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Polymerisation of Acrylic Acid using atmospheric plasma jets

Group meeting 1

23th of May 2014

Outline

1. Acrylic acid
2. Experimental Setup
3. Mass spectrometry
   a. Time-averaged
   b. Time-resolved
4. Deposition
   a. XPS
   b. TOF-SIMS
5. Future
   a. Frequency & duty cycle
   b. Deposition
   c. Monomer

Objective:

→ Polymerise acrylic acid using a atmospheric plasma jet.

→ Deposit poly(acrylic) coating

Acrylic acid and its polymer

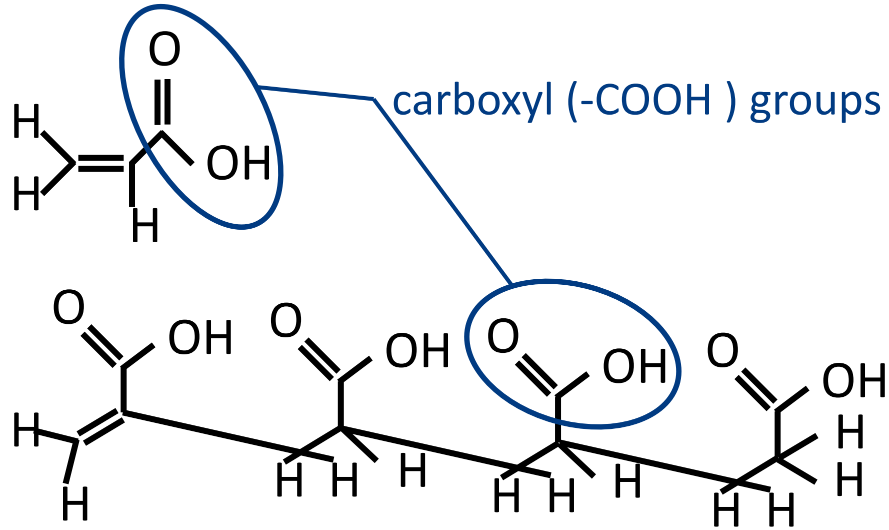
Acrylic acid (AA):

AA is a standard monomer being produced for over 30 Years.
AA **coatings** are used for: hydrophilic properties, good adhesion to metallic surface, sensor technologies, protein and cell adhesion,…

