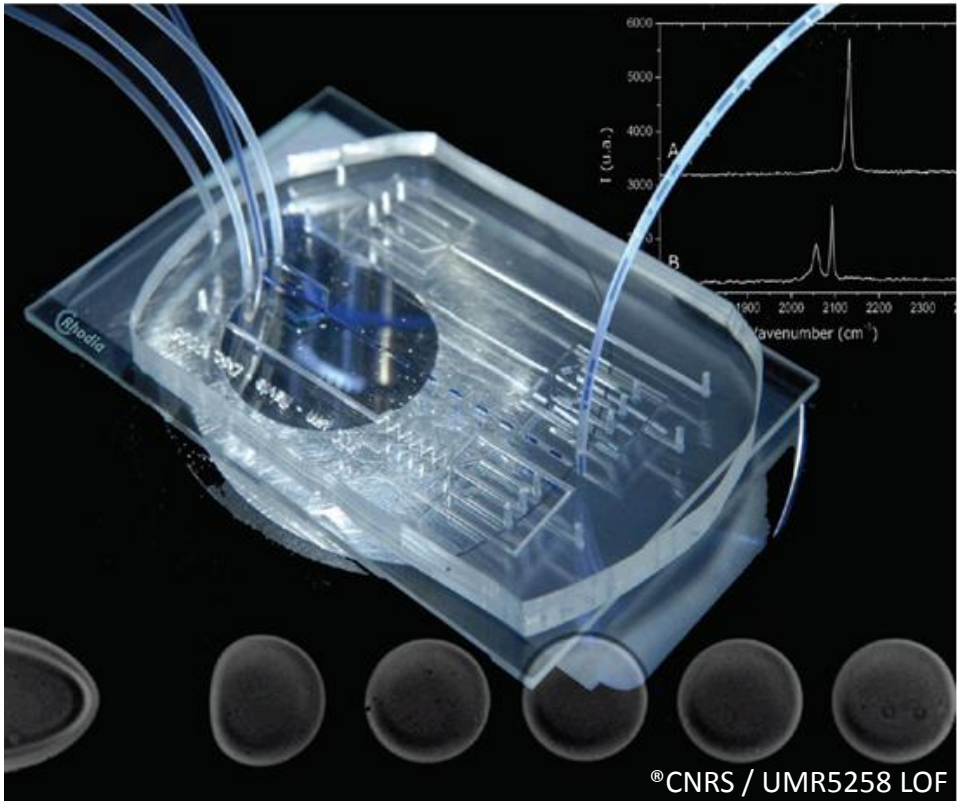
Radical (Co)polymerization Kinetics Obtained From Droplet-Based Microfluidics



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asking more from chemistry®

Outline

Miniaturized tools - Process & Analysis

Introduction

- Concept of droplet-based microfluidics for chemistry
- Coupling *inline* analytical tools

Polymerization reactions within droplets

Methodology

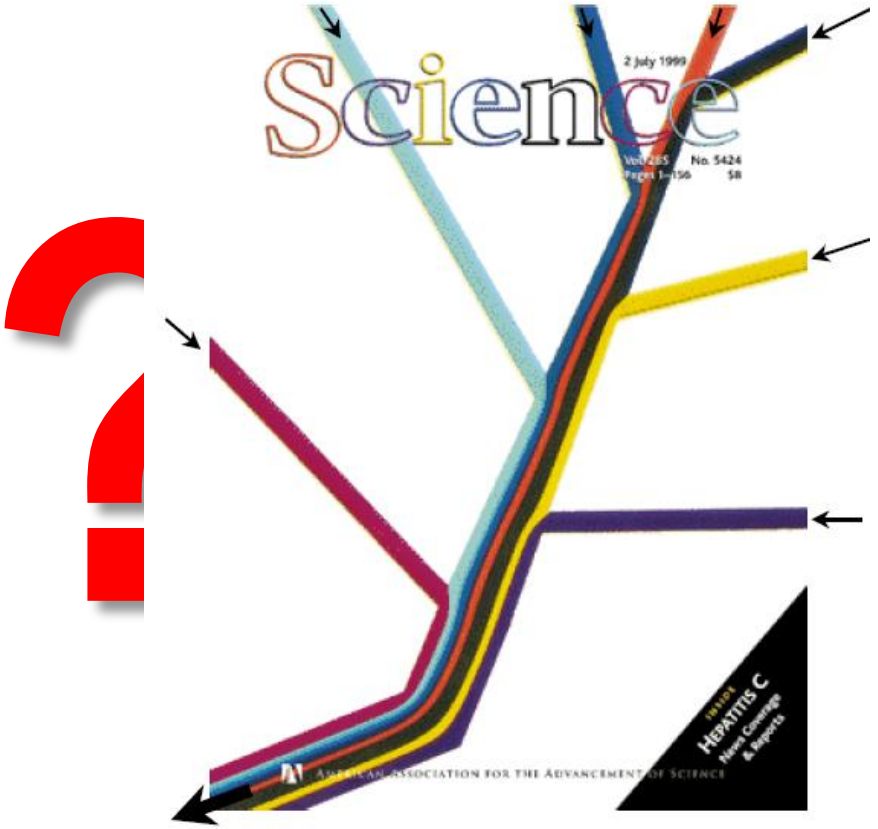
- Polymerization of acrylic acid
- Copolymerization of acrylic acid with Sodium Styrene sulfonate

Conclusion and outlooks

Radical Copolymerization Kinetics Obtained From Droplet-Based Microfluidics

- **Microfluidics**

  ↳ *The science and technology of systems capable to handle fluids, and where at least one of their characteristic dimensions is of the micrometer*

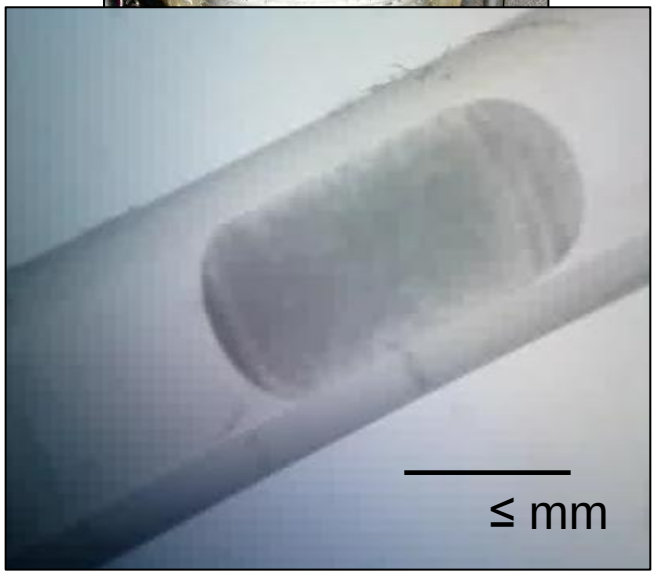


At small length scales, transport phenomena can be precisely controlled:

