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Report on Raman spectroscopic monitoring of emulsion polymerisation with particle size and morphology information

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1 Introduction

The application of Raman spectroscopy for characterisation of the polymerisation process has been investigated. Knowing the concentration of monomers in the reactor during the polymerization is important for several reasons. First, this measurement can be used for model predictive control in order to control the reaction kinetics. Kinetic models use concentration information for the determination of reaction rates. If concentrations are available directly in real time, these model states do not have to be estimated, e.g. by means of calorimetry. It has been shown earlier that using concentrations obtained by Raman spectroscopy leads to better results compared to the case when concentrations are estimated from the calorimetry data [1]. Second, the amount of free monomers is critically important at the industrial scale due to increased safety issues. As polymerisations are usually strongly exothermic reactions, a cooling failure together with high amounts of free monomers may lead to catastrophic thermal runaways.

2 Conducted experiments

The reaction experiments for collecting the Raman data were conducted at the University of Cambridge. In total, four reaction experiments with inline Raman monitoring have been conducted, all using the same recipe. The experiments are labled UC4-7. The recipe includes in total five monomers. The main monomers are styrene, butyl acrylate and methyl methacrylate. In addition, small amounts of acrylic monomers (acrylic acid and acryl amide) are used. The recipe has constant feeds and two different monomer mixtures are fed subsequently. This is referred to as first and second polymerisations. The period of time following the end of the second addition is called post-polymerisation.

2.1 Offline characterization

All samples were analysed by gravimetric analysis to obtain values of the overall conversion and solid content, gas chromatography (GC) for monomer concentrations, dynamic light scattering (DLS) for particle size and transmission electron microscopy (TEM) for particle size and morphology evolution. The samples were collected every 15 minutes during the feeding period and 30 minutes during the post polymerisation. Calibration experiments for Raman spectroscopy for individuals and mixed monomers and water were conducted at various temperatures.

2.2 Setup of Raman device

A Horiba Jobin Yvon LabRAM HR Raman with 16 mW 532 nm laser was used. The resolution was about 4 to 6 cm^{-1}. Due to geometric constraints, the Raman probe could not reach the reaction mixture from the start of the reaction. Only as the level in the reactor increased during feeding, the probe reached the reaction mixture. Therefore, only a later part of the first polymerization could be observed. The second polymerisation could be observed well.

Figure 1. An image of the 500 mL reactor at UCAM during a semi-batch polymerization experiment, with an immersion Raman probe.

For the experiments UC4-6, the sampling rate of the Raman device was set to 5 minutes. In the experiment UC7, 3.5 minutes sampling interval was used. The data was obtained as measured and no spectral correction was applied.

3 Analysis of monomer concentration based on Raman signal

The used recipe runs the reaction under starved conditions meaning that only small amounts of free monomer outside the particles are present. In the first polymerisation, the conversions are very high, well above 95% for all the samples taken, see Figure 2. The second polymerization has a slightly higher concentration of free monomer but the conversions are still above 80% most of the time. The low concentration of monomers in semi-batch operation makes it difficult to measure concentration by Raman in comparison to a batch operation where the monomer is abundant in the beginning [3].

