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Comprehensive Analysis of Oligomeric Impurities, Monomer Composition, and End-Group Information in ArF Photoresist Block Copolymers Using Q-TOF High-Resolution Mass Spectrometry

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Introduction

Argon fluoride (ArF) photoresists, widely used in 193 nm photolithography, play a pivotal role in semiconductor manufacturing by enabling the fabrication of sub-100 nm features. The performance of these photoresists is highly dependent on the purity and structural precision of their polymeric and oligomeric constituents[1]. However, during synthesis, processing, or storage, undesirable oligomeric impurities—such as incomplete reaction products, degradation byproducts, or catalyst residues—can form, negatively impacting critical properties like photosensitivity, etch resistance, and pattern fidelity. Identifying and characterizing these impurities is essential for optimizing photoresist formulations and ensuring consistent lithographic performance.

Traditional analytical techniques like gel permeation chromatography (GPC) and nuclear magnetic resonance (NMR) spectroscopy provide valuable bulk property information but lack the sensitivity and specificity required to detect and identify the low-abundance and structurally similar oligomeric species present in block copolymer photoresists. The inherent limitations of these methods become particularly apparent when analyzing: (i) isobaric oligomers with identical mass but different monomer sequences, (ii) end-group variants that differ by subtle mass differences, and (iii) cyclic versus linear topologies that significantly impact photoresist performance. Recent studies have demonstrated that even parts-per-million (ppm) levels of specific oligomeric impurities can alter the dissolution kinetics and acid diffusion characteristics of photoresists, highlighting the need for advanced analytical solutions.

High-resolution mass spectrometry (HRMS) has become an indispensable analytical technique for the detailed structural elucidation of synthetic polymers and advanced materials[2]. Unlike conventional methods such as GPC and NMR, HRMS enables the discrimination of isobaric species and the detection of trace-level impurities. This study leverages Q-TOF HRMS to identify oligomeric impurities, decipher the monomer composition, and characterize end-group functionalities in ArF photoresist block copolymers.

Experimental

Sample Preparation

5 mg photoresist samples were dissolved in 1 mL of high-purity tetrahydrofuran (THF), and sonicated for 10 min at 25°C to ensure complete dissolution. After that, the samples were centrifuged at 10,000 rpm for 5 min to remove insoluble particles. Then, the supernatant was used for LC-MS analysis.

Data Acquisition

Agilent 1290 Infinity II UHPLC coupled with 6546 LC/Q-TOF system was employed for separation and identification of the compounds in ArF photoresist samples.

Table 1 The method parameters for LC-MS/MS.

Method	
LC	1290 Infinity II
Injection	1 µL
Flow rate	0.5 mL/min
Mobile Phase	5mM ammonium acetate +0.1% formic acid in THF
Column	ResiPore (4.6 × 250 mm, 3.5 µm)
MS	6546 Q-TOF Mass Spectrometer
Ionization	ESI (Agilent Jet Stream, AJS)
Polarity	Positive
MS Mass range	m/z 400-2500
MS Acq rate	3 spectra/s
MS/MS Mass range	m/z 40-2500
MS/MS Acq rate	5 spectra/s
Isolation width	Medium (~4 amu)
Precursors/cycle	6
Collision energy	Fixed: 10, 20, 40 V

Data Analysis

The Agilent MassHunter Qualitative Analysis 12.0 software was used for peak picking, formula assignment, and MS/MS fragment annotation.

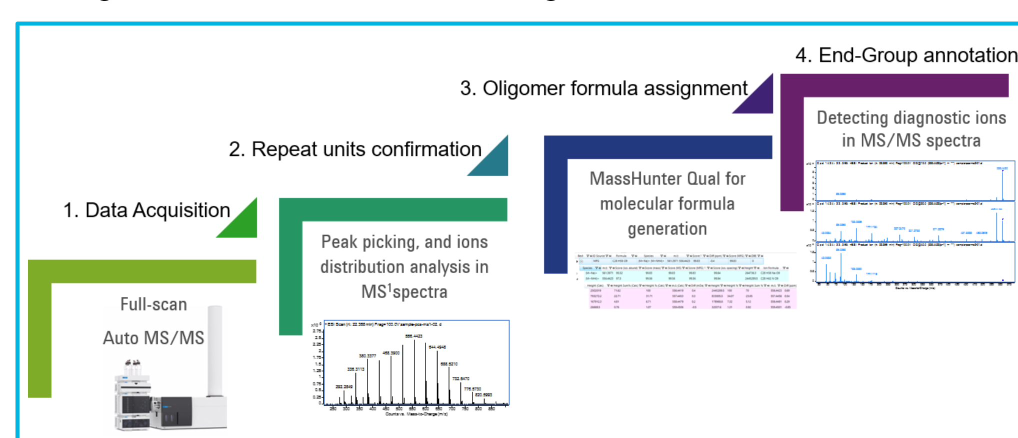

Figure 1 The workflow for oligomeric MS/MS analysis.

