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Investigation of Marine Degradation Characteristics of Bioplastics using MALDI-TOFMS and MALDI-DITMS

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1. Introduction

Recently, the accumulation of plastic waste in the ocean has been known to have an adverse effect on marine environment and ecosystem. An ecological impact of microplastics ingested by marine animals is a current global concern. The other problem is "Ghost net" caused by abandoned fishing net made of plastics. Marine animals suffer from serious and direct damages through the entanglement by plastic fibers.

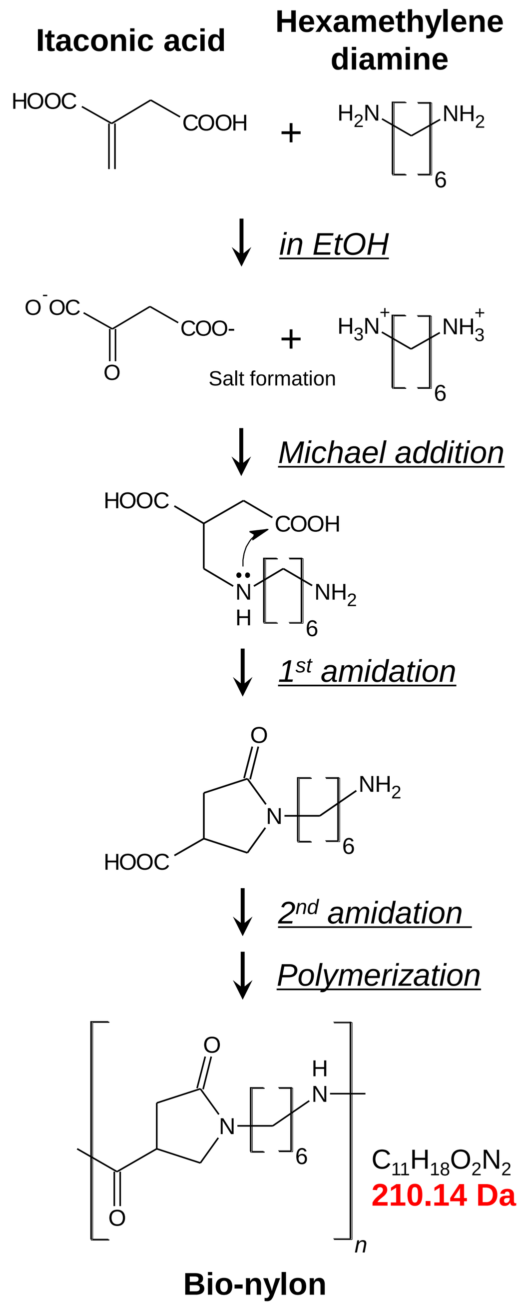
One solution for this is to replace conventional plastics by **biodegradable plastics**. A significant effort is being consecrated in tailoring the key properties of the biodegradable plastics such as physico-chemical properties and biodegradability in the marine environments. Here, marine degradation properties of a degradable nylon derived from a biomolecule, itaconic acid, were evaluated using MALDI-MS.

2. Methods

2-1. Newly designed polyamide

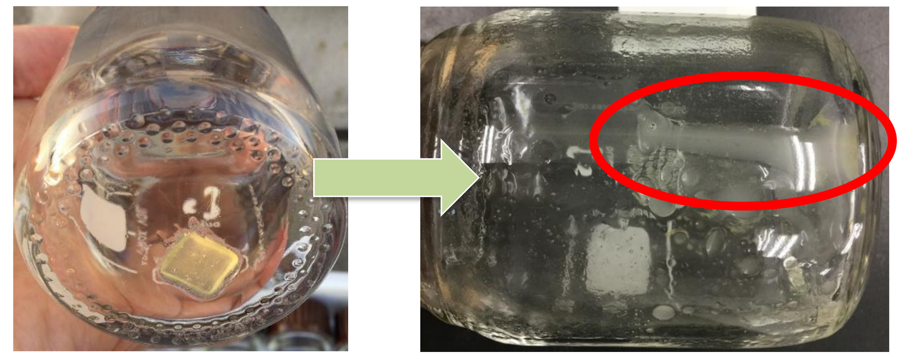
A newly designed polyamide (bio-nylon), which has photocleavable pyrrolidone rings and readily decomposes in water by ultraviolet irradiation, was used. This bio-nylon was made from **itaconic acid**, which can be produced by mold fermentation, and **hexamethylene diamine**.