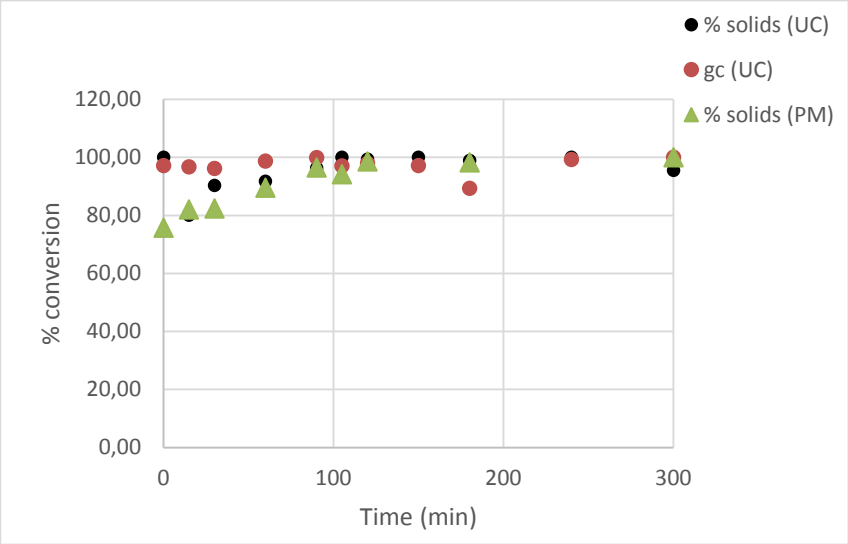

Figure 2. Instantaneous conversion and % solids during polymerization experiment UC4. 'UC' corresponds to the data obtained at UCAM. 'PM' corresponds to an experiment with the same recipe performed at Polymat.

3.1 Data analysis by means of identifying peaks associated to species

In Figure 3, the evolution of the obtained Raman spectra over time is shown. The spectra shown are normalised by a standard normal variation, meaning the data has a standard deviation of 1, to improve the comparability. Generally, it can be seen that peaks appear and disappear over time, indicating that reactions occur. The first polymerisation does not show strong Raman scattering species as compared to the second polymerisation. The peak associated to styrene at 1000cm $^{-1}$ clearly indicates the start of the second copolymerisation. During the first 50 minutes, the obtained spectra show only very few peaks that are corrupted by the measurement noise. In Figure 3, strong peaks of double bond at around 1600 cm^{-1} are observed. This indicates that the conversion had dropped, which was confirmed by the GC measurements.

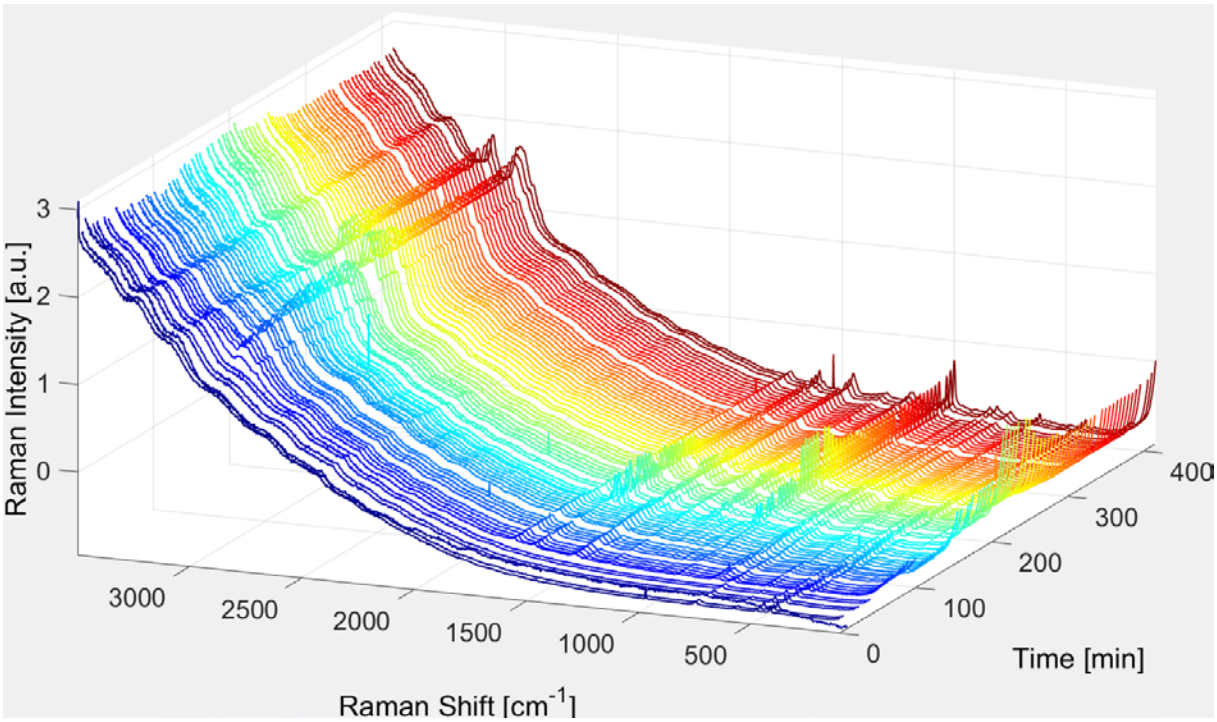

Figure 3. Raw Raman data from experiment UC5.

