Experimental report

13/03/2020

Proposal: **EASY-581** **Council:** 10/2019

Title: In-situ observation of the emulsion polymerisation of poly(vinyl acetate) for wood glues

Research area: Methods and instrumentation

This proposal is a new proposal

Main proposer: **Anja HOERMANN**

Experimental team: Anja HOERMANN
Albert PRAUSE
Dominic HAYWARD

Local contacts: Sylvain PREVOST

Samples: Emulsion of vinyl acetate in D2O

Instrument	Requested days	Allocated days	From	To
D11	12	12	25/02/2020	26/02/2020

Abstract:

The new chemical reactor for in-situ observation developed by Dominic Hayward has so far been used to e.g. study pH titration of surfactant solutions and polymerisation induced self-assembly (PISA). To test the applicability to concentrated reactions as used in the chemical industry, we want to do a test experiment on the example of the emulsion polymerisation of poly(vinyl acetate), which is used for wood glues. This test requires exclusion of oxygen, temperatures up to 90°C as well as pumping a relatively viscous solution. If the experiment proves to be feasible under these conditions, we know the setup covers a wide range of possible reaction conditions.

1 experiment

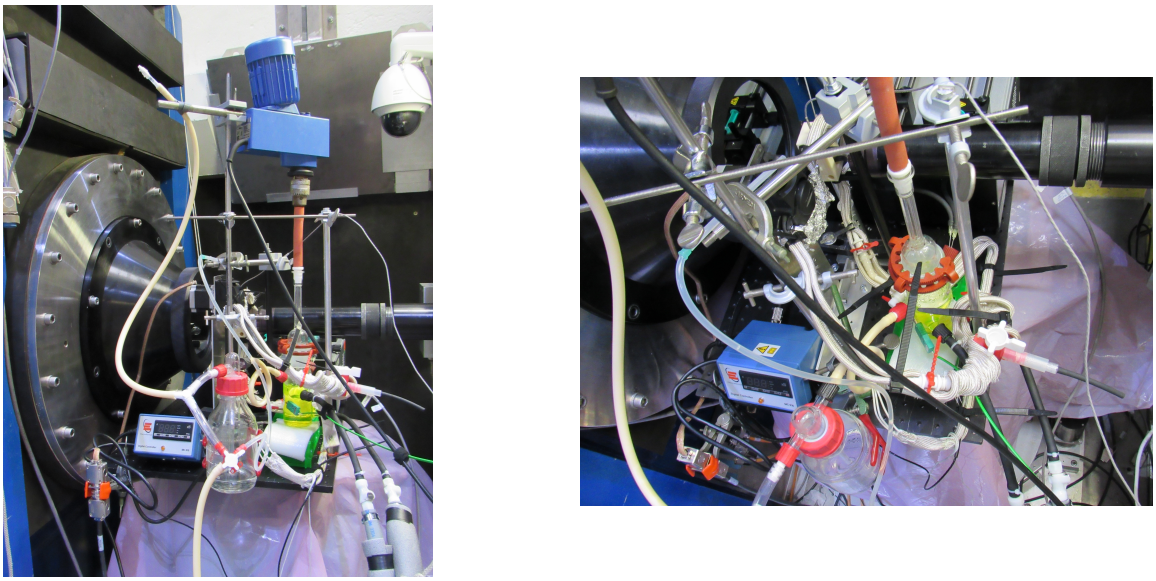

Figure 1: Setup for the experiment with the result of the 2nd reaction in the circuit.

We used a custom-made flow-through chemical reaction vessel with a glass propeller stirrer (2 pairs of tilted blades). Vessel and stirrer were made by Carsten Hirschfeld at TU Berlin as a modification of Dominic Hayward's initial flow-through reactor. The stirrer was rotated at 200 rpm. A peristaltic pump (Williamson model 250) was used to pull the solution through the cuvette (2 mm path length) at 80 rpm (1st reaction) and 60 rpm (2nd reaction). For the continuos addition of monomer and initiator we used a double syringe pump (Harvard) with syringes of 24 and 5 mL capacity, respectively. The setup was heated using a water bath (ThermoScientific AC200-A40, for the reactor vessel) and a heating tape (Electrothermal, for the tubing). Both were set to 62 °C, 78 °C and 95 °C to reach temperatures of 60 °C, 75 °C and 90 °C. The cuvette holder could not be thermalized either way as the current prototype is not leak-proof. Therefore, the temperature of the reaction mixture was approximated as the temperature of the thermalized reactor wall as measured by a thermocouple. The entire setup was kept under nitrogen using a bottle of nitrogen and a gas wash bottle to keep the atmosphere in the reactor while also allowing for additions of large volumes through a septum without a significant change in pressure.

We used one configuration ($\lambda = 5\,\text{Å}, SD = 39.85\,\text{m}, coll = 40.5\,\text{m}$), covering a q -range of about $0.0014\,\text{nm}^{-1}$ to $0.018\,\text{nm}^{-1}$o.

1.1 reaction trial 1

The first trial aimed at a total volume of 40 mL for the reaction, such that the sample would stay below the inlet at all times and emptying the cuvette would be possible to see if something (or how

much) is stuck in the cuvette. Unfortunately, the corresponding volume of initial solution (20 mL) was too little to fill both the space between the reactor bottom and the stirrer blades as well as the tubing. Homogenization could therefore only occur due to the peristaltic pump, which may have changed the properties of the particles produced.

1.2 cleaning

Cleaning was easy as the reaction had not continued. The reactor was cleaned with water, which was also pumped through the circuit until the cleaning water remained clear. Some droplets of water remained in parts of the circuit even after the removal of water from the bottom of the reactor by a syringe.

