

## Investigating atmospheric-pressure polymerization using mass spectrometry

J.W. Bradley, F. Moix and K. McKay

University of Liverpool, Department of Electrical Engineering and Electronics, Brownlow Hill, U.K.

**Abstract:** Using an atmospheric-pressure plasma jet operated in a mixture of helium and acrylic acid vapour thin films of poly-acrylic acid can be produced. Here, we investigate the gas phase chemistry involving positive and negative ions created in the discharge outflow by means of molecular beam mass spectrometry. The results show that heavy oligomers of the form  $[nM+H]^+$  and  $[nM-H]^-$  can be formed in the stream with  $n > 5$ .

**Keywords:** plasma jets, atmospheric-pressure, plasma polymerisation, mass spectrometry

### 1. Introduction

In recent years, the use of atmospheric-pressure plasmas have become more commonplace in industry as they remove the need for the complex and expensive vacuum systems required by low pressure plasma processes [1]. Although the use of atmospheric pressure plasmas has increased, the physics and chemistry of the polymerisation process is still not well understood. Here, we investigate the simple ion chemistry present in a pulsed dielectric barrier discharge (DBD) helium jet with acrylic acid monomer introduced into the gas flow using mass spectrometry.

### 2. Experimental arrangement

The plasma jet used in this study was a cylindrical DBD. It consisted of a quartz tube, 10 cm in length, with an outer diameter (OD) of 4 mm and an inner diameter (ID) of 2 mm. A custom-built copper ring of 4mm ID was positioned at 5 mm from the end of the capillary as shown in Fig. 1. The electrode was powered using a custom-made voltage amplifier. The signal was a monopolar positive pulse DC of 5 kHz generated by a digital pulse generator (DG645, Stanford Research Systems). The peak-to-peak amplitude of the excitation was fixed at 4 kV. The feed gas used was pure helium (99.996 %). Helium was split into two lines, 940 sccm going directly to the quartz capillary and 13.13 sccm bubbling up through 100 ml of anhydrous acrylic acid (99%, sigma-aldrich). The Antoine equation allows the calculation of the acrylic acid concentration in the final flow [2]. Using the Antoine coefficients of acrylic acid from NIST and a liquid temperature of  $23 \pm 2$  °C the calculated concentration was  $60 \pm 9$  ppm. The gas mixture was allowed to interact with the ambient air after exiting the capillary. The distance between the end of the quartz tube and the mass spectrometer extractor orifice was fixed at 10 mm. The mass spectrometer used for chemical analysis of the plasma was a quadrupole-based molecular beam mass spectrometer HPR-60 (HIDEN Analytical Ltd), providing a mass resolution of  $\sim 0.2$  m/z.

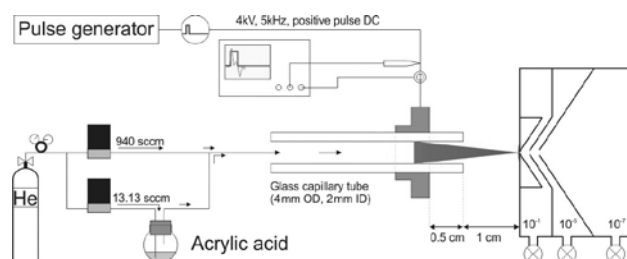


Fig. 1. A schematic diagram of the pulsed plasma jet system and molecular beam mass spectrometer.

### 3. Results and Discussion

The main helium (940 sccm) and monomer + helium flow (13.13 sccm) were chosen to create stable plasma and provide an optimised residence time for the monomer in the plasma. Fig. 2 shows the positive ions detected for a duty cycle of 2.5% from 1 to 550 Da, no ions with a mass higher than this were detected for the conditions considered here. Fig. 2a shows the mass peaks between 1 and 97 Da, the main ions detected in this mass range were  $He^+$ ,  $N^+$ ,  $O^+$ ,  $H_2O^+$ ,  $N_2^+$ ,  $O_2^+$  and  $CO_2^+$ , these ions were created through the interaction of helium species with the air molecules [10]. The acrylic acid protonated monomer  $[M+H]^+$  was also detected in this mass range along with other monomer fragments,  $C^+$ ,  $C_2H_3^+$  and  $C_3H_3O^+$ . In Fig. 2b, the mass peaks detected were created through the polymerisation of acrylic acid. The main peaks detected correspond to the protonated oligomers  $[nM+H]^+$  where  $n = 2$  to 5. The other visible peaks are ions formed through combination of oligomers and other molecules coming either from air or from acrylic acid fragments, the larger ones are labelled at the bottom of Fig. 2. Negative ions were also detected (see Fig. 3), showing clear oligomer peaks  $[nM-H]^-$  amongst many other peaks. However, negative ions were only detected when the plasma jet was moved significantly closer to the extraction orifice (0.5 mm). The negative ions detected are mainly from the acrylic and poly (acrylic) acid with the exception of the  $O^-$  peak. These negative ion peaks indicate a high degree of