3.2 Indirect hard modelling

Indirect hard modelling aims at explaining the measured spectra by a weighted sum of the raw component spectra [2]. Therefore, the pure component spectra must be known. Due to the low concentrations of the acrylic monomers, the detection was found to be infeasible for offline GC and online Raman measurements.

3.2.1 Construction of parametric models for spectra

For the monomers a series of calibration experiments were conducted with pure monomers and mixtures of monomers measured at 80 ºC and in a few cases at different temperatures to check the temperature dependence of the spectra. A summary of GC monomer data is given in Table 1. Based on these spectra, parametric models were constructed using Peaxact (v. 4.0.0, S-PACT GmbH, Aachen, Germany). The spectral range 110 to 3000 cm^{-1} was used. The noisiness was reduced by smoothing by a moving window approach using a width of five samples.

Table 1. A summary of GC monomer concentrations for the Raman calibration samples.

Concentrations (v/v)				
Butyl Acrylate	Methyl Methacrylate	Styrene	Allyl Methacrylate	Acrylic Acid (*)
0.490	0.000	0.000	0.000	0.510
0.027	0.000	0.000	0.000	0.973
0.076	0.000	0.000	0.000	0.924
0.514	0.000	0.000	0.000	0.486
0.038	0.624	0.000	0.000	0.337
0.131	0.500	0.000	0.000	0.368
0.228	0.471	0.000	0.000	0.301

0.243	0.502	0.000	0.000	0.255
0.287	0.400	0.000	0.000	0.313
0.282	0.376	0.000	0.000	0.342
0.287	0.374	0.000	0.039	0.299
0.000	0.135	0.000	0.560	0.305
0.000	0.231	0.000	0.458	0.310
0.000	0.345	0.000	0.349	0.306
0.156	0.295	0.000	0.308	0.240
0.249	0.226	0.000	0.238	0.286
0.241	0.209	0.000	0.230	0.321
0.000	0.284	0.000	0.000	0.716
0.000	0.536	0.000	0.000	0.464
0.000	0.045	0.000	0.000	0.955
0.000	0.000	0.000	0.000	1.000
0.000	0.000	0.000	0.000	1.000
0.026	0.000	0.666	0.000	0.308
0.030	0.000	0.846	0.000	0.125
0.242	0.000	0.743	0.000	0.015
0.256	0.000	0.421	0.000	0.323
0.697	0.000	0.000	0.000	0.303
0.728	0.000	0.000	0.000	0.272
0.586	0.000	0.000	0.000	0.414
0.580	0.000	0.000	0.000	0.420
0.000	0.615	0.000	0.000	0.385
0.000	0.575	0.000	0.000	0.425
0.000	0.480	0.000	0.000	0.520

The copolymer spectra were not available as pure components. For IHM, a crucial point is the assumption that the measured spectrum is the sum of weighted pure component spectra. Therefore, it is necessary to provide pure component spectra for all main species in the mixture, i.e., monomers and polymers. The pure monomer spectra were obtained in offline Raman experiments. The polymer spectra had to be reconstructed from the reaction spectra. For the first copolymer, full conversion was assumed just before feeding the second monomer mixture. It was assumed that only the copolymer and water are present in the mixture. Initiator, crosslinker and emulsifier were neglected due to their low weight fractions. The copolymer spectrum was reconstructed by fitting a hard model additionally to a water spectrum. The assumption is that the model of a copolymer and water create the mixture spectrum.