1.3 reaction trial 2

The second trial aimed at 48 mL reaction mixture, which was enough to stirr and fill the circuit even at the beginning. The continuous addition of monomer and initiator was started manually from the pump interface.

The reaction protocol could be followed without problems, but the beam had to be shut off for manual addition of further additives (sodium acetate and antifoam agent at the beginning; sodium isoascorbate and tert-butylhydroperoxide at the end), starting the continuous addition and changes in temperature of the heating tape.

In the end, the sample was allowed to cool by shutting off all heat sources and measured at rest during cooling.

2 results

2.1 first reaction trial

Data were acquired every 2 minutes with listmode activated. We observed an increase of intensity ($\sim q^{-4}$) soon after the initial addition of monomer and initiator (KPS). Intensity increased over the course of ≈ 1 h at 75 °C when it was noted that further addition hat not occured due to some error in the electronic communication to the syringe pump. Although the addition was started again from the syringe pump interface (without Nomad), only vinyl acetate was added, resulting in further increase of the Porod scattering presumably from monomer droplets.

2.2 second reaction trial

Data were acquired every two minutes and transmission after five measurements each. Listmode was activated.

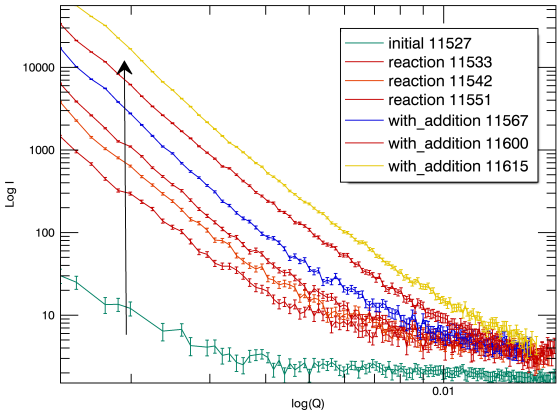

Figure 2: 1st reaction: increase of q^{-4} scattering.

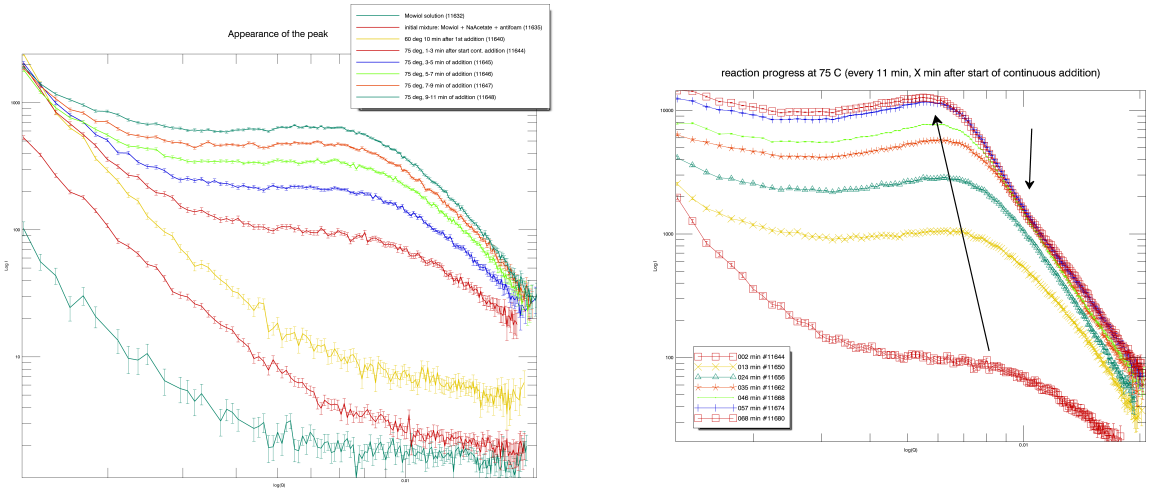

Figure 3: 2nd reaction: Appearance and growth of latex particles with structure factor (75 °C).

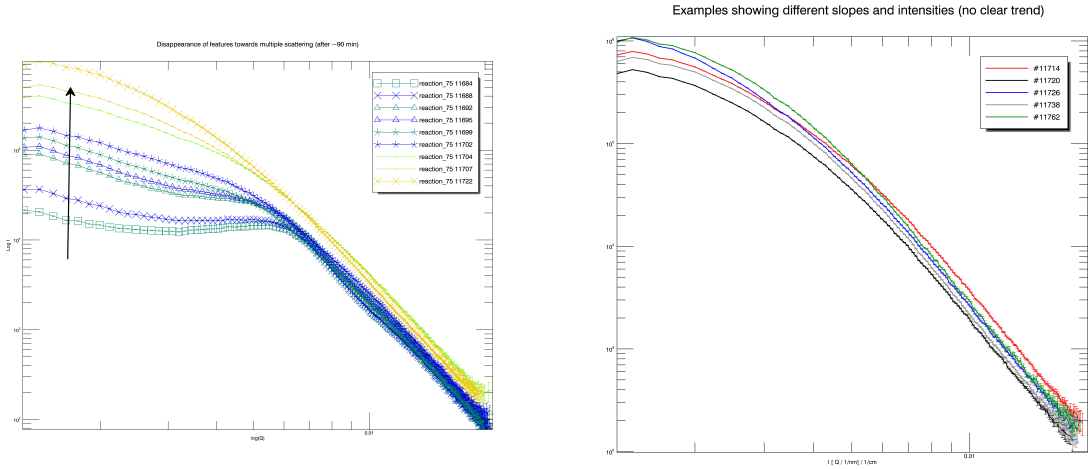

Figure 4: 2nd reaction: Appearance of signs of multiple scattering and its changes (75 °C).