

Supercritical Heat Flow Reaction Calorimetry: A Comprehensive Tool for Monitoring Reactions in Supercritical Fluids

Charalampos A. Mantelis, Thierry Meyer

Ecole Polytechnique Fédérale Lausanne, Institute of Chemical Sciences and Engineering, Group of Macromolecular Processes

The technique of supercritical heat flow reaction calorimetry is the fusion of three scientific fields, namely of the reaction calorimetry, the supercritical fluids (SCFs) and polymer science. A combination of characteristics from all three and the comprehension of the results of their implication are essential.

The first step in the development of supercritical reaction calorimetry was the identification of the particularities linked to the physical state of supercritical fluids. The source of these particularities is primarily the fact that the entire reactor volume is occupied by the reaction mass. This observation not only demanded further development of the apparatus but also identified the points where special attention has to be paid during calorimetric calculations and the effect of using correct reaction mixture properties values.

Based on the above, the study is taken one step further by carrying out a term-by-term analysis of the heat flow equation during the free-radical dispersion polymerization of methyl methacrylate (MMA) in $scCO_2$. The overall heat transfer coefficient between the reactor and the temperature regulating jacket is found to be the most important parameter, therefore several approaches were studied to either measure or calculate its variation during the reaction and for the first time the temperature oscillation technique was applied with SCFs. This variation is relatively strong due to the changing properties of the reaction mixture. Furthermore, it is shown that the injection of additional reactants can considerably disturb the system, unless the pressure change rate is kept at very low levels. Finally, a significant improvement of the monitoring results is achieved and reveals the correct reaction evolution.

This improvement is apparently more important during the initial stage of the polymerization reaction, where the polymer particles are formed through a coagulative nucleation phase. Previous studies have shown that only the number density of the particles formed increases and their size is constant but for the first time the heat released by the reaction during this phase was measured.

Furthermore, a series of experiments was conducted to isolate the effect of the pressure on the reaction evolution. It is found that the pressure affects the partitioning of the monomer between the continuous and the polymer-rich phase and consequently the reaction rate. Under marginal dispersion stability conditions the heat rate can be seen to decelerate just before the gel effect becomes predominant. These observations in combination with previously reported comprehensive mathematical models led to the formation of a theoretical explanation, which also explains the pressure variation during the polymerization. The pressure difference between the final and the initial pressure is found to be positive when the reaction is carried out at relatively low pressures and negative at higher reaction pressures. Furthermore, the point of transition depends on the composition of the initial reaction mixture and the reaction temperature.