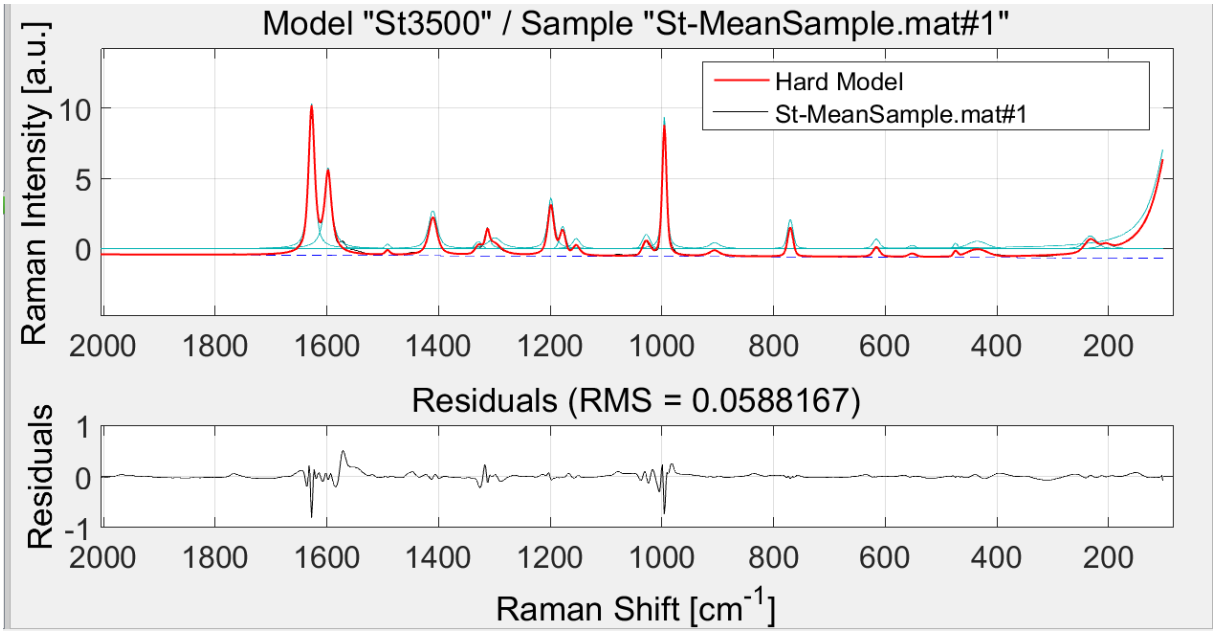

Figure 4. Spectral fitting of styrene using Voigt functions with Peaxact.

In Figure 4 the fit of the styrene monomer with peak-shaped functions is shown together with the measured spectrum. It can be seen that the spectral model and measured spectrum are in fairly good agreement. There is a fitting error at the bands around 1600 and 1000 cm^{-1}. Increasing the peak height of the underlying spectral Voigt model decreases the error at the peak value. However, the overall fitting error increases and the fitting routine prefers to have these errors. An explanation could be that the measured peaks are not symmetrical around their peak value, but the used basis functions are symmetric.

3.2.2 Calibration and prediction of the IHM model

The IHM model was calibrated against the available GC data. The gravimetric data had not been used due to the large difference observed when compared to the GC data and the observation of a reduction in solids content at the end of the polymerisation, which is not justifiable and is likely a measurement artefact. The origin of the artefact may be explained by coagulated polymer that was observed at the end of reaction.

Due to the very low weight fractions of the monomers, small absolute errors lead to very large relative errors. The average weight fraction of butyl acrylate and methyl methacrylate is found to be only about 0.2 wt% during the polymerization. Due to the comparatively large number of different species in the reaction mixture, namely three monomers, two copolymers and water and their spectral similarity, no good fit was yet obtained.

One problem may be that due to the measurement noise, the spectral model fit does not take into account the important peaks but a least squares error of the considered

wave length interval. For a similar system, IHM resulted in better estimates of the concentration [3]. In [4] good agreement for a microgel system using IHM was found.

3.3 Partial least squares models for concentrations

In addition to the more physically-motivated IHM models, a data-driven model using partial least squares (PLS) was also investigated. It was found that the PLS model predicted the concentrations well. The predictions of the PLS model benefit from the fact that all conducted experiments were based on the same recipe. The ability to extrapolate is, however, very limited since a PLS model describes only the variance it was trained with. For online optimizing control, it is necessary to extrapolate since new operating procedures may be found. Faster feeding rates, varying reactor temperatures and abrupt changes in the feeds may lead to operating regions that are outside of the trained data. Therefore, it would be better to have data analysis methods based on physical principles than on statistical data fitting.