Results and Discussion

Agilent 1290 Infinity II UHPLC coupled with 6546 Q-TOF MS system was employed for separation and identification of the compounds in ArF photoresist samples. The Figure 2 was the base peak chromatogram (BPC) of the sample, which shows the oligomers has a good separation on ResiPore (4.6 × 250 mm, 3.5 µm) column.

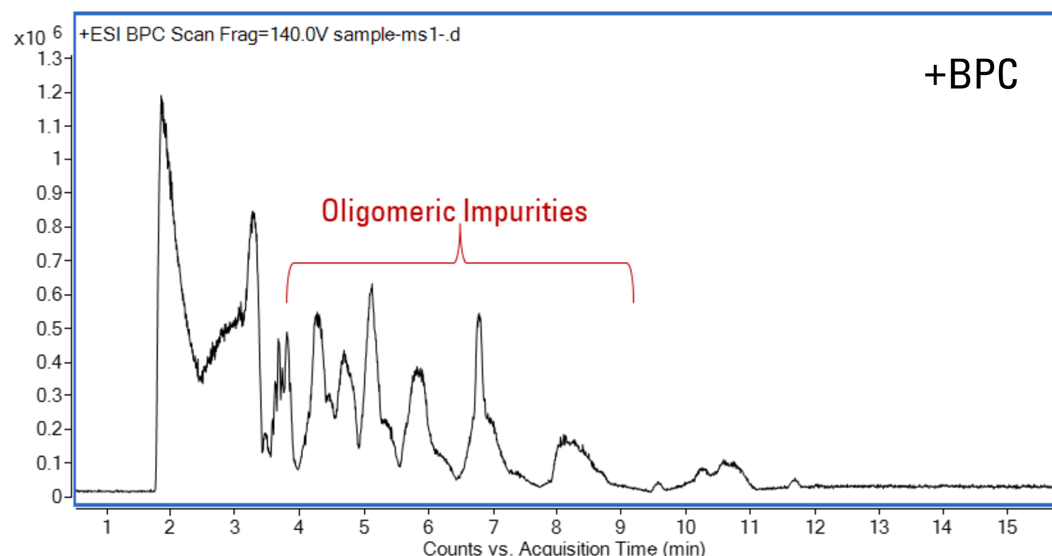

Figure 2 The base peak chromatogram (BPC) of the sample.

Oligomer Impurities Profiling

Due to the disproportionation reaction in the polymer synthesis process, the dominant ion species are $[M+H]^+$ and $[M+H-2H]^+$. The MS^1 spectra analysis revealed the presence of a variety of oligomeric impurity species in the photoresist resin samples. Take the peaks at Rt=4.3~5.1 min as an example, a series of ions at m/z 704.4321, 874.4932, 1044.5524, 1214.6107, 1384.7367, 1554.7961, 1724.8574 were showed in MS^1 spectra (Reference Figure 3), which indicated the repeat units was 170 Da. The exact mass of these ions generated molecular formulae as $C_{39}H_{63}NO_{10}$ + n($C_8H_{10}O_4$) by MassHunter Qual molecular formula generation algorithm.

Combined with the molecular formula, double bond equivalent, and other relevant sample information, the degrees of polymerization of this oligomers were elucidated ranging from 3 to 9.

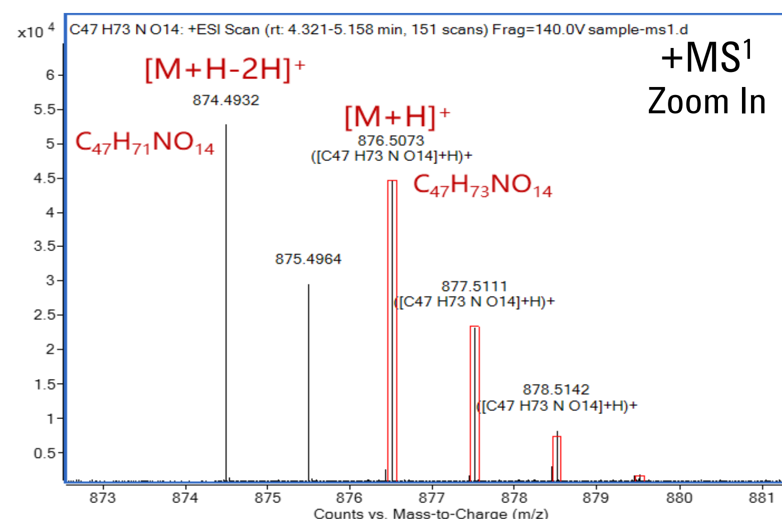

Figure 4 The zoom in MS^1 spectra at Rt=4.3~5.1min.