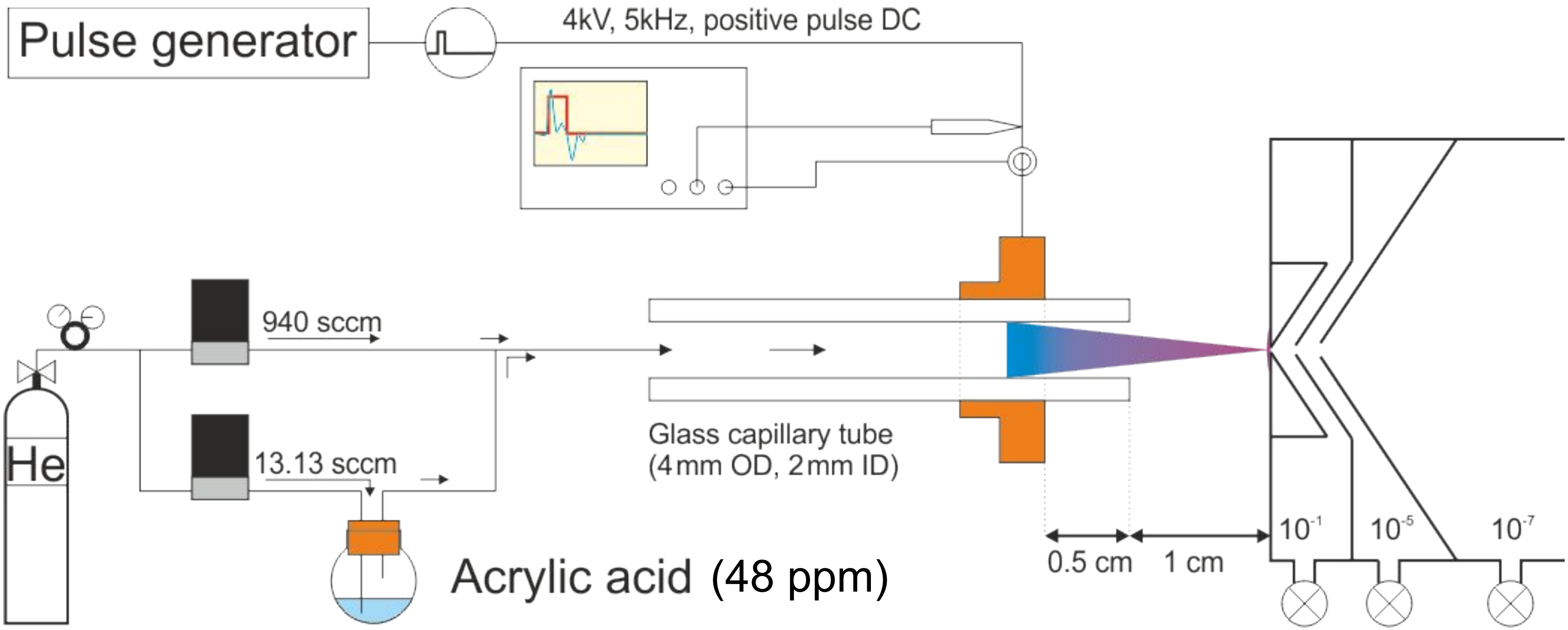
These properties mainly come from the **–COOH group**

Acrylic acid:
$C_3H_4O_2$ (72 amu)

Poly(acrylic acid):
$n[C_3H_4O_2]$ (72n amu)



