PAT SEQUIP AND

EMULSION POLIMERIZATION APPLICATIONS

Kinetics of heterogeneous reactions depends critically on phase boundaries of constituent phases. In cases of liquid-liquid heterogeneous systems, droplet size distribution is one of the most important parameters to follow and therefore feedback controls of dynamic processes. This application will demonstrate cases of emulsion polymerization of which dynamic variations in term of droplet/particle population are observed in real time and inline via a PAT sensor of Sequip. The robustness and sensitivity of this PAT tool will assist rapid development of efficient dispersion processes since the multi capture signal analysis technology of PAT Sequip is fully capable to capture dynamic behavior of liquid-liquid heterogeneous systems.

1. An organic oil/water system:

A dispersion process of a special oil (solvent for polymerization process) in water is in real time observed via an experiment setup as shown in Figure 1. Measurement was carried out at ambient temperature. A stirrer Ultra-Turrax was used.

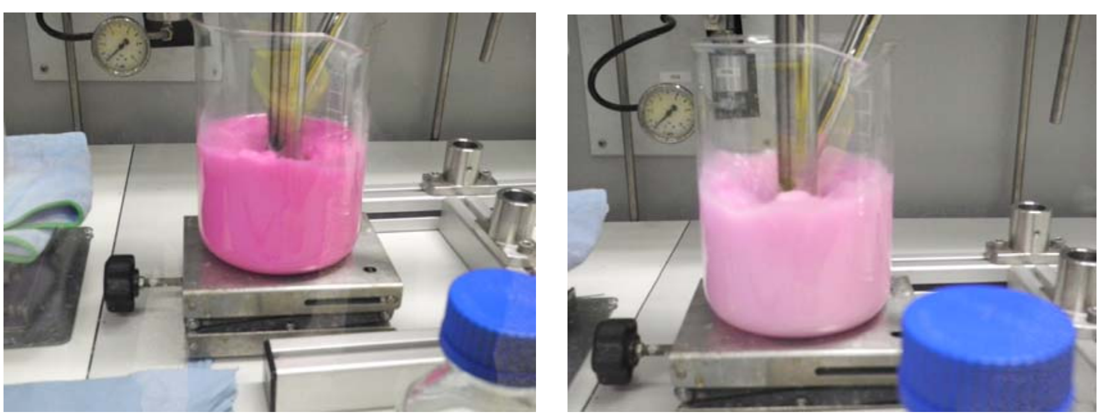

Figure 1*: Emulsion of oil in water after changing pH value to 12. Measurement sample contains indicator phenolphthalein (left and right photos for short and long mixing periods, respectively).*

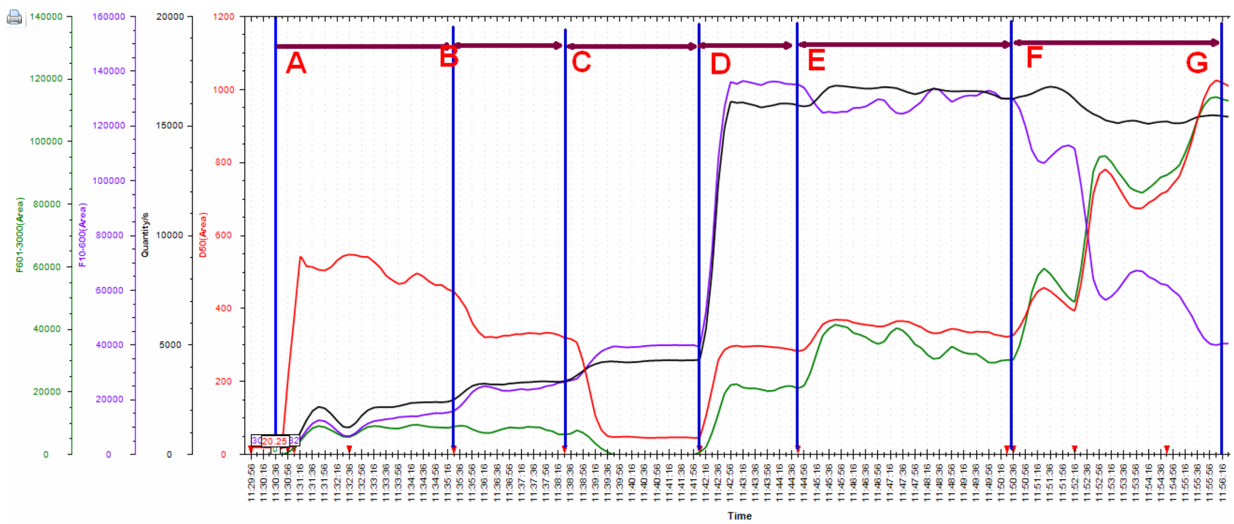

***Figure 2**: Dispersion process is observed trough variation of total count (Quantity, **black**), D50 (**red**), a small fraction F1-600 (**violet**), a bigger fraction F601-3000 (**Green**). All data were area-weighted.*

The measurement results are presented as Figure 2. Relevant events are interpreted in Table 1.