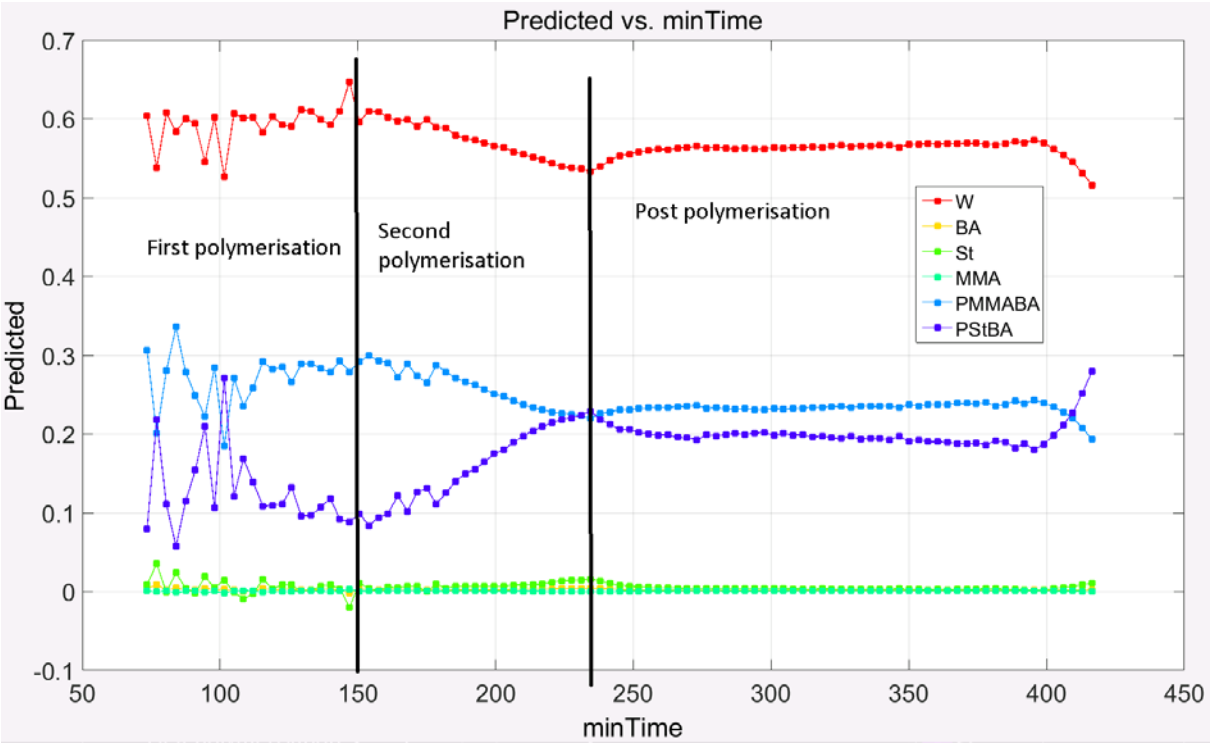

Figure 5. Weight fraction prediction by PLS model.

In Figure 5, the predictions for the weight fractions for the polymerisation UC7 are shown. It can be seen that the first polymerisation is harder to observe than the second polymerization. This is most likely due to the presence of styrene as strong Raman scattering species in the second polymerization.