Experimental setup



Grade A Helium 99.996%, BOC

Flow controller, MKS

Acrylic acid 99%, Sigma-Aldrich

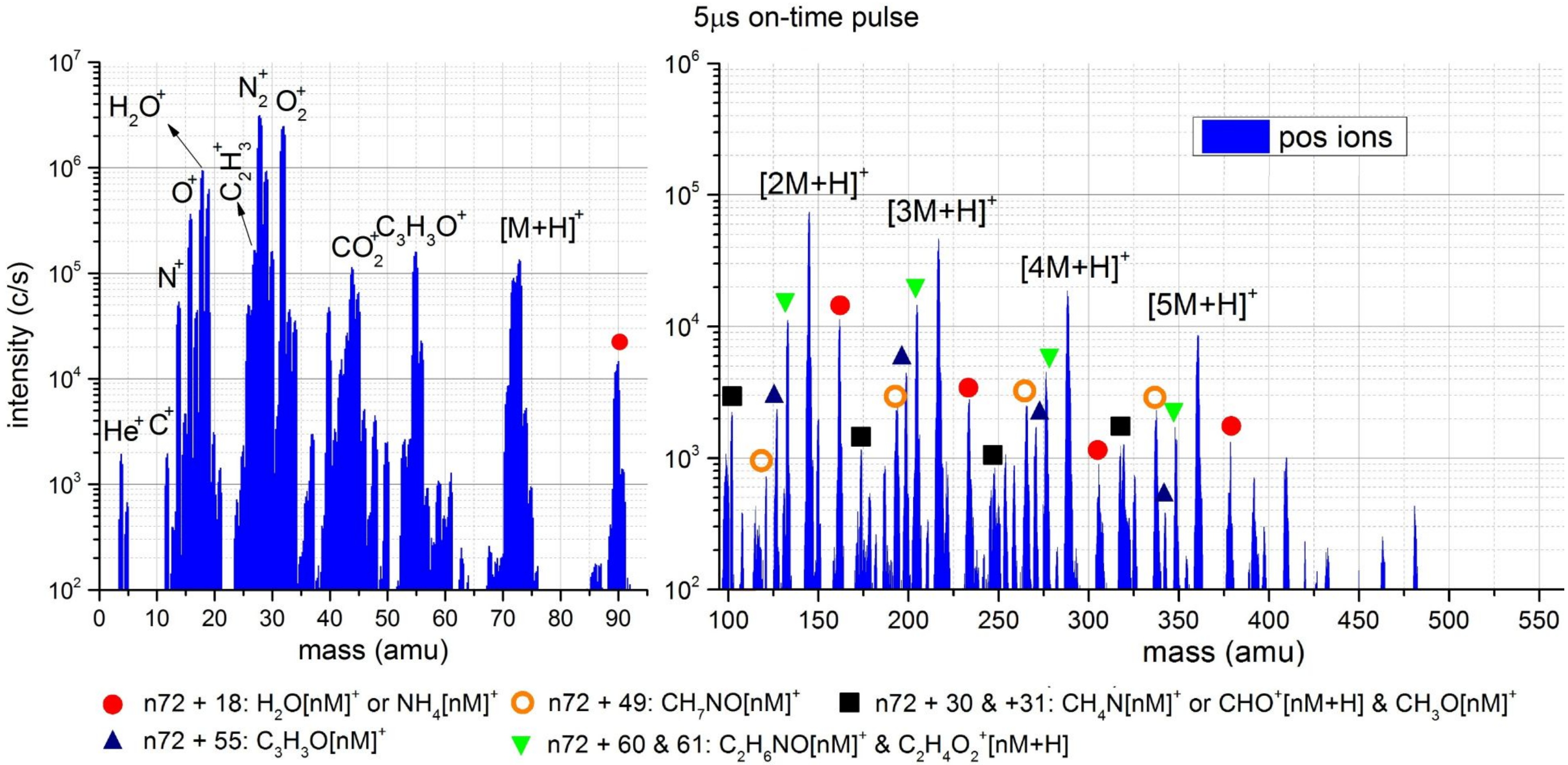
Homemade power supply & copper electrode

Quartz tube, Robson Scientific

HPR-60 molecular beam mass spectrometer, Hiden

Mass spectrometry

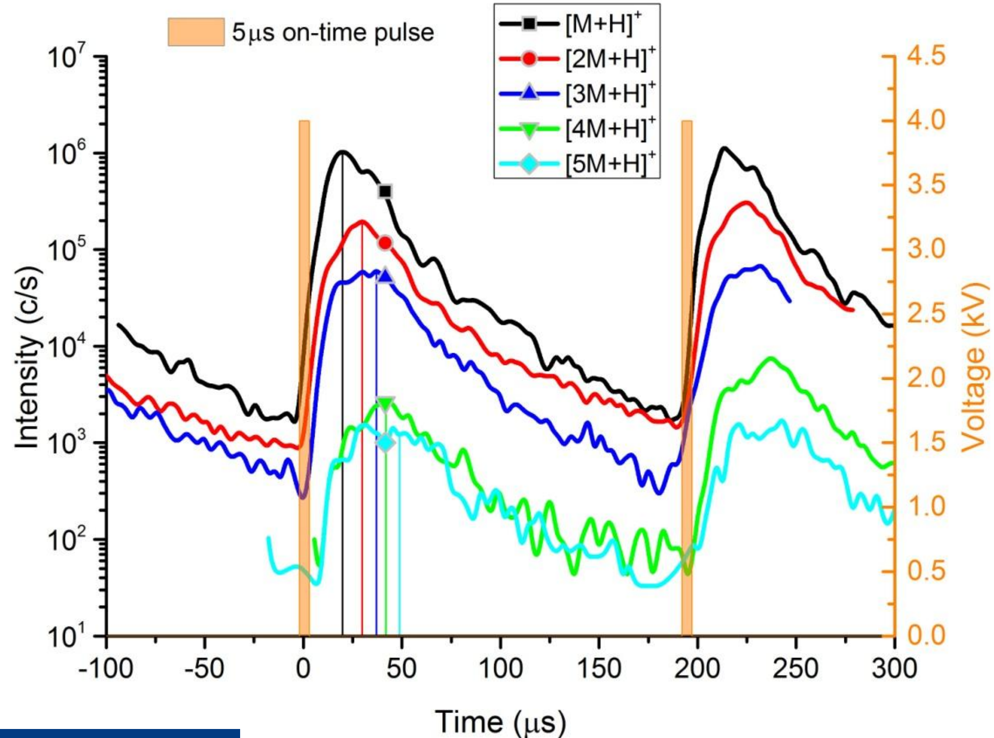
Time-averaged, positive ions, [M = $C_3H_4O_2$] (AA)