Mixing - Thermal transfers - Concentrations - Flows

Radical Copolymerization Kinetics Obtained From Droplet-Based Microfluidics

Size of the reactor



Mass & heat transfer

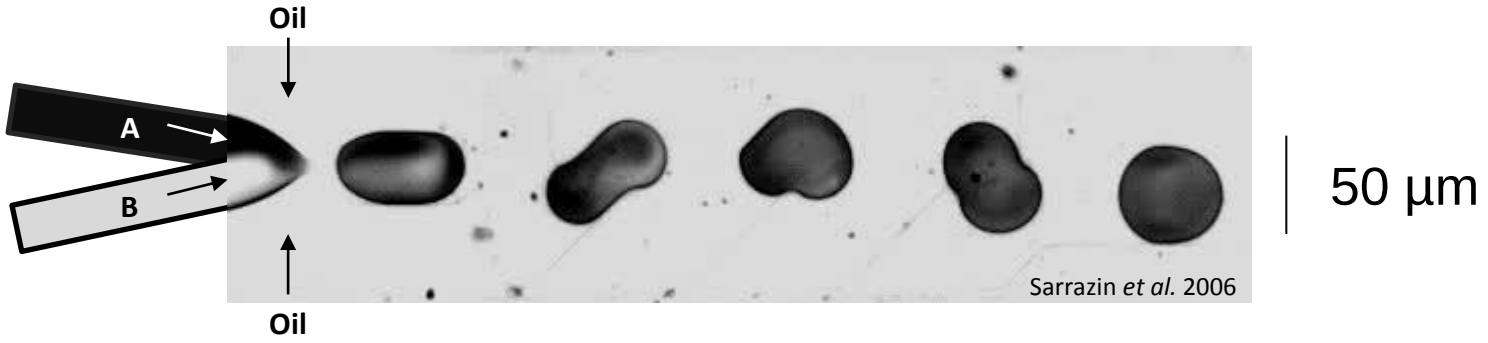
Lab Tools: Droplet-Based Microfluidics

✓ Importance of the size of the microreactor

	micro		milli	batch
	50 µm	**500 µm**	**1 mm**	**19 cm**
	0.3 nL	**0.3 µL**	**3 µL**	**3 L**
Flow-rates	0.1 mL/h	2 mL/h	6 mL/h	-
Surface/Volume	30000	3000	1500	10
Residence time	30 s	1 h	> h	> h
Mixing time	10 - 60 ms	0.4 - 1.5 s	3 -10 s	6 s
Reactions				
fast	++	+	-	-
slow	-	+	++	++
sampling	-	-	++	+
exothermic	++	++	++	-

Droplet-Based Microfluidics

✓ Microfluidics : a miniaturized continuous approach



Droplets = independent chemical microreactors

Analysis = *inline* monitoring in 'real time' by using non-intrusive techniques

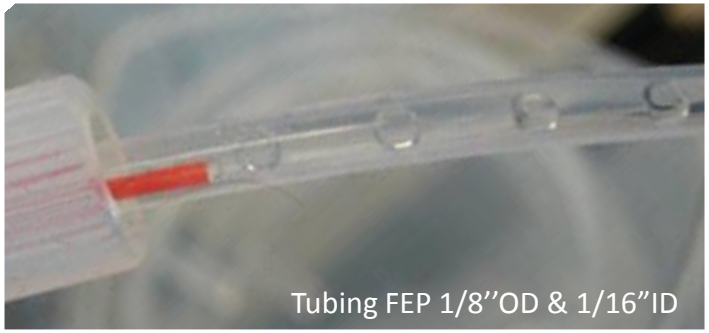
- Control of flows/mixing ⇨ Control of concentrations
  Compartmentalization ⇨ Control of residence times
- Transparency ⇨ Microscope, spectroscopy, IR Thermography
  Sequential production ⇨ Potential for High Throughput Experiments
  Very high S/V ratio ⇨ Favors heat exchange
  Temporal resolution ⇨ Time/space correspondence
  Small volumes ⇨ Improve safety, less waste

Mixing inside by wall forced convection
Management of viscosity issues

Ideal tool for kinetic data acquisition

Droplet-Based Microfluidics

✓ Low cost & user-friendly Droplet-Based Micro- or Millifliduics



- "Same" microreactors, hydrodynamic properties and possible "inline" analysis
  ↳ High S/V ratio, space/time correspondence, …

- Higher residence times (about hours)

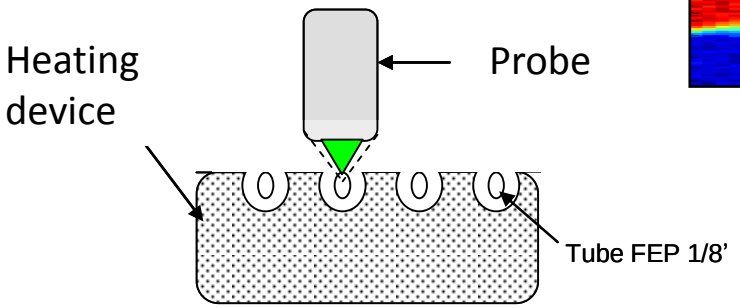
- Good chemical resistance (PTFE, glass, …)

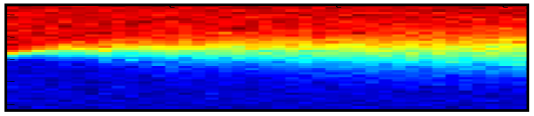
- Large choice of commercial tubing, capillaries and connectors

- No need of a cleanroom nor expensive microfabrication machines

Coupling *inline* analytical tools

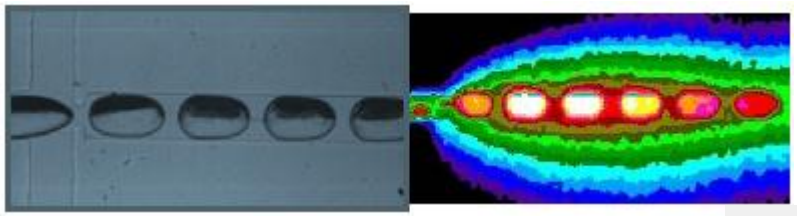
- **Raman (back scattering)**
  - Identification
  - Conversions





Mixing by Raman imaging (false colors)

- **Thermal Infra-Red CCD**
  - Heat of reaction



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- **Spectroscopy UV-Vis**
  - Turbidity (frequency of droplets)
  - Absorption

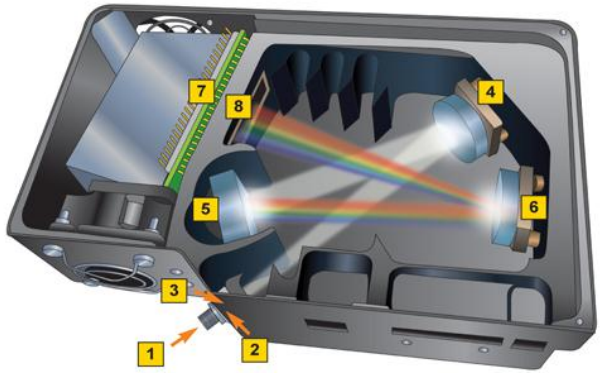
Coupling *inline* analytical tools

✓ For a qualitative determination

- OceanOptics Laser: 532nm, 500mW

$

- InPhotonics probe
  - Optical fiber: polyurethane, length: 5m, Ø: 200µm
  - Material: stainless steel and quartz
  - Backscattering
  - Focus distance: about 7,5mm



- OceanOptics QE65000 Spectrometer
  - **Resolution: 18cm^{-1}**
  - Software: SpectraSuite
  - USB

- Possible sample holder

Coupling *inline* analytical tools

✓ In depth quantitative analysis by Raman spectroscopy

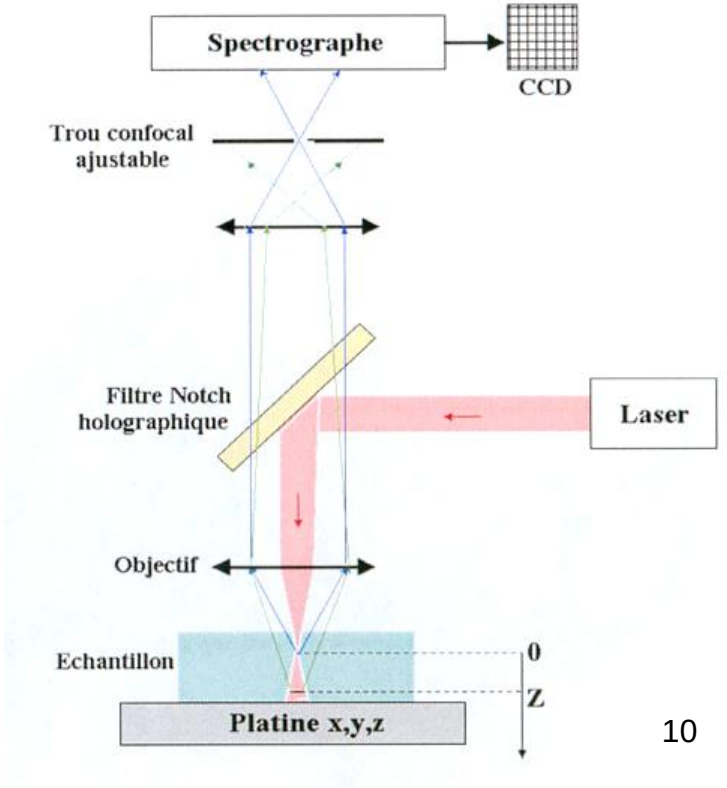
- Laser NdYAG
  - 632 nm, 500mW
  - Doubled frequency

$$$

- Olympus BXFM Microscope:
  - **Objectives: x10 ; x50 ou 100x**
  - Backscattering