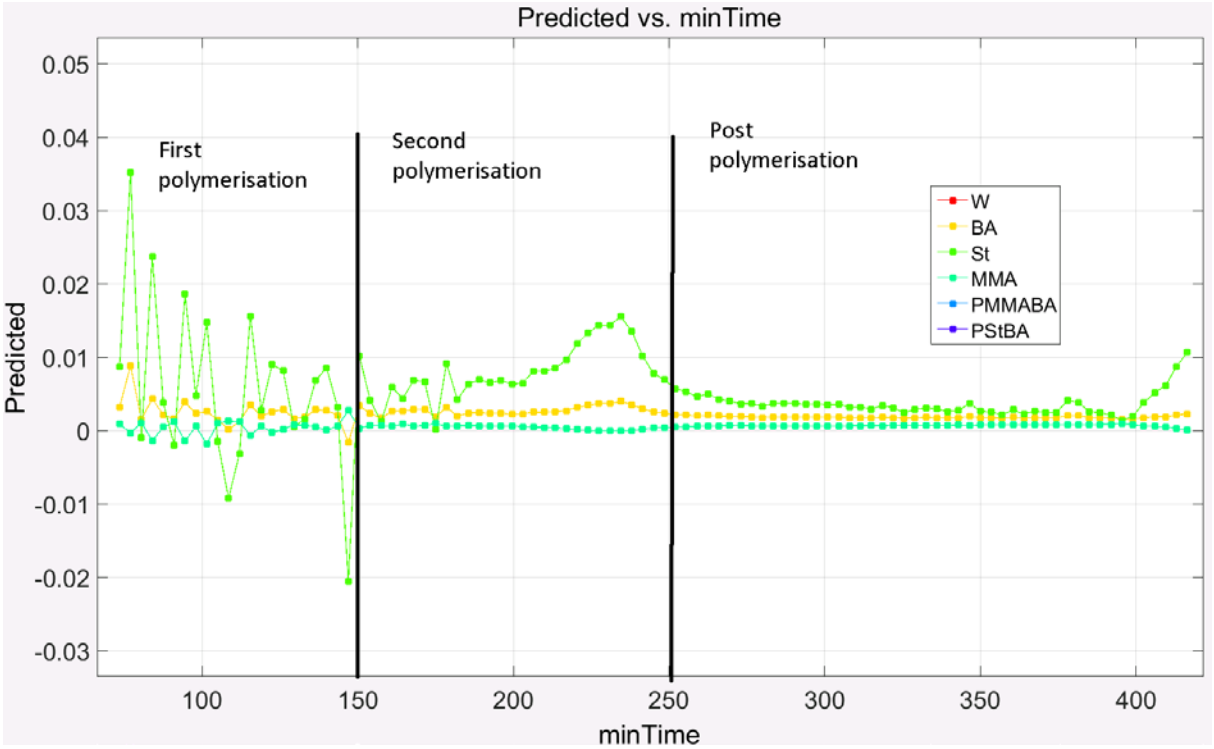

Figure 6. Monomer weight fractions predicted by PLS model.

In Figure 6, only the monomer weight fractions are shown. It can be observed that styrene is misidentified during the first polymerisation. Again, the second polymerization is in good agreement with the offline GC data. In the post polymerization, the monomer fractions are overestimated. At the very end, the artefact of increasing styrene weight fraction can be observed.

4 Particle size determination

One of the quality parameters for latex is the particle size distribution. One of the goals for this project is to obtain an agreement of the particle size between the online Raman measurements and offline DLS or TEM data.