Polymerization pathway



2-2. Degradation of the bio-nylon

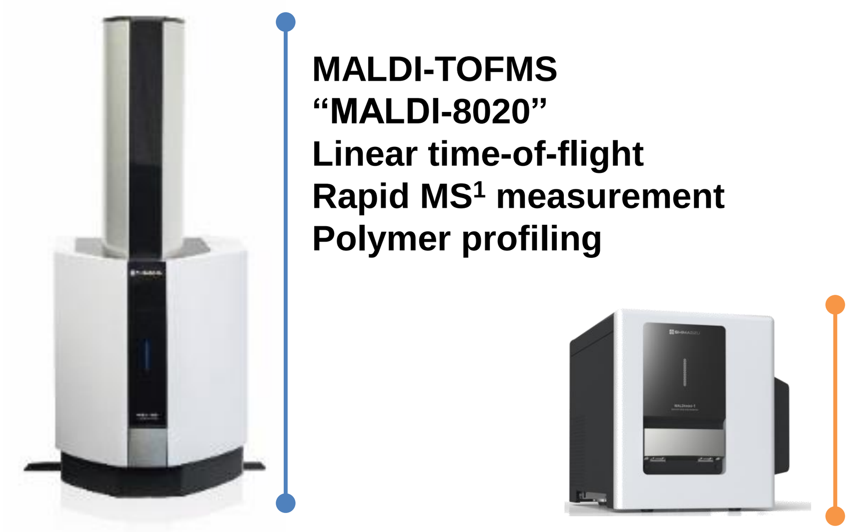
Photodegradation of the bio-nylon immersed in seawater was induced by exposing to sunlight for 14 days. This degradable bio-nylon immerged in water becomes hydrophilic by sunlight irradiation, and finally dissolves in water completely. This was also true under the condition of sunlight/seawater combination.



Immediately after immersion / After 14 days

2-2. Mass Spectrometry

The resulting sample in the seawater was diluted 10-fold by ultrapure water and measured using a CHCA matrix without any desalting pretreatment. Benchtop-type two instruments, MALDI-TOFMS (MALDI-8020, Shimadzu) and MALDI-DITMS (MALDImini™-1, Shimadzu) were used for the identification of the degradation products.



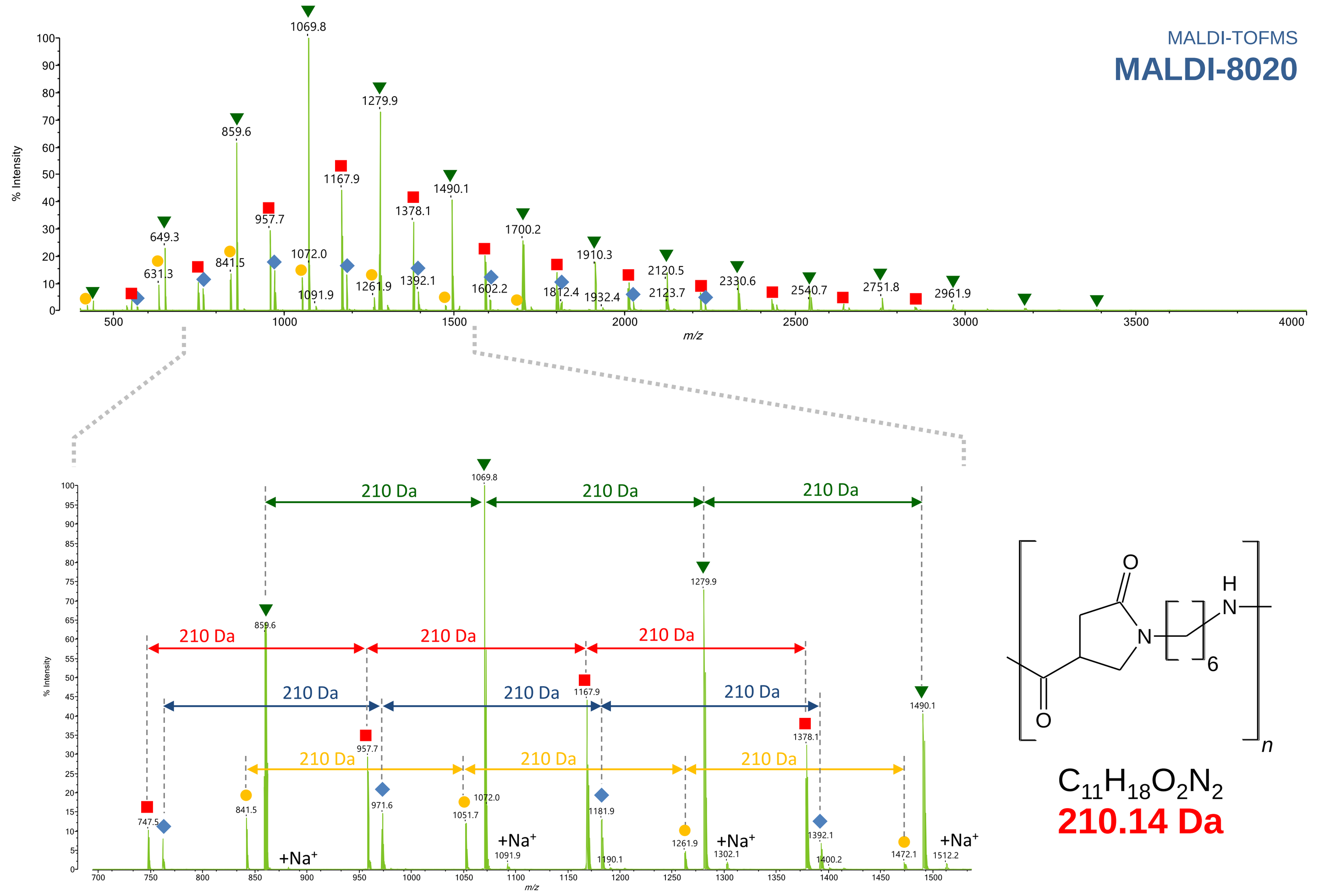
MALDI-TOFMS
"MALDI-8020"
Linear time-of-flight
Rapid MS[1] measurement
Polymer profiling