- Jobin-Yon LABRAM HR800 Spectrometer
  - **Resolution: 1 cm^{-1}**
  - Software: Labspec

- Motor drive control of x-y-z table



- Possible sample holder

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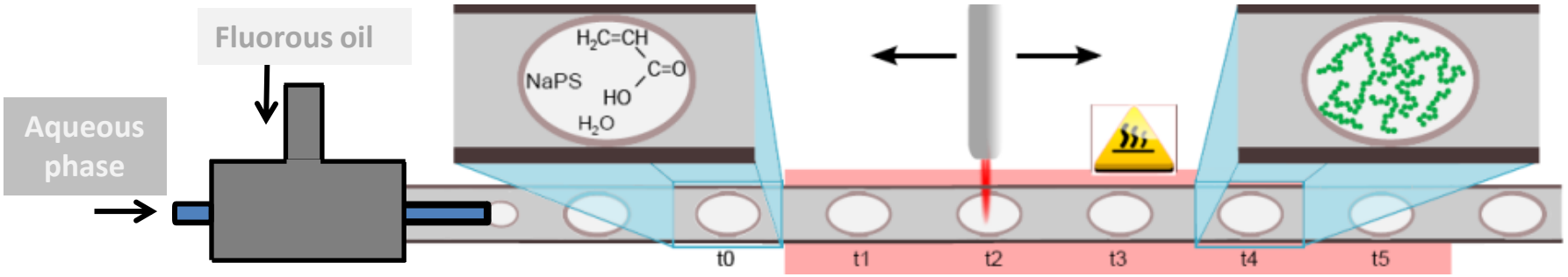
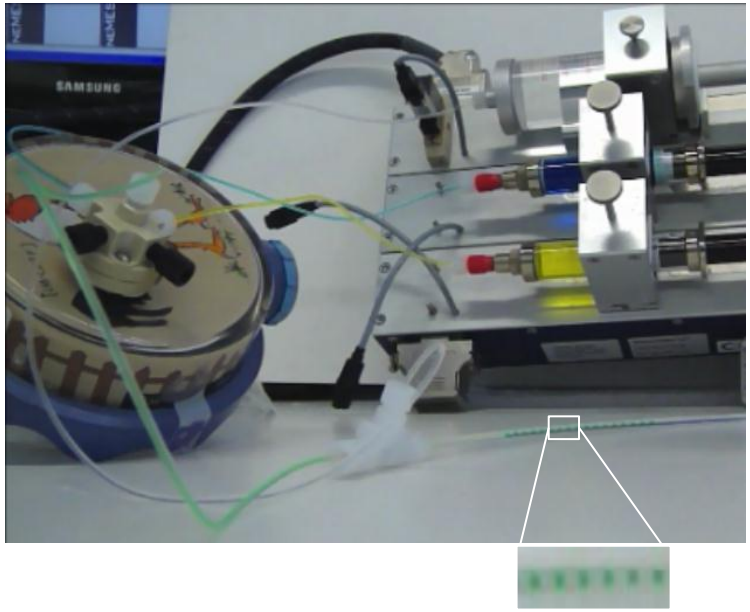
Monitoring of acrylic acid polymerization