Mass spectrometry

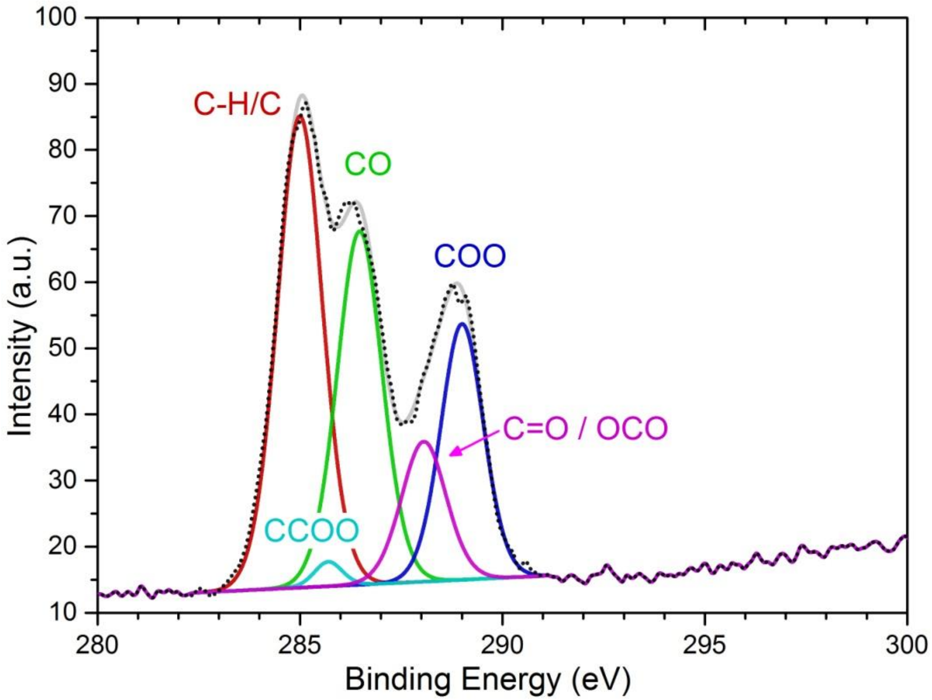
Time-resolved

- Polymerisation between the pulse and 50µs to 75 µs for heavy mass.