MALDI-DITMS
"MALDImini™-1"
Digital ion trap
MS[1-3] measurements
Structural analysis

3. Results & discussion

3-1. MALDI-TOF MS of photodegradation products

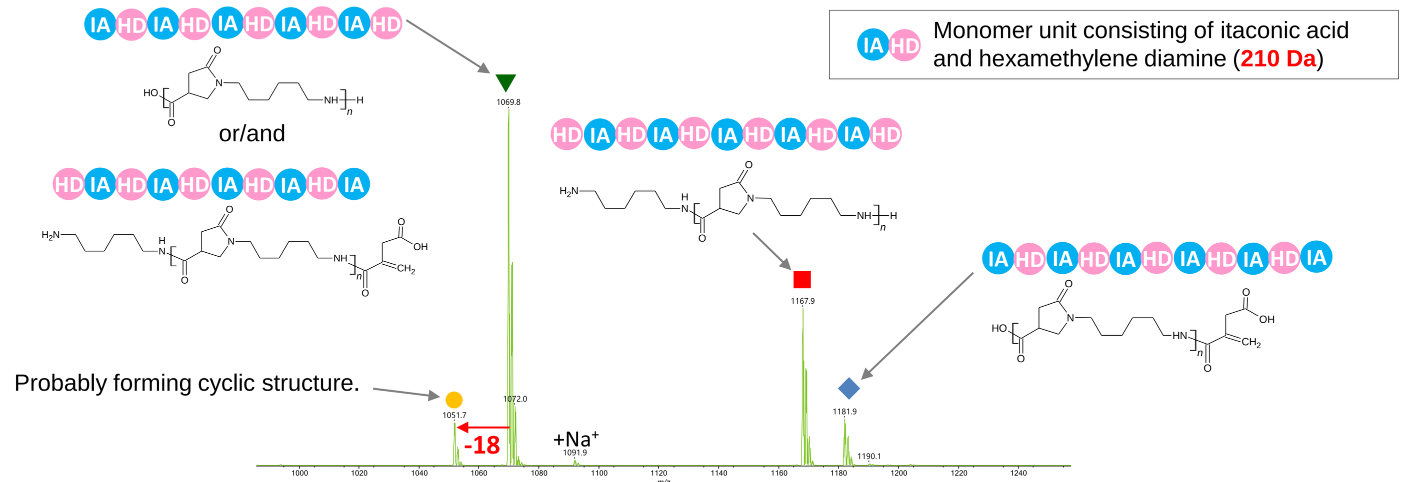
The results of MALDI-TOFMS analyses of the degradative products of the bio-nylon in seawater showed **four-types of polymers having monomer unit Δm = 210 Da**, which corresponds to a 1:1 condensation monomer of itaconic acid and hexamethylene diamine. Due to the presence of a basic constituent (hexamethylene diamine), all degradative polymers are ionized as **[M+H]$^+$**, not as cationized forms in spite of the high level of salt constituents in seawater.