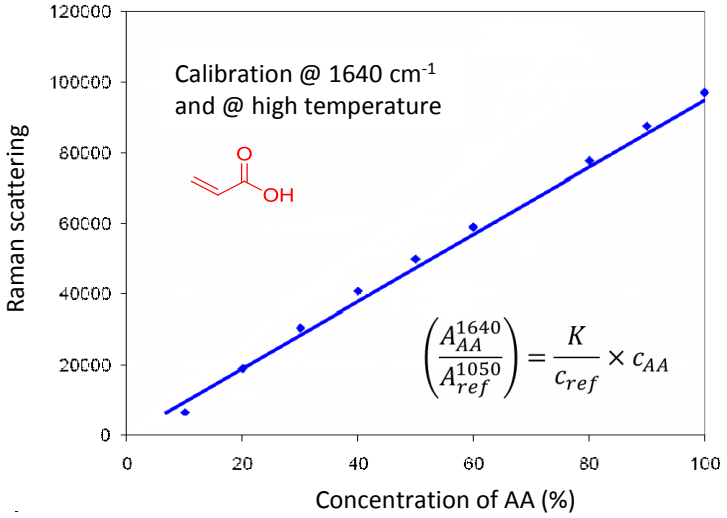
✓ Experimental set-up



Generation of droplets

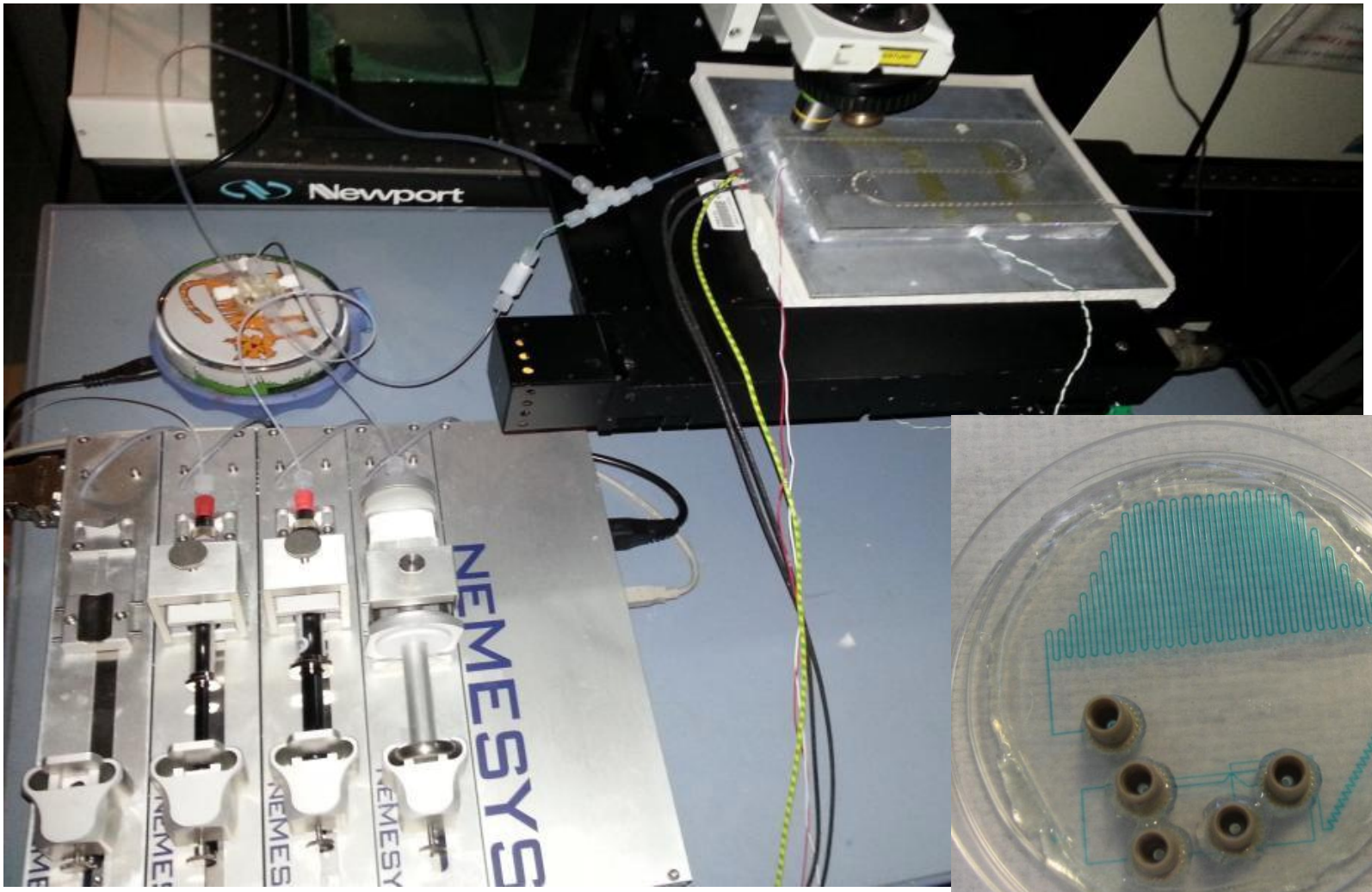


Calibration based on Raman spectroscopy



Monitoring of acrylic acid polymerization

✓ Experimental set-up

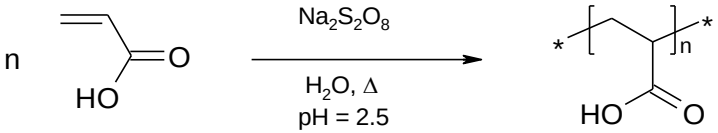


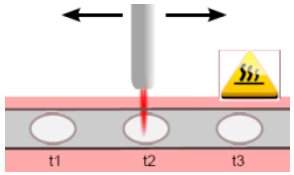
Monitoring of acrylic acid polymerization

- ✓ **Droplets allow using the time vs space correspondence**

Monitoring of acrylic acid polymerization

✓ Kinetics



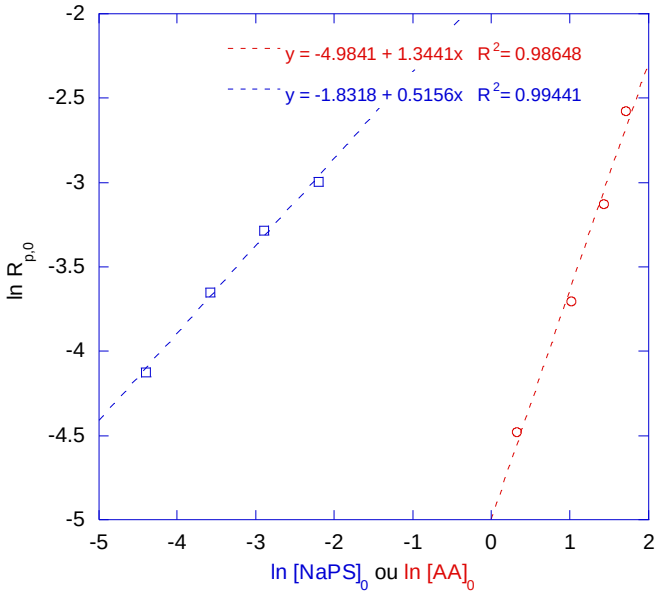


Conversion:

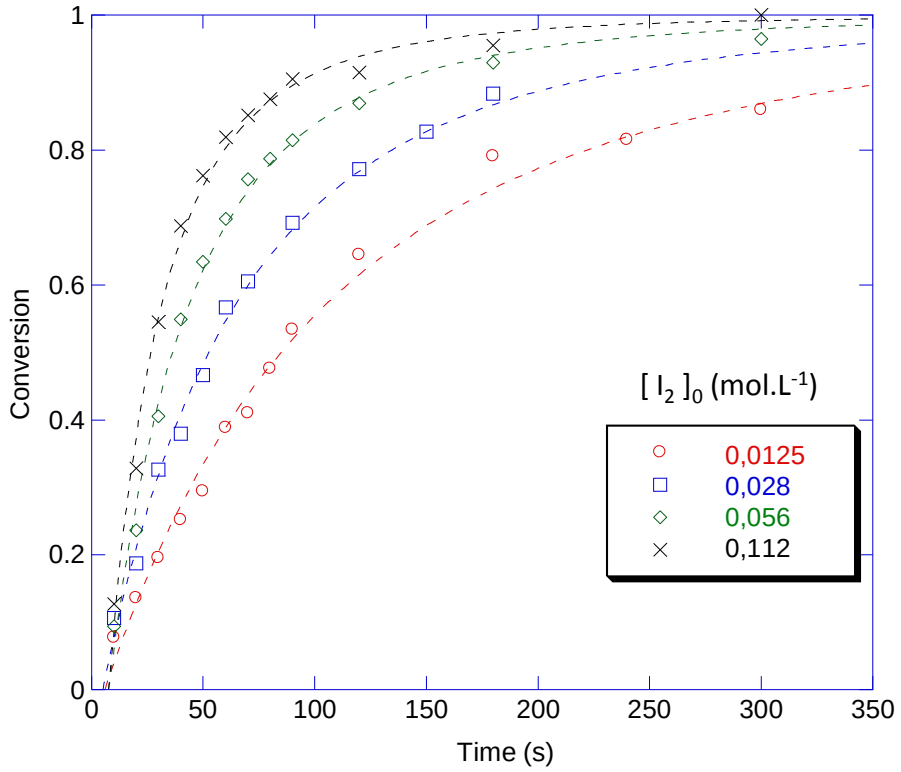
$$\rho = 1 - \frac{n_{m,t}}{n_{m,0}} = 1 - \frac{C_{m,t}}{C_{m,0}} = \frac{\left(I_t^{1640cm^{-1}} / I_t^{1050cm^{-1}} \right)}{\left(I_0^{1640cm^{-1}} / I_0^{1050cm^{-1}} \right)}$$

Polymerization rate:

$$R_p = -\frac{d[AA]}{dt} = k_p \sqrt{\frac{f k_d [I_2]_0}{k_t}} \times [AA]^{\alpha}$$



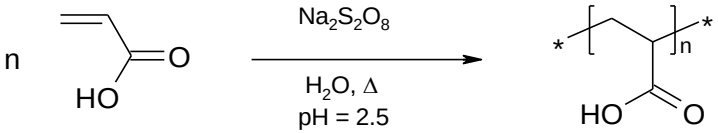
$[AA]_0$ = 2.8 mol.L^{-1} (20 wt. %)
pH = 1.8 ; 81 °C

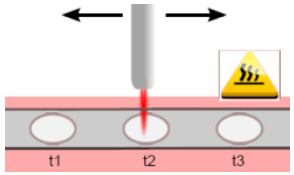


Macromolecules, **43 (2010) 5524**
Macromolecular Symposia, **296 (2010) 203**

Monitoring of acrylic acid polymerization

✓ Kinetics



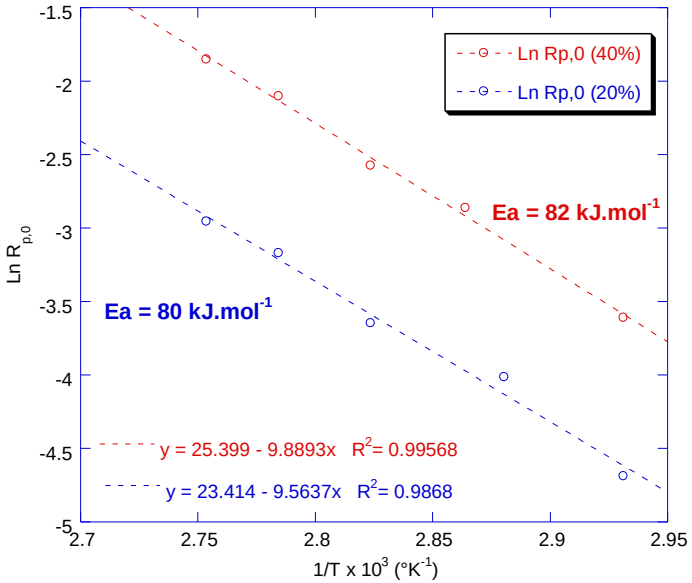


Conversion:

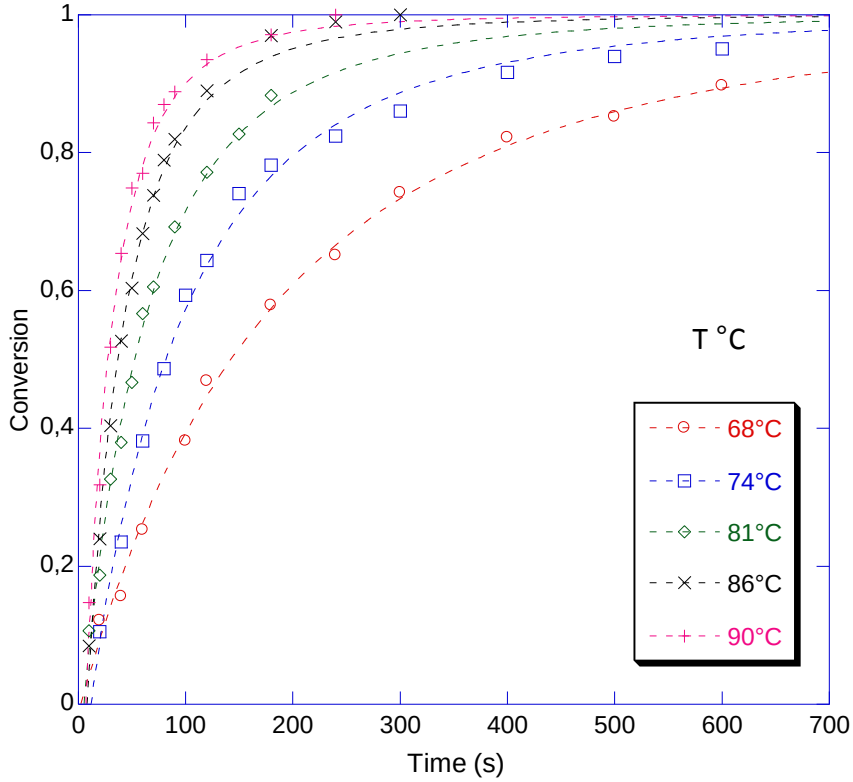
$$\rho = 1 - \frac{n_{m,t}}{n_{m,0}} = 1 - \frac{C_{m,t}}{C_{m,0}} = \frac{\left(I_t^{1640cm^{-1}} / I_t^{1050cm^{-1}} \right)}{\left(I_0^{1640cm^{-1}} / I_0^{1050cm^{-1}} \right)}$$

Overall activation energy of the poly rate:

$$\ln(R_{p,0}) = \ln A - \left(E_a / RT \right)$$



$[AA]_0$ = 2.8 mol.L^{-1} (20 wt. %)
pH = 1.8 ; $[I_2]_0$ = 0.028 mol.L^{-1}



Macromolecules, **43 (2010) 5524**
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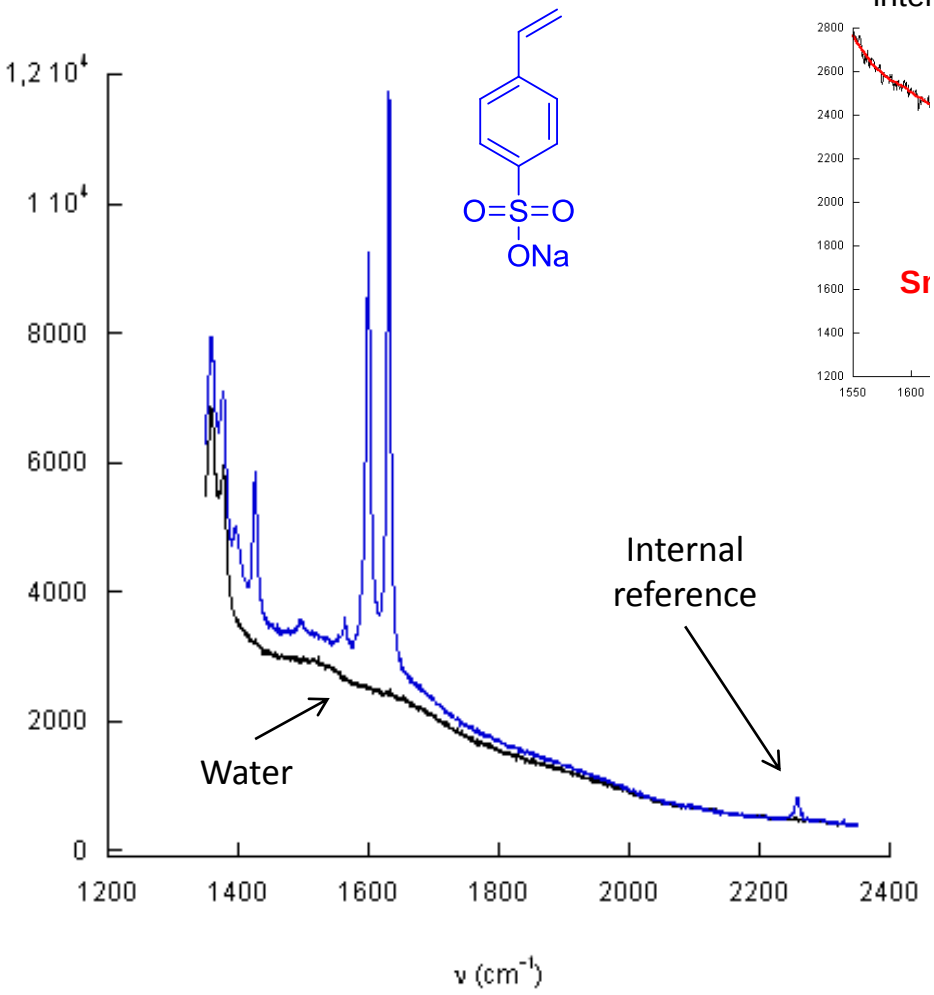
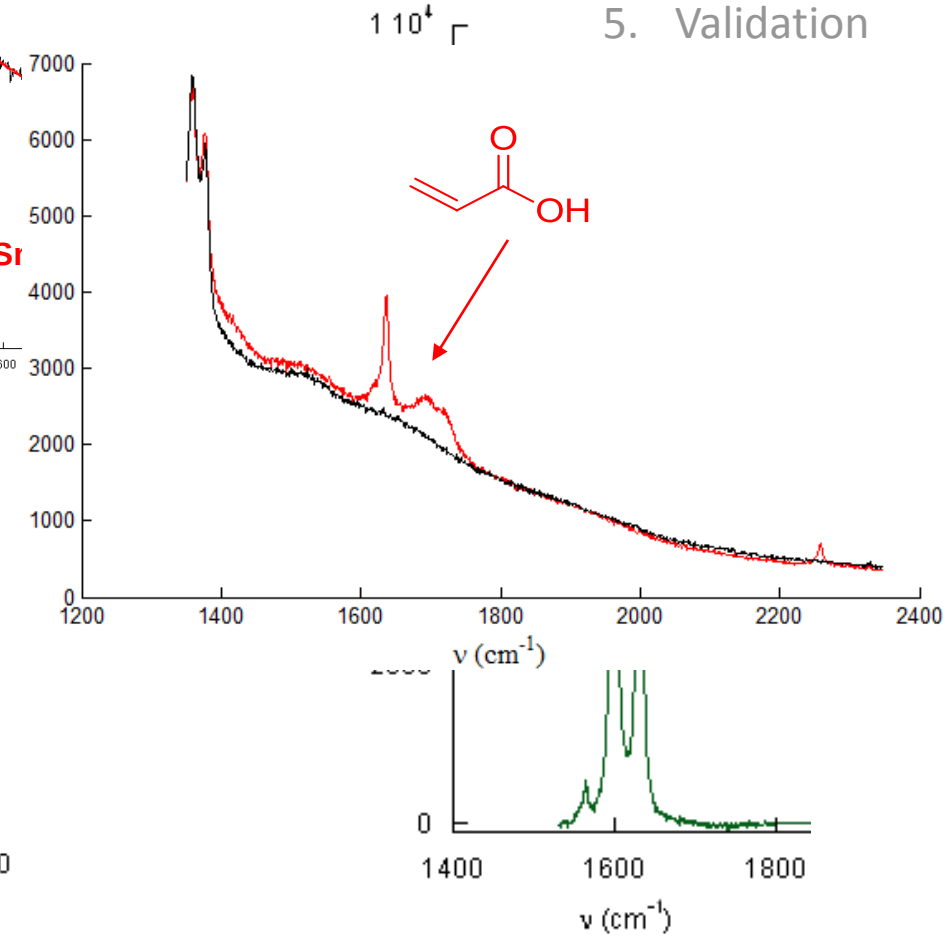
Monitoring of the copolymerization