***Table 1**: Relevant events of dispersion process*

No	Process	Event	Interpretation
1	A	Start stirring • Ultra-Turrax • 3000 rpm	All parameters significantly increase (e.g. D50(Area-weighted), Quantity, Fractions) due to droplet formation via mixing effects of two immiscible liquids.
2	A→B	Keep stirring	General tendency: large droplets were divided into small ones under shear force. Therefore: • Number of count increasing. • Small fraction increasing

			• Large fraction decreasing • D50 decreasing
3	B	Increase shear force • Ultra-Turrax • 4000 rpm	Increasing shear force leads to breakage of bigger droplets. More fine droplets are formed. • Number of count increasing. • Small fraction increasing. • Large fraction decreasing. • D50 decreasing.
4	B➔C	Keep stirring at 4000 rpm	A new equilibrium is quickly established. Emulsion remains good homogeneity.
5	C	Add 20 mL NaOH 3.5%	Increased pH to 12. The stability of colloidal is affected by pH value since OH^- anion can change zeta potential of colloidal. Result: droplet size is getting smaller. • Number of count increasing. • Small fraction increasing. • Large fraction decreasing. • D50 decreasing.
6	C➔D	Remain emulsion C with constant stirring rate 4000 rpm	Fast respond, a new equilibrium is quickly established. All signals are getting stable levels.

7	D	Add phenolphthalein	Significantly increasing in all data fields. Phenolphthalein can change the emulsion state. More materials of oil phase disperse into water phase. • Number of count increasing. • Small fraction increasing. • Large fraction strongly increasing. • D50 increasing.
8	D➔E	Remain emulsion D with a stirring rate of 4000 rpm	A new equilibrium is established.
9	E	Add again NaOH	System change against increasing of pH.
10	E➔F	Remain emulsion E with a stirring rate of 4000 rpm	Establish a new equilibrium which tends to create more fine droplets.
11	F➔G	Increase stirring rate to 10000 rpm	The system is interrupted by air bubble and cavity due to violently stirring. The events are captured by PAT Sequip as seen in Figure.

2. Polydispersed phases

This measurement is carried out with a multi dispersed system. A water-oil-polymer system is premixed in a mixer with different frequencies. Then, this emulsion is bumped into a special measurement cell as shown in Figure 3. The PAT Sequip sensor is set with an angle in order to increase the measurement quality.

Figure 3: *Experimental setup for the measurement of a water-oil-polymer system (left picture). Then, this emulsion is changed into a 250 mL glass beaker (right picture).*

The measurement result shows multi-modal behavior of the water-oil-polymer dispersion system. Big droplets are visible in Figure 3 (right).

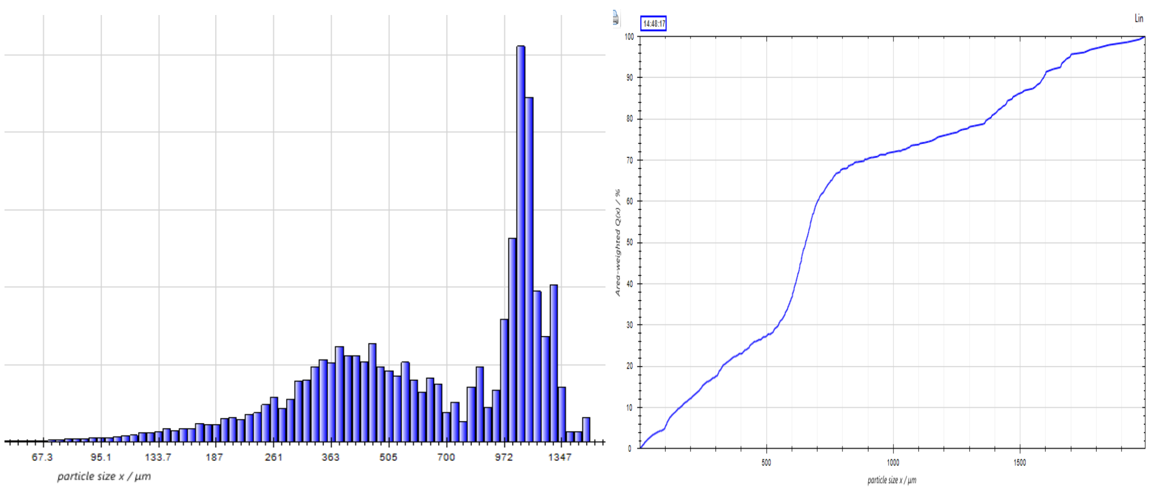

Figure 4*: Multi-modal distribution is observed for multi-dispersed system water-oil-polymer. Left and right diagrams represent histogram and cumulative distributions.*