$C_{11}H_{18}O_2N_2$
210.14 Da

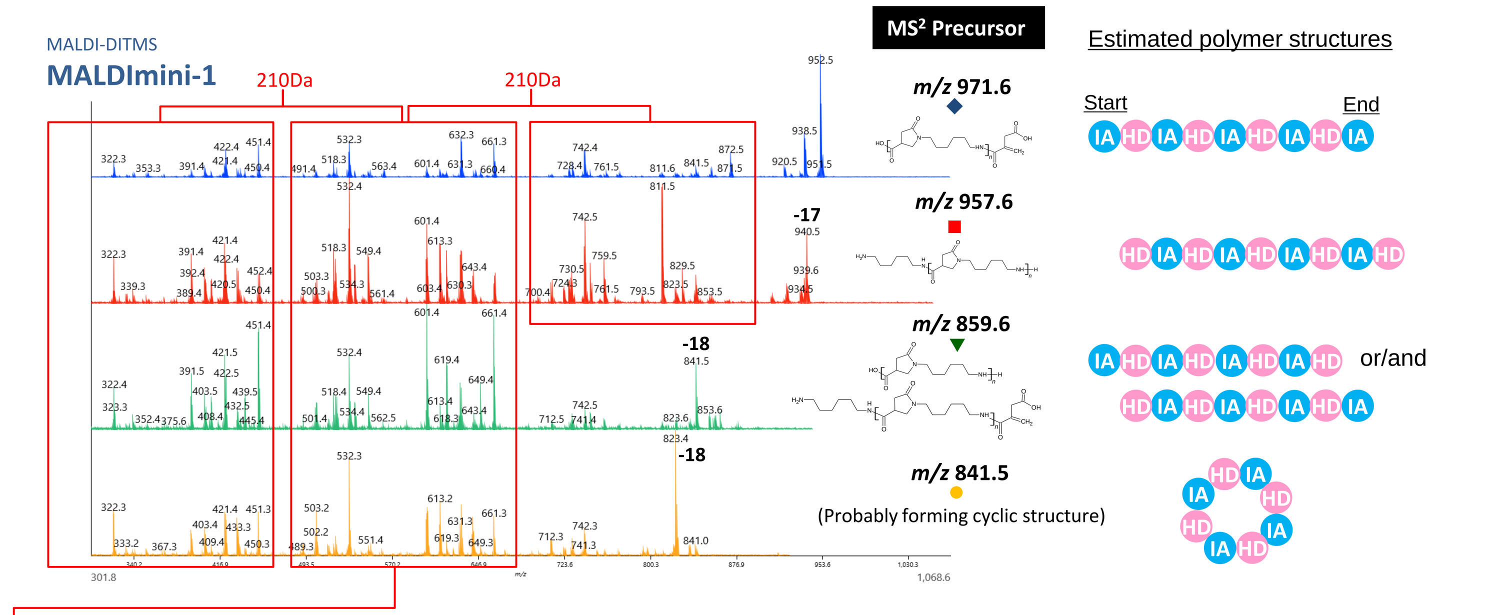
3-2. Estimated structures of the degradative products

Considering the polymerization pathway and estimated cleavage sites during the photo-degradation process, it was inferred that the four-types of polymers were the polymers with different terminal structures or a dehydrated product (probably forming cyclic structure).

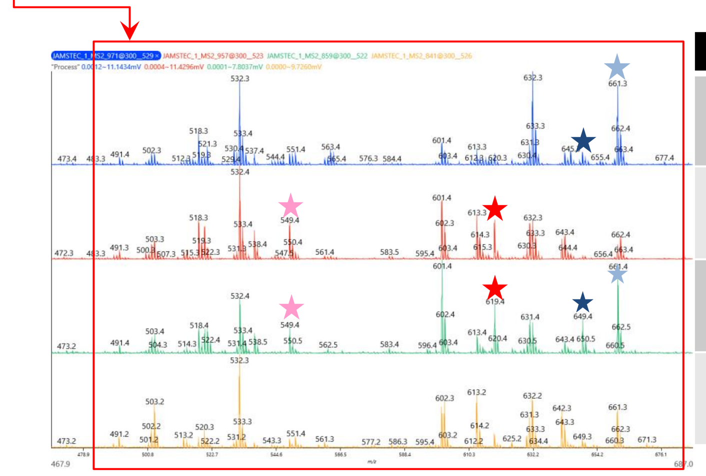


3-3. MS^2 of the degradative products

We measured same samples by a different type of mass spectrometer, MALDI-DITMS (MALDImini-1). MALDImini-1 has the digital ion trap, enabling us to perform MS^2 and MS^3 analyses under low-energy CID conditions. Each MS^2 mass spectrum of degradative products was obtained using MALDI-DITMS, and the results supported the structures estimated above.