✓ Raw Raman spectra from monomers

1. **Baseline**
2. Deconvolution
3. Calibration
4. Test
5. Validation



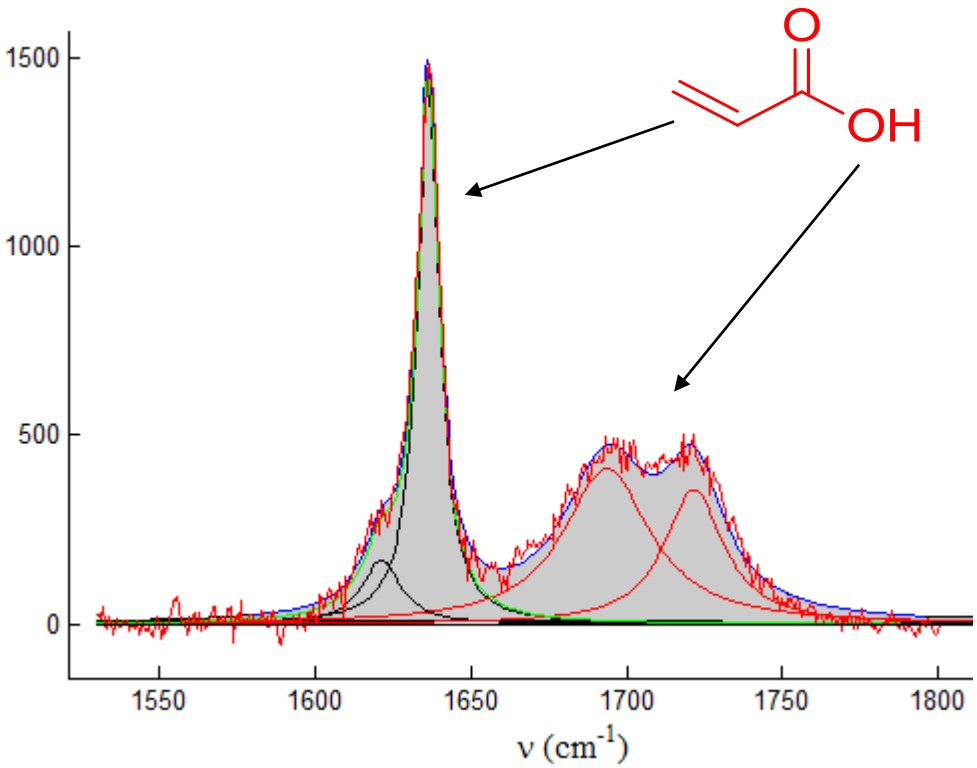
Water spectra in the interest area (zoom)



Monitoring of the copolymerization

✓ Corrected Raman spectra from monomers

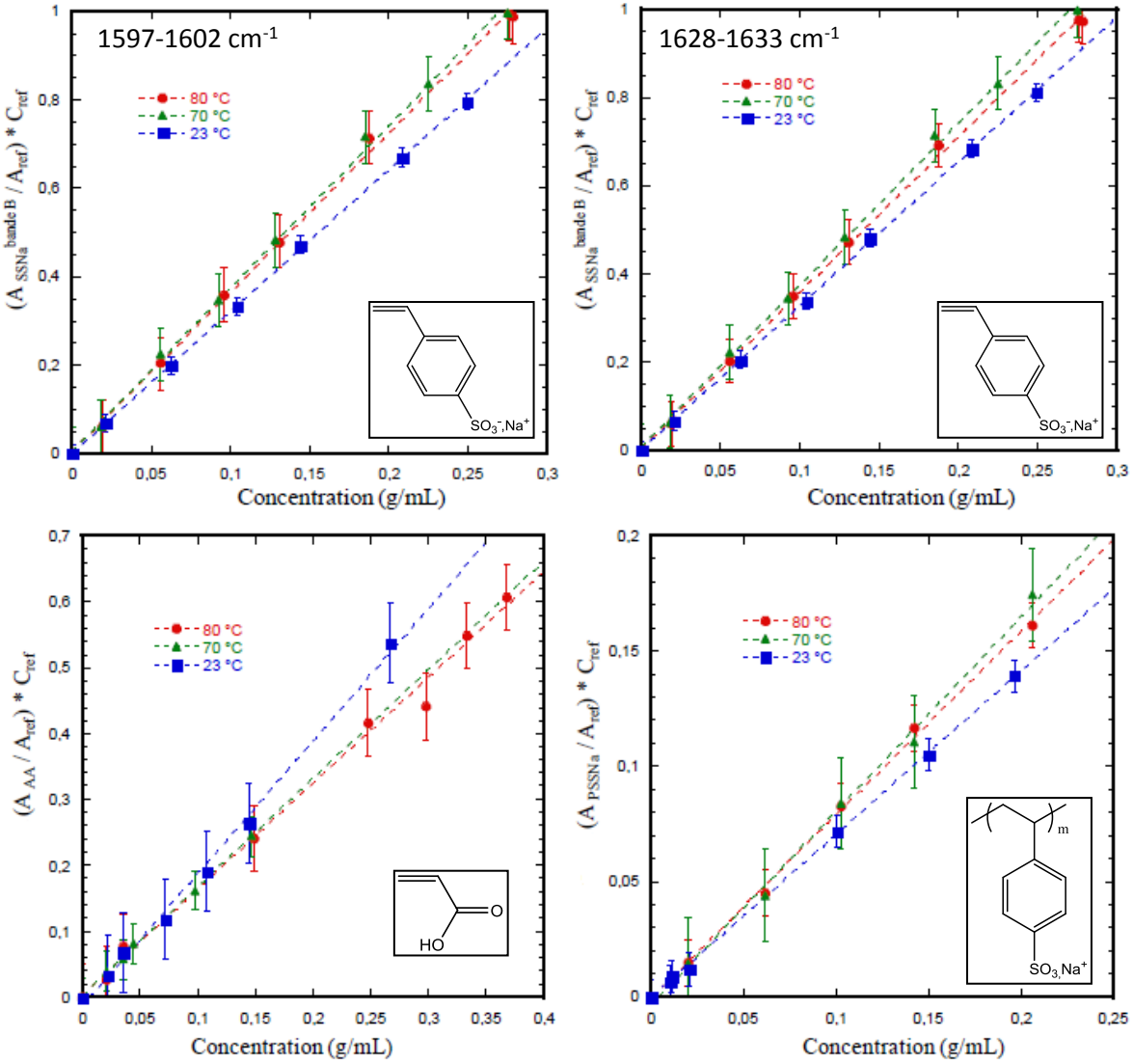
1. Baseline
2. **Deconvolution**
3. Calibration
4. Test
5. Validation