Deposition

XPS for a 6µs on-time deposition



Measurement: [%]				
C=O / O-C-O	CCOO	CO	COO	C-H/C
11.3	1.1	29.3	19.75	38.55

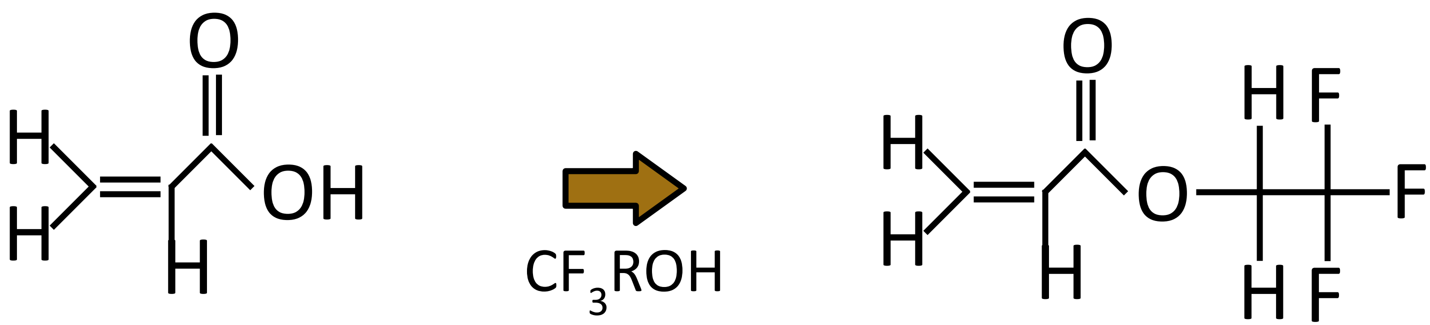
Expected for pure PAA: [%]				
C=O / O-C-O	CCOO	CO	COO	C-H/C
0	33	0	33	33

Kratos Axis Ultra (Kratos, UK) with a monochromated Al kα source (1486.7 eV) using an emission current of 10 mA and an anode potential of 12 kV. High resolution C 1s scans use a pass energy of 20 eV.

Derivatisation performed by the University of Nottingham

Deposition

Trifluoroethanol derivatisation :



underivatised carboxylic acid

derivatised carboxylic acid

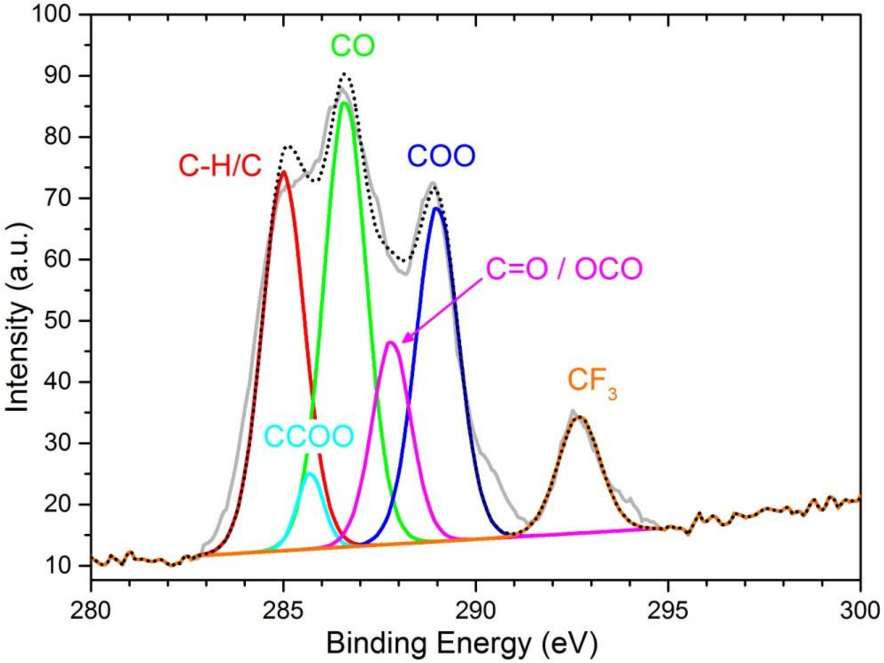
Percentage of carboxyl group (COOH) over all the other C group: 33%

Ratio of CF_3 over the COOX group: 1/1

$$\text{Retention: } \frac{[COOX]_{under}}{33} \bullet \frac{[CF_3]_{der}}{[COOX]_{der}} : 1 \bullet 1 = 100\%$$

Deposition

XPS for a 6μs on-time deposition



Measurement: [%]					
C=O /O-C-O	CCOO	CO	COO	C-H/C	CF_3
13.94	3.16	29.75	22.05	23.97	7.13

