



Avis de Soutenance

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Soutiendra publiquement ses travaux de thèse intitulés

Recherche de traceurs spécifiques de la fabrication d'explosifs par spectrométrie de masse à très haute résolution

Soutenance prévue le **mercredi 30 octobre 2024 à 14h00**

à l'Amphithéâtre de l'Institut Supérieur d'Électronique et d'Automatique (ISEA), 7 Rue Marconi,
57070 Metz Technopôle

Abstract

Fluoropolymers are used in a wide variety of applications, both civil and military. Certain polymers, such as polyvinylidene fluoride (PVDF), are known to be used for industrial applications (e.g. Li-ion batteries), but also as a binder in explosive compositions.

This work focuses on the analysis of PVDF by mass spectrometry. As it is well-known to be poorly (or non-soluble) in common organic solvents, an ambient ionization source, direct analysis in real time (DART) was used. To allow the unambiguous assignment of an elemental composition to each ion produced by DART, it was hyphenated to a Fourier transform ion cyclotron resonance mass spectrometer.

In order to evaluate the capacity of DART-MS to analyze PVDFs, three telomers samples, with known structures and average molecular weight were firstly analyzed. They were successfully ionized, and oligomer distribution were observed as $[M-H]^-$, $[M+O_2]^-$, $[M+NO_2]^-$, $[M+CO_3]^-$, $[M+HCO_3]^-$, $[M+HCO_4]^-$.

Once the capacity of the DART ion source was established, four PVDF samples were analyzed. Two of them were standards at known average molecular weight (71 000 and 107 000 Da), and two were commercial sample for which no information were provided. The obtained mass spectrum displayed ions distributions from the DART ionization of small oligomers trapped in long PVDF chains. Oligomeric distributions were attributed to $[(C_2H_2F_2)_n C_4H_8O_2 + HCO_{3-4}]^-$ for the two standards and $[(C_2H_2F_2)_n C_3H_8 + HCO_{3-4}]^-$, $[(C_2H_2F_2)_n H_2O - H]^-$ or $[(C_2H_2F_2)_n H_2O + NO_2]^-$ for the two other samples. The end groups formula $\alpha + \omega = C_4H_8O_2$, C_3H_8 , H_2O were linked to the use of ethyl acetate, isopropanol as chain transfer agents, and persulfate as initiator, respectively.

For in-depth PVDF characterization, a thermodesorption/pyrolysis (TD/Py) device was added to the DART ion source. A temperature gradient from 35 °C to 600 °C ensured to observe both thermal desorption and pyrolysis products. The latter were typically $H(C_2H_2F_2)_n F$ and $H(C_2H_2F_2)_n CH_2F$. In one of the investigated PVDFs, an unexpected amount of fluorine revealed the presence of a perfluorinated comonomer, which was not evidenced by "simple"-DART analysis. This result was confirmed by ^{19}F NMR, which demonstrated the presence of 5 % of hexafluoropropylene (HFP) comonomer. A correlation between the HFP content in the polymer and the number of CF_2 units measured in pyrolysis product was observed, showing the capacity of TDPy-DART to evaluate the comonomer composition of a copolymer.