**Online monitoring of emulsion polymerization by SRS and Raman spectroscopies**

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**Highlights**

* Monitoring of emulsion polymerization with NIR and Raman spectroscopies
* Spatially resolved spectroscopy (SRS) for heterogeneous process
* Prediction of the polymer fraction and particle size with PLS

**1. Introduction**

Online monitoring of polymerization processes is essential to ensure the process security, product quality and process productivity by allowing process control and reconfiguration of the operating conditions when necessary. Monitoring of emulsion polymerization is particularly challenging due to the multiphase nature of the reaction. In this kind of systems, it is important to monitor the different concentrations (monomer, polymer, and surfactant) as well as the key product properties, like the polymer molecular weight or the particle size. Currently, calorimetry constitutes the primarily online technique used for monitoring of polymerization processes. Spectroscopies, like Raman and Near Infrared (NIR), are becoming widely employed online. Based on NIR spectroscopy, the Spatially Resolved Spectroscopy (SRS) has been developed to study heterogeneous media and obtain information related to the light scattering and thus the particle. SRS and Raman spectroscopies are investigated in this study to evaluate the potential of SRS to predict the polymer fraction and the particle size online in emulsion polymerization.

**2. Methods**

A batch polymerization period was first conducted, during which polymer particles were nucleated, followed by a semi-continuous reaction to allow their growth follows. The reactions were done in a 1 L reactor with mechanical stirring, between 300-400 rpm. First, the surfactant was dissolved in water and degassed using nitrogen and the mixture was heated to 70 °C using a thermostated bath with silicon oil. The co-monomer mixture was then added and the polymerization was initiated by adding the initiator, KPS. During the reaction, the nitrogen gas flow was moved out of the reaction medium to the top of the reactor to maintain an atmosphere saturated with nitrogen. At the end of particle nucleation, the semi-continuous phase was started by adding the monomer mixture under starved conditions. Samples were collected at specific time intervals to measure the solids content (SC, i.e. mass fraction of solid) using a thermobalance and the particle size using dynamic light scattering (DLS, Malvern Nano ZS®).

Throughout the reaction, online analysis was provided with Raman spectroscopy using an OceanOptics QE65000 and an immersion probe with a wavelength laser excitation of 785 nm. SRS spectroscopy, based on NIR spectroscopy, from Indatech-Chauvin Arnoux was used with angles of measurement to the light source at 180° (for transmission), 175°, 170° (for scattering) and 30° (for backscattering).

**3. Results and discussion**

The results presented in the following figure show the prediction of masse fraction of polymer by both the SRS and Raman spectroscopy. Extensive data analysis combined with multivariate calibration using Partial Least Square (PLS) regression was necessary to exploit the online data. The figure shows that the prediction of the polymer fraction can be established by both spectroscopies and fits well with the reference measurement made offline on the thermobalance.



**Figure 1.** Polymer fraction estimated by gravimetry, Raman and SRS.

The prediction of the diameter of particles was also investigated by both spectroscopies. The SRS was more adapted for this study than Raman spectroscopy mainly due to the specific probe configuration that makes it particularly sensitive to light scattering due to particles and is therefore sensitive to the particle size distribution.

**4. Conclusions**

Online monitoring of the polymer fraction and the diameter of polymer particles was established by using Raman and SRS spectroscopies. Both methods gave rather good predictions of the chemical information, like the polymer fraction, but the SRS was more suitable for the prediction of physical parameters like the mean diameter of particles.

**References**

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