$[CF_3]/[COOX] = 0.323$

Expected for pure PAA: [%]					
C=O / O-C-O	CCOO	CO	COO	C-H/C	CF_3
0	20	20	20	20	20

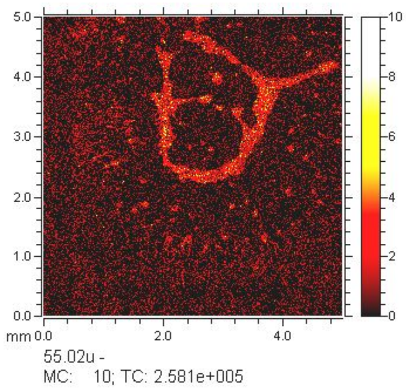
Retention : 19.75/33 • 0.323 = 19.33%

Analysis performed by the University of Nottingham

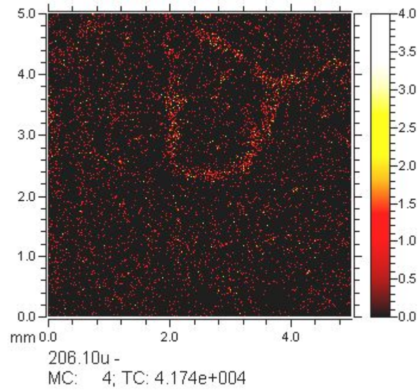
Deposition

TOF-SIMS (on a 6µs on-time deposition)

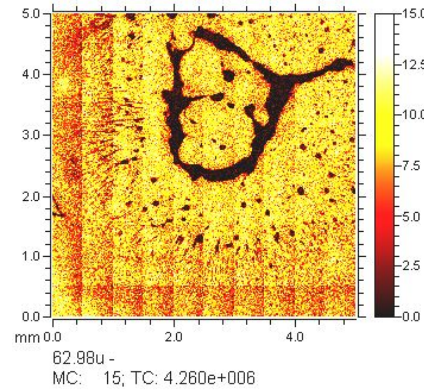
$C_3H_3O^+$



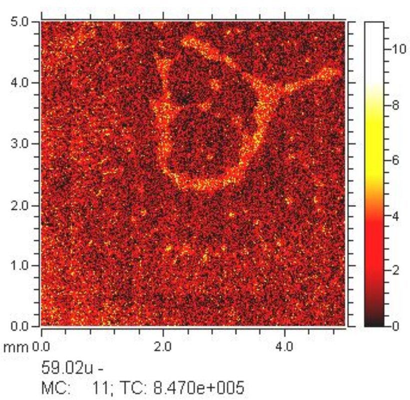
206.1^+



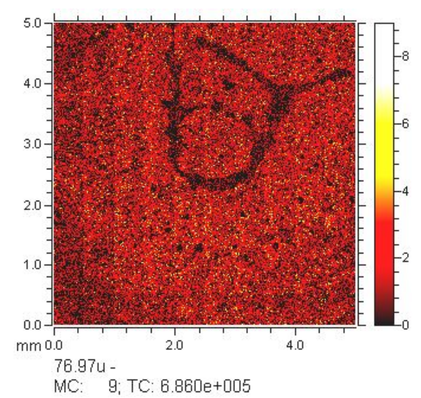
Na_2OH^+



$C_2H_3O_2^-$



$SiHO_3^-$



Near-future

- + pulse signal
  - Using 2 frequencies: 5 kHz & 10 kHz
  - Using different duty cycle [5,10,25,45,50,75,90] % & [10,25,50,75,90] %
- Continuous wave
  - Using different frequencies: 5, 5.5, 6.6, 10, 11.1, 13.3, 20 kHz

Future - deposition

- Using the x-y stage (thank you MJ) to deposit homogenous coating
  - Measuring the coating ?
- Deposit on different substrate material: glass, plastic (polystyrene, acrylic), metal (aluminium, silicone)

Future - monomer

- Do similar experiments with different monomers:
  - Heptylamine, allylamine,
  - Styrene