Monomer Composition Analysis

Accurate mass data and fragmentation patterns enabled reconstruction of monomer composition. The series of ions at Rt=4.3~5.1 min shows the oligomer contain a monomer with formular $C_8H_{10}O_4$, which is consistent with butyrolactone methacrylate. The MS^2 spectrum of m/z 874.4932 (Reference Figure 5) shows loss of $C_{12}H_{18}$ to get the characteristic fragment at m/z 712.3574. What's more, the dominant fragment ion was found at m/z 163.1476 in the low mass range with formular $C_{12}H_{19}^+$. The above two fragments corroborated that the structure contained substituent 2-ethyl-2-adamantyl, which can be derived from the monomer 2-ethyl-2-adamantyl methacrylate. Combined with the molecular formula and other relevant sample information, it is known that this oligomer structure contains monomers with butyrolactone methacrylate, 2-ethyl-2-adamantyl methacrylate, and methacrylic acid.

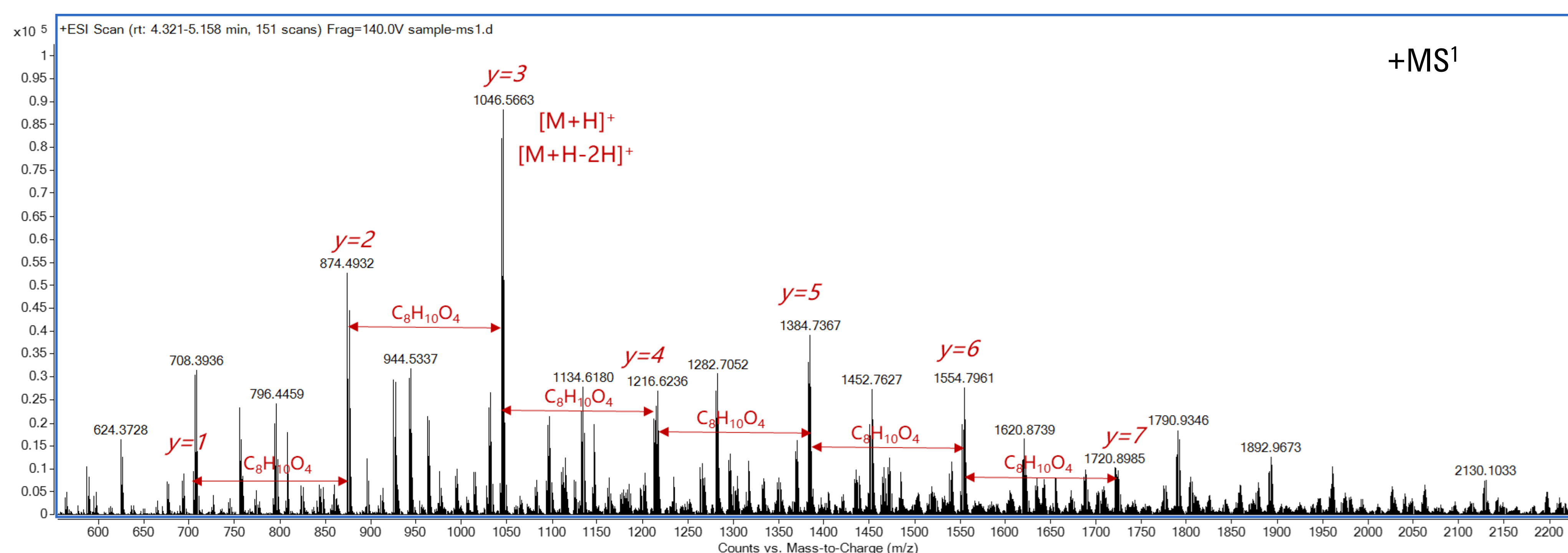

Figure 3 The MS^1 spectra at Rt=4.3~5.1min.