Intensity (area) is proportional to the concentration

Monitoring of the copolymerization

✓ Validation of the calibration

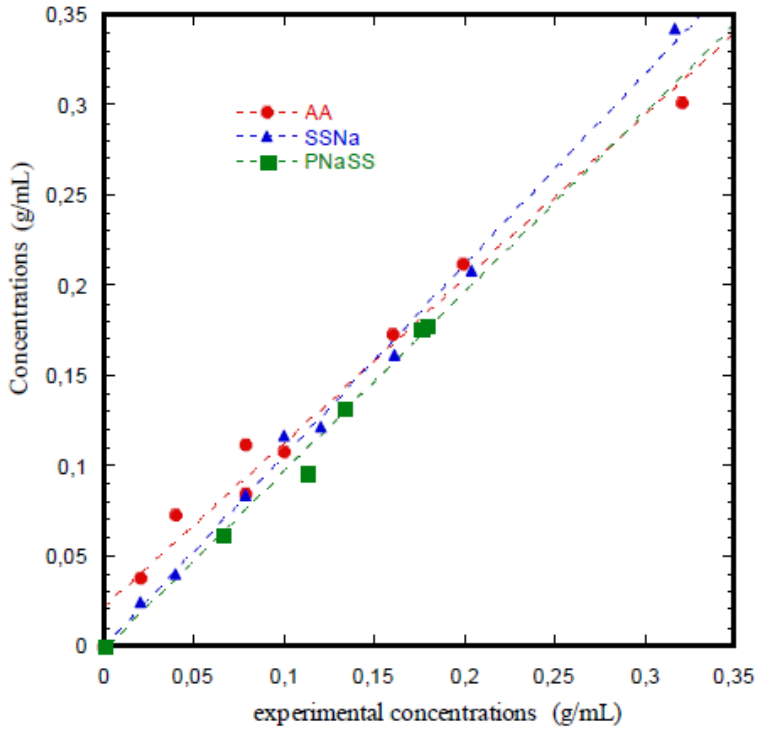


1. Baseline
2. Deconvolution
3. **Calibration**
4. Test
5. Validation

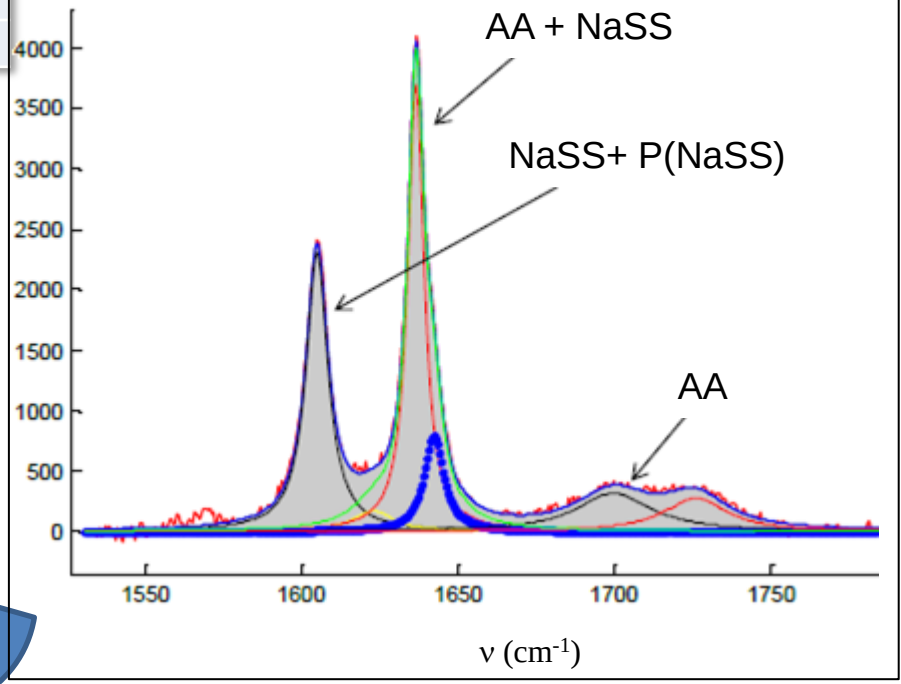
Monitoring of the copolymerization

✓ Validation of the calibration

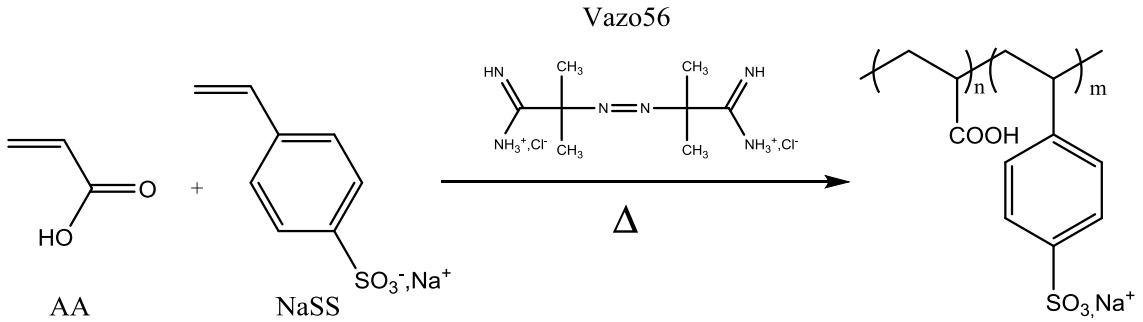
		Temperature					
		23 °C		70 °C		80 °C	
SSNa	1597-1602 cm^{-1}	3,21	±0,02	3,68	±0,06	3,6	±0,06
	1628-1633 cm^{-1}	3,27	±0,02	3,67	±0,06	3,53	±0,05
AA		2,01	±0,06	1,65	±0,03	1,61	±0,05
P(NaSS)		0,71	±0,01	0,84	±0,03	0,8	±0,02



Simulations with model solutions



Monitoring of the copolymerization



Assume terminal model of copolymerization:

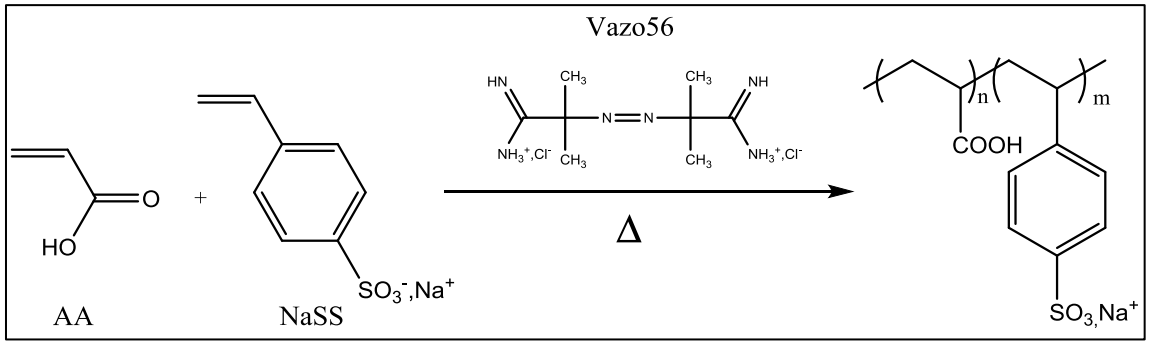
$$--M_1^* + M_1 \xrightarrow{k_{11}} ---M_1^*$$
$$--M_2^* + M_1 \xrightarrow{k_{21}} ---M_1^*$$
$$--M_1^* + M_2 \xrightarrow{k_{12}} ---M_2^*$$
$$--M_2^* + M_2 \xrightarrow{k_{22}} ---M_2^*$$

$$-\frac{d[M_1]}{dt} = k_{11}[M_1^*][M_1] + k_{21}[M_2^*][M_1]$$
$$-\frac{d[M_2]}{dt} = k_{12}[M_1^*][M_2] + k_{22}[M_2^*][M_2]$$

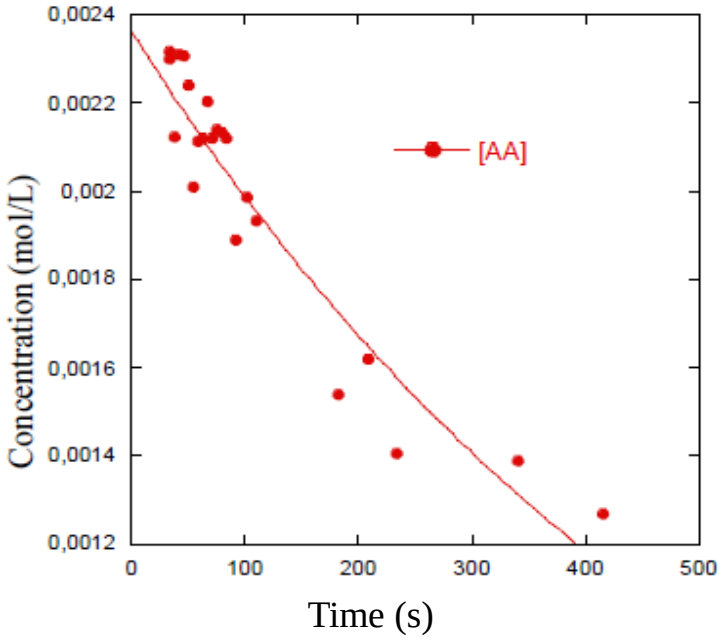
$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2]([M_1] + r_2[M_2])}$$

