was also found to be much less of a problem in the system when the water content is low.

The results showed that at water-rich final solutions, micelles were formed at times shorter than the deadtime (22 ms). Moreover these micelles were stable over a long period of time indicating no further growth. Interestingly, the micelles prepared by mixing the polymer powder directly in the final solvent mixture displayed a larger micellar size. Hence this means that the micelles are always not in equilibrium. We can correlate this behaviour with the results from equilibrium kinetics studies using small angle neutron scattering. Those results indicate that the unimer exchange is essentially frozen at high water content [1,2].

Thus, these results lead to the important conclusion that formation kinetics is likely to be dominated by unimer step-like growth and not fission/fusion mechanisms as alternative pathways. By decreasing the water component (smaller interfacial tension jump) the initial growth of the micelles could be directly followed by TR-SAXS. This is shown in Figure 1.

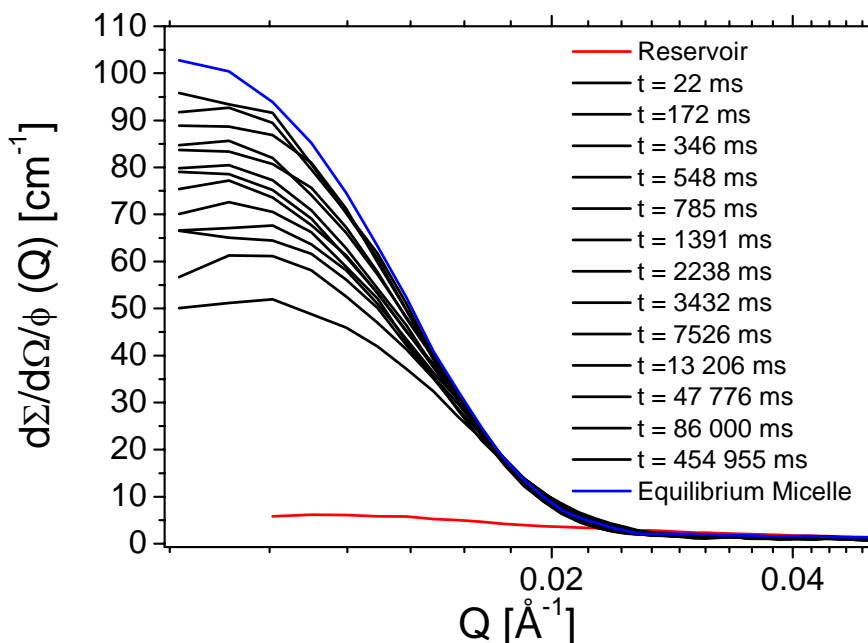


Figure 1. Time evolution of the normalized intensity of PEP-PEO block copolymers after rapid mixing of polymer solution with 80:20 DMF-water solvent mixture in a 1 :1 proportion. The lowest red line displays the scattering from the reservoir (PEP-PEO unimers) and the highest blue line displays the scattering of the micelles prepared by dissolving bulk PEP-PEO directly in the final solvent mixture (90:10).

As seen the kinetics of formation can now be evaluated by detailed fitting with a core-shell model including a star-like density profile [4]. The results of these fits are given in terms of the aggregation number (P) and the overall radius of the micelle (R_M) in Figure 2.

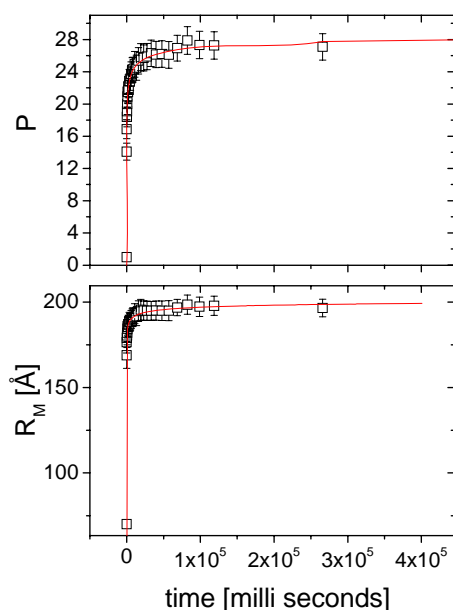


Figure 2. The aggregation number (P) and the radius of the micelle (R_M) evaluated by fitting a core-shell model to the micellar scattering. The solid line displays a fit to a stretched exponential growth.

The data shows an extremely broad distribution of relaxation times manifested by a stretched exponential growth with a stretching exponent of about 0.2-0.3. It is interesting to compare these results with existing theories. Considering only unimeric growth, Nyrkova and Semenov [4] show that the effective collective activation energy of forming micelles is an increasing function of the supersaturation, i.e. the excess number of free unimeric chains in the solution. This naturally leads to an increasing relaxation time with the size of the micelles which explains the stretched exponential growth. A detailed modelling with these ideas in mind are being performed and will be published at a later stage.

Future experiment is planned to access shorter initial times (lower dead time) by varying injection times and the triggering point of data acquisition. In future experiments also the polymer concentration will be varied in order to check predictions from theories considering the relationship between supersaturation and micellization rates

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2. Lund R, Willner L, Richter D, Dormidontova EE MACROMOLECULES **39** (13): 4566-4575 (2006)
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4. Nyrkova IA, Semenov AN. MACROMOLECULAR THEORY AND SIMULATIONS 14 (9): 569-585 NOV 23 2005