PRECIPITATION POLYMERIZATION USING $scCO_2$ IN A CONTINUOUS MINIATURIZED TUBULAR REACTOR

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ABSTRACT

Supercritical carbon dioxide ($scCO_2$) has emerged as a viable "green" alternative to organic solvents for polymer synthesis and processing as carbon dioxide is inert, abundant, inexpensive, nonflammable and nontoxic. At temperature and pressure above its critical point (Tc = 31.1 °C and Pc = 7.38 MPa), it has unique properties such as liquid-like density, gas-like viscosity, and "zero" surface tension. These properties can be tuned by varying the pressure or the temperature. Besides, miniaturized continuous processes gain much attention as a promising alternative to conventional lab-scale reactors. They enhance the control of reaction conditions which is essential to characterize a chemical reaction. Furthermore, they improve safety and increase product yield.

In this work, a high pressure co-axial capillary microreactor has been designed and used in several reaction conditions (up to 80 °C and 25.0 MPa). First, technical challenges concerned the control of the very low flow rates of both liquid and $scCO_2$ fluids in such small scales. Then, the phase behavior of the reaction mixture (acrylic acid (AA), $scCO_2$, water, co-solvent) has been investigated using an *in-situ* FTIR method. Complete phase diagrams for these mixtures have been established by combining the literature data (if any)[1] and our experimental results. The partition coefficient of each component in biphasic system has been determined. Then, precipitation polymerizations of AA using $scCO_2$ as solvent were performed either by using homogeneous or segmented flows, i.e. by adding water, in the microfluidic device. It has been showed that good yield of low molecular weight of poly(acrylic acid) can be obtained easily without plugging the system : for instance, 20 vol.% of 10:90 weight ratio of AA:water in $scCO_2$, the molar conversion was 65 % and Mw = 50 000 g/mol in 1h00 at 75 °C.

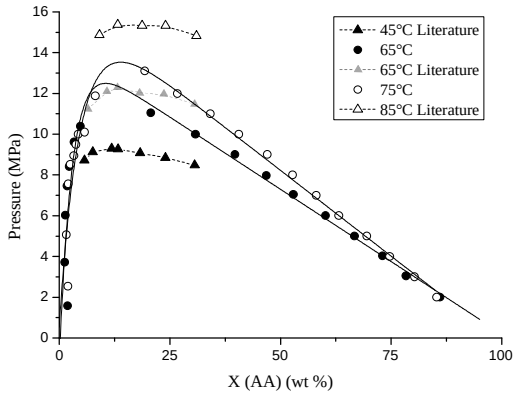

Fig. 1: Phase diagram of binary mixture: acrylic acid (AA) in carbon dioxide

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Reference:

[1]European Patent EP0301532 A2, 1988.