Results and Discussion

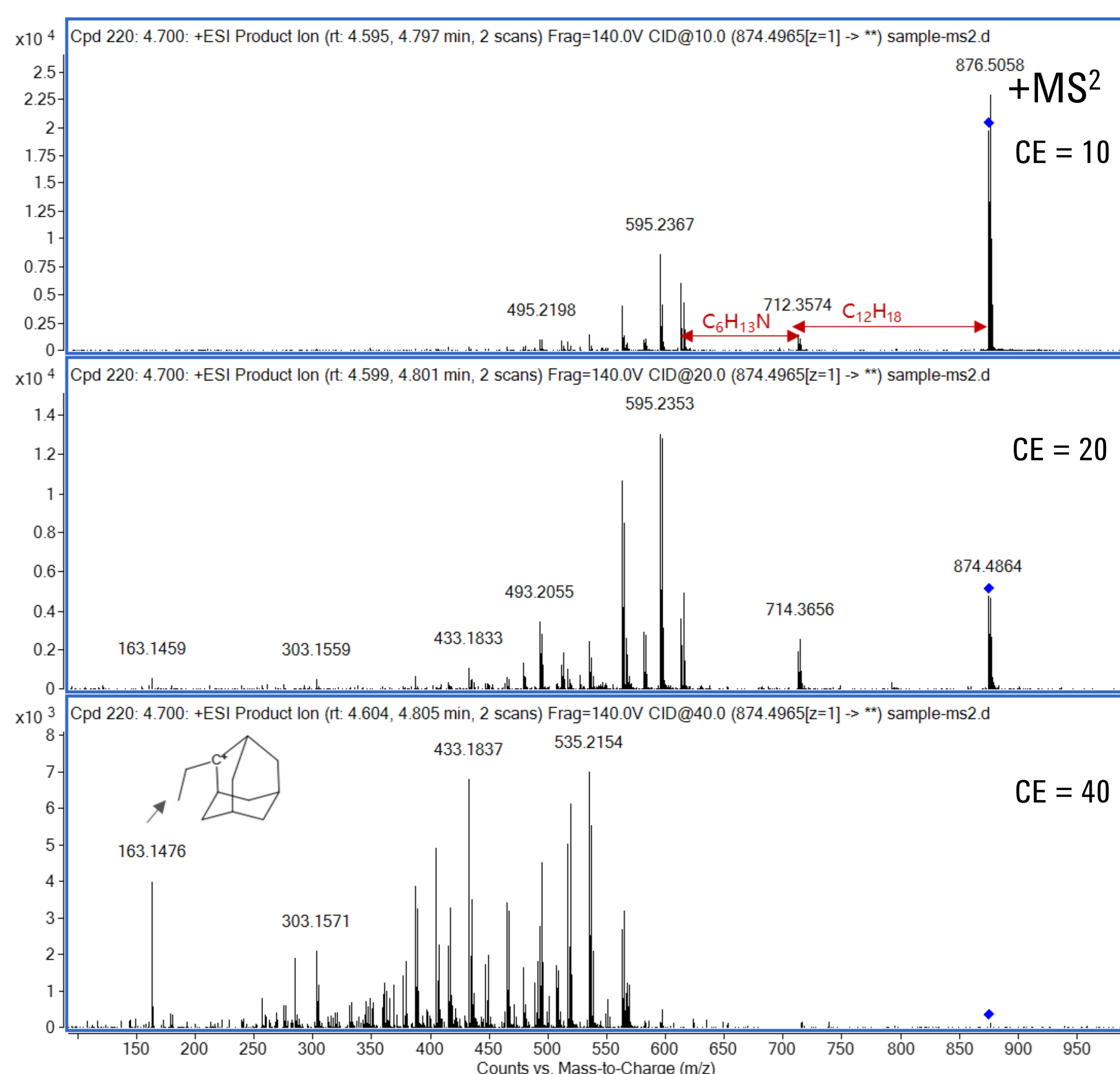

Figure 5 The MS^2 spectrum of m/z 874.4932.

End-Group Functionalities Characterization

Tandem MS/MS experiments can provide end-group functionalities information through the analysis of fragment ions. The MS^2 spectrum of m/z 874.4932 at peaks Rt= 4.3~5.1 min shows loss of $C_{12}H_{18}$ to get the characteristic fragment at m/z 712.3574, this fragment can further generate neutral loss of $C_6H_{13}N$ to get the diagnostic fragment ion at m/z 613.2444 (as showed in Figure 5). This information indicated that the structure of m/z 874.4932 has an end-group cyclohexanamine. The structure of oligomeric impurities at Rt=4.3~5.1 min and the fragmentation pathways of m/z 874.4932 were showed in Figure 6 and Figure 7, respectively.