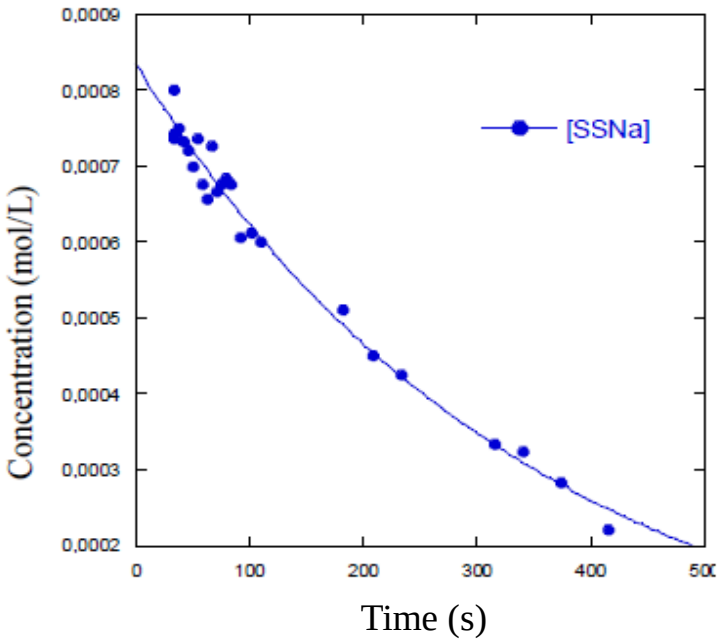
et $r_1 = \frac{k_{11}}{k_{12}}$ $r_2 = \frac{k_{22}}{k_{21}}$

Monitoring of the copolymerization



- $[AA]_0$ = 2.8 mol.L^{-1} (20 wt. %) ; pH = 1.8 ; 70 °C
- AA / NaSS = 80 / 20 (wt. % ratio)





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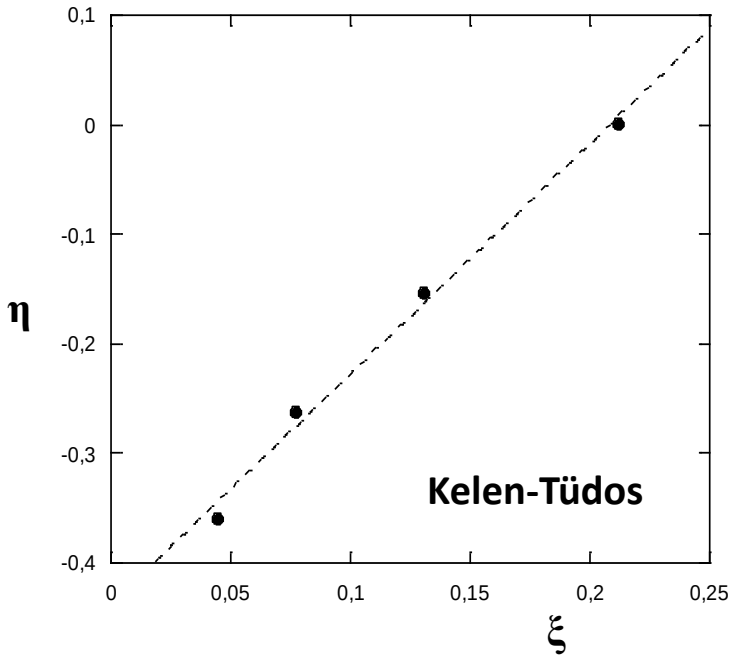
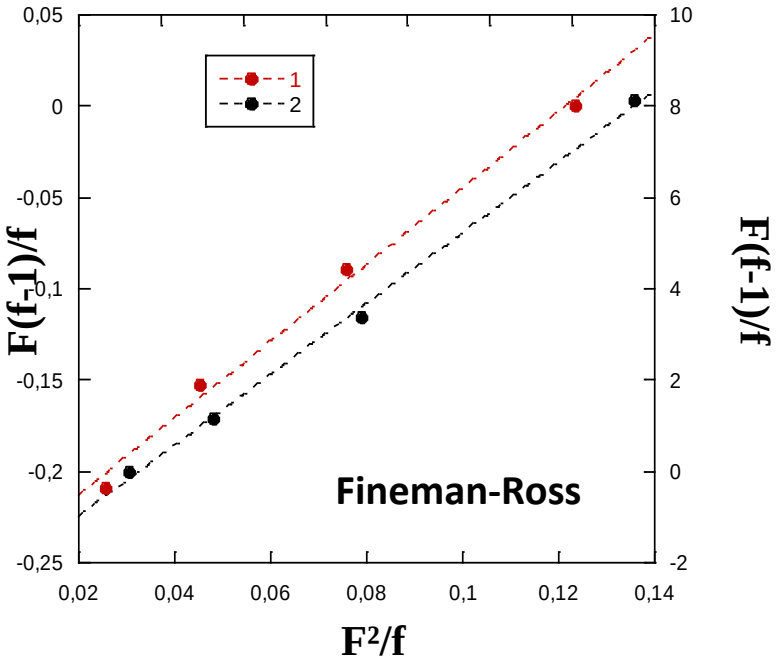
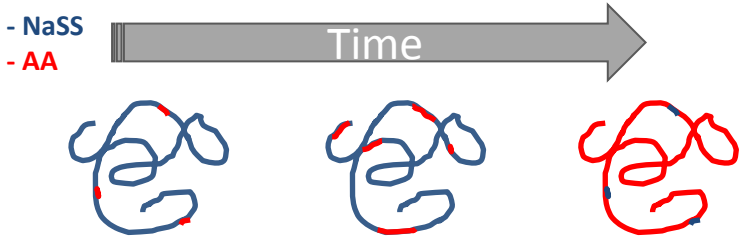


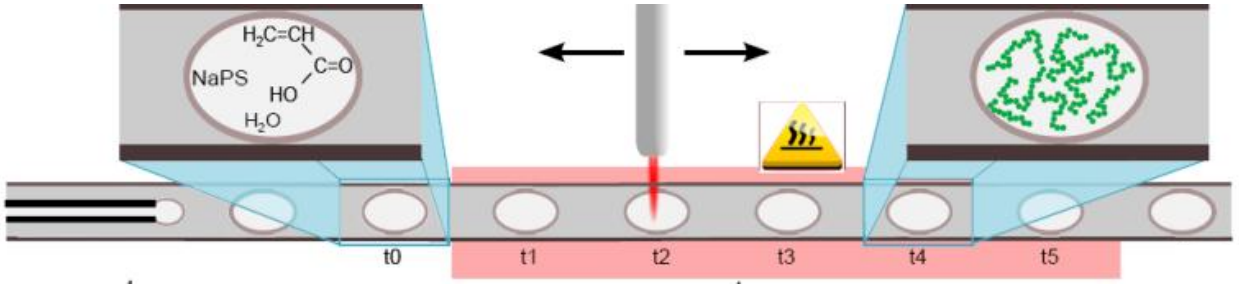


	$r_{AA} = \frac{k_{11}}{k_{12}}$	$r_{SSNa} = \frac{k_{22}}{k_{21}}$
Droplet-based microfluidics	0.26	2.10
Wiley *et al.* (1958)	0. 2	4.5
Grabiel et Decker (1962)	0.1	1.0

Drift in composition with residence time



Conclusion and outlooks



- ✓ **Continuous synthesis of (co)polymers within droplets in a wide range of conditions**
- ✓ **Reaction monitoring by Raman confocal microspectrometry**
- ✓ **Straightforward data acquisition platform**
  - ↳ **No manual handling of samples**

    Data non-accessible in 'conventional' batch reactors
- ✓ **Better heat transfer allows performing fast/exothermic reactions**

❖ **Molecular weights with residence time by off-line SEC**

Thank you for your attention!

Thanks to

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Dr. Pierre Guillot
Dr. Flavie Sarrazin

Solvay RIC-Paris:
Dr. James Wilson

IPREM – UPPA:
Dr. Oihan Garagalza
Dr. Bruno Grassl
Dr. Stéphanie Reynaud