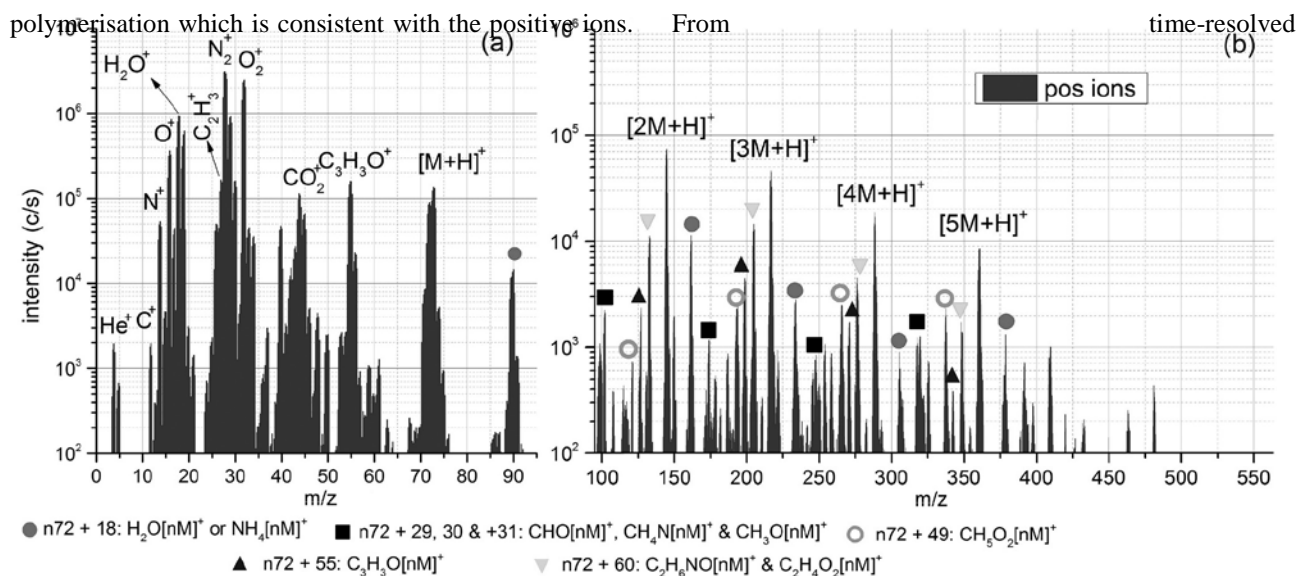


Fig. 2. Positive ions mass spectrum for 2.5% pulse duty cycle in the mass range 0-550 Da.

measurements of the ion chemistry (not shown here) it was found that the negative ions were only produced after the falling edge of the pulse. During this off-phase of the discharge there is no applied electric field, as a result the negative ions are not accelerated towards the extraction orifice as is the case for the positive ions and therefore they cannot propagate as far.

the plasma was significantly closer to the mass spectrometer. This was a result of the negative ion formation occurring during the off-phase of the discharge, when the applied electric field is zero. Future work will consist to thin films deposition using the same parameters and analysis of carboxyl retention in these films using time-of-flight secondary ion mass spectrometry (TOF-SIMS), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR), contact angle measurement and ellipsometry.

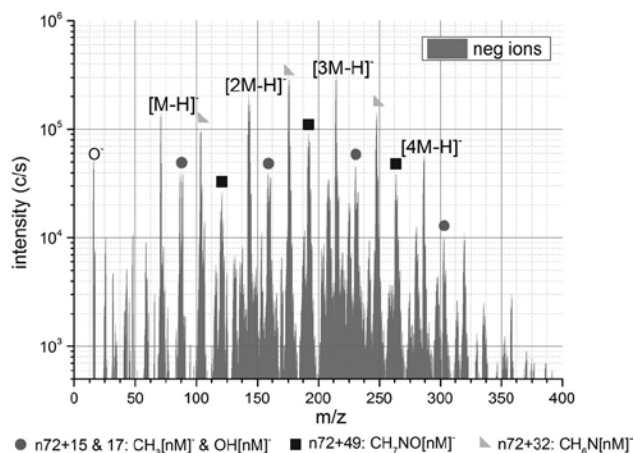


Fig. 3. Negative ions mass spectrum for 2.5% pulse duty cycle in the mass range 0 - 400 Da.

#### 4. Conclusions

A mass spectrometric study of the positive and negative ions created during the polymerisation of acrylic acid has been conducted using a pulsed DBD plasma jet. It was found that large acrylic positive oligomer ions,  $[\text{M}+\text{H}]^+$  ( $n = 2$  to  $5$ ), of acrylic acid were formed in the plasma under various operating conditions. Negative oligomer ions were also detected, however, these were only seen when

#### 5. References

- [1] I.O. Carton, D. Ben Salem, S. Bhatt, J. Pulpytel and F. Arefi-Khonsari. *Plasma Process. Polymers*, **9**, 984 (2012)
- [2] K. Nasirzadeh, D. Zimin, R. Neueder and W. Kunz. *J. Chem. and Eng. Data*, **49**, 607 (2004)