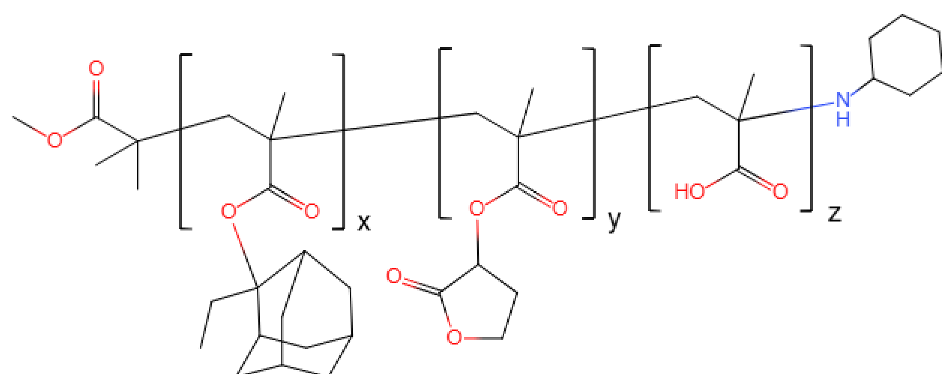

Figure 6 The structure of oligomeric impurities at Rt=4.3~5.1 min.

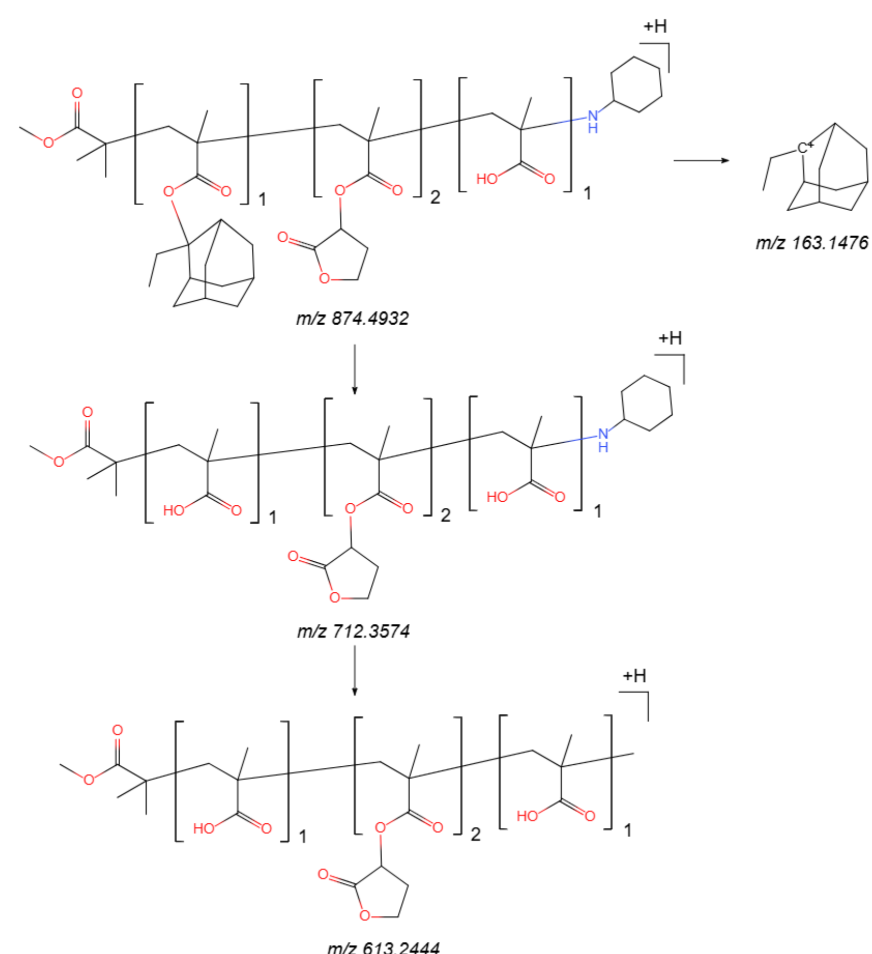

Figure 7 The fragmentation pathways of m/z 874.4932. .

Conclusions

This study presents a comprehensive Q-TOF HRMS workflow for the simultaneous analysis of oligomeric impurities, monomer composition, and end-group functionality in ArF photoresist block copolymers. The results provide valuable insights into the composition of photoresist resins and highlight the importance of rigorous quality control in their production.

References

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