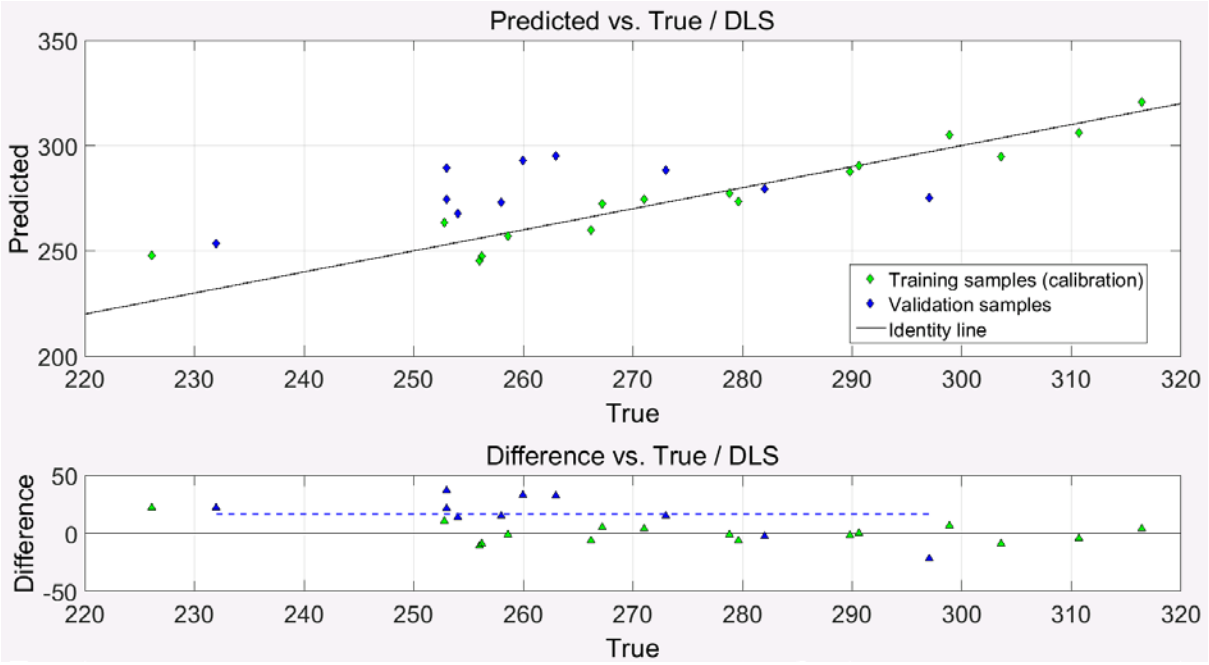

Figure 7. Particle size prediction for experiment UC7 with training data from UC5 and UC6.

In Figure 7, the plot for the validation of the particle size for the experiment UC7 is shown. It can be seen that the predictions are on average within 10% of the reference dynamic light scattering (DLS) measurements. It must be noted that the experiments are based on the same recipe, from which the statistical PLS model benefits.

5 Morphology

One goal of the RECOBA project is to control the evolution of particle morphology. As an example, Figure 8 shows a non-equilibrium morphology of particles with the final mean particle diameter of 300 nm obtained by transmission electron microscopy. The features of morphology in this case are (i) the overall particle diameter and (ii) the size and (iii) number of the clusters that make up the particle. It may further be desired to identify composition of the clusters. In other morphologies, such as core-shell, the features would include the sizes of (i) core and (ii) the shell with respect of (iii) the overall particle size and their compositions.

At the current state of development of Raman as *in situ* sensor for emulsion polymerisation only one morphology characteristic – the overall particle size – could be determined on the basis of statistical models, *i.e.* strictly within a single polymer recipe for which the calibration model had been developed. It is not feasible to identify the sub-structure morphological features from Raman measurements and this

limitation is restricting the use of Raman sensor for monomer concentration and particle size determination.

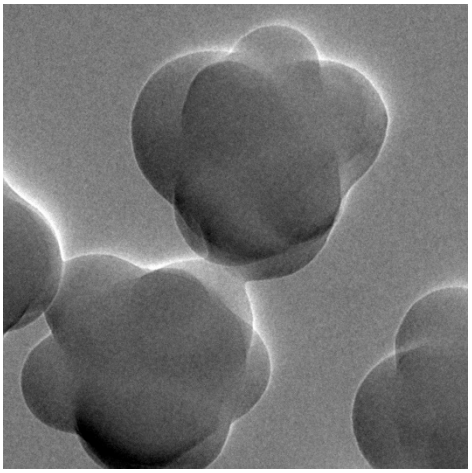

Figure 8. An example of non-equilibrium morphology obtained in polymerization UC4.

6 Conclusions

Four data-rich polymerization experiments were conducted at the University of Cambridge in order to generate the necessary information about the evolution of particle size and morphology during a complex two-stage semi-batch emulsion polymerization. The monomer concentrations for these reactions can be predicted using a statistical PLS model. This implies the opportunity for closed-loop control of residual monomer concentration, which is critical in the manufacture of particles with a specific morphology.

Using the indirect hard modeling method (IHM) did not result in satisfactory predictions of concentrations. However, this is likely to be due to the limited set of calibration spectral data.

Therefore, for the continuation of work on Raman in situ sensor for control of emulsion polymerization processes the following lines of development will continue:

1. Generation of a reliable calibration model for predicting residual monomer concentrations in semi-batch co-polymerisation, specifically for the system to be used in demonstration (spectrometer, probe, reactor, polymerization recipe).
2. Development of a hybrid physical-empirical model, e.g., based on IHM, for semi-predictive rather than statistical calibration model for residual monomer concentrations.
3. Improving the statistical calibration model for particle size determination.

7 Bibliography

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