BASIC CHEMICAL DATA FROM RADICAL COPOLYMERIZATION USING DROPLET-BASED MILLIFLUIDICS

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ABSTRACT

A conventional batch reactor can be miniaturized to the size of a droplet of a few microliters or less by using milli- or micro-fluidic devices.¹ Indeed, one can generate a sequence of monodisperse droplets, i.e. individual micro batch reactors, containing well-controlled amounts of reagents due to the flow rates applied upstream of the droplet generator. Chemicals are thus compartmentalized within droplets since there is no exchange through the inert carrier fluid. Furthermore, using droplets allows one to control exactly the residence time, i.e. the time of the reaction, as well as improving heat transfer thanks to their high surface-to-volume ratio. Finally, using droplets induces a correspondence between space and time, i.e. all droplets reaching a particular position along the channel will have the same time of reaction and hence the same composition. Coupling a non-intrusive analytical system thus allows fast and easy in-situ determination of concentrations.



Fig. 1: Concentrations of acrylic acid (AA) and sodium styrene sulfonate (SSNa) vs. time (total concentration is 2.8 mol.L⁻¹ for a 80/20 wt% mixture at 70 $^{\circ}$ C

The aim of this presentation is to show how these tiny droplets can be easily generated "on a bench" and be useful for the chemist in order to obtain basic chemical data from rather fast or exothermic reactions, in particular in radical copolymerization.² Examples of the determination of kinetics and reactivity ratios from hydrophilic comonomers at high concentration and temperature, using droplet-based millifluidics coupled to confocal Raman microspectrometry, will be presented. Off-line analysis by SEC coupled to a triple detection will also be discussed according to the effect of this miniaturized process on molecular weights and polydispersity of the polymers.

References

¹ Lorber, N.; Sarrazin, F.; Guillot, P.; Panizza, P.; Colin, A.; Pavageau, B.; Hany, C.; Maestro, P.; Marre, S.; Delclos, T.: Avmonier, C.: Subra, P.: Prat, L.: Gourdon C.: Mignard E. Lab Chip 2011, 11, 779.

² Lorber, N.; Pavageau, B.; Mignard E. *Macromolecules* **2010**, *43*, 5524.