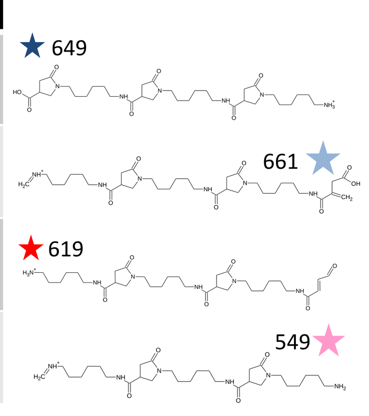


MS^2 spectra were somewhat complicated, but can be interpreted as bellow.
Detected MS^2 fragments can be classified into two groups, **internal fragments** and **terminal fragments**.
Cyclic ● should mainly produce the internal fragments. Here, we focus on the terminal fragments.
◆-specific and ■-specific fragments can be interpreted as the terminal fragments (star-symbols)
MS^2 of ▼ contains characteristic terminal fragments detected in MS^2 of ◆ and ■.
This indicates that ▼ is the mixture of IA-start and HD-start polymers, (IA HD)$_n$ and (HD IA)$_n$.



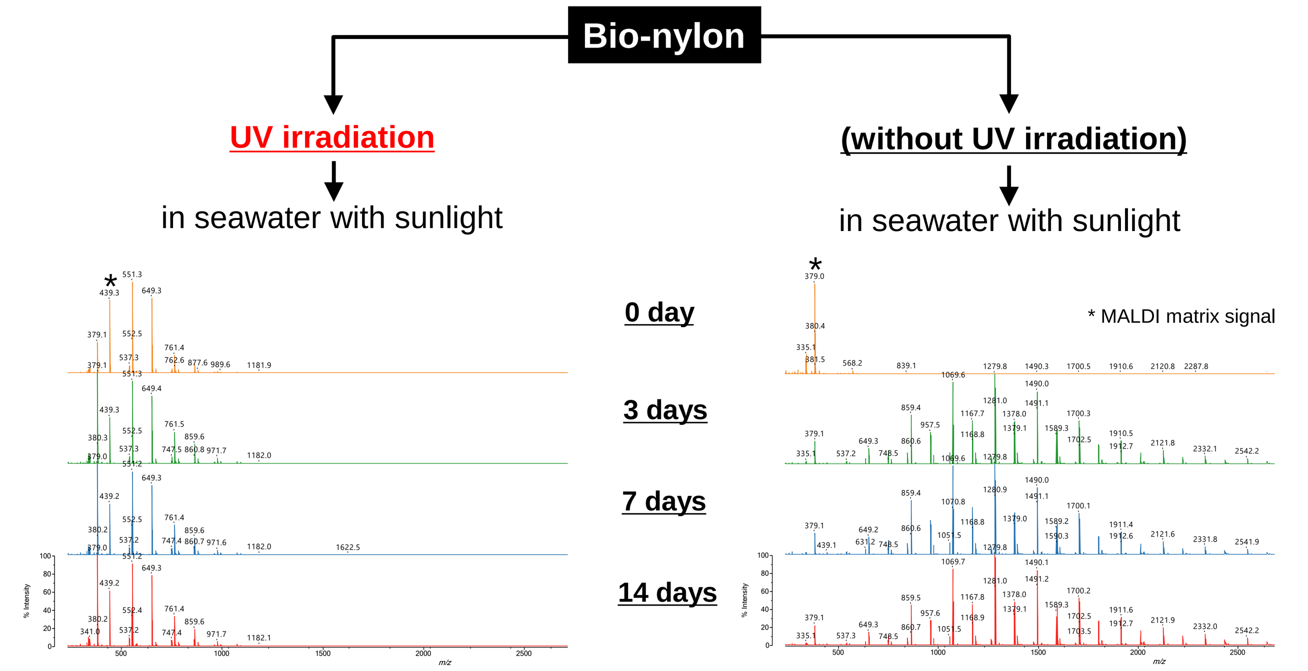
	Internal	Terminal fragments
◆	✔	
■	✔	
▼	✔	Both of the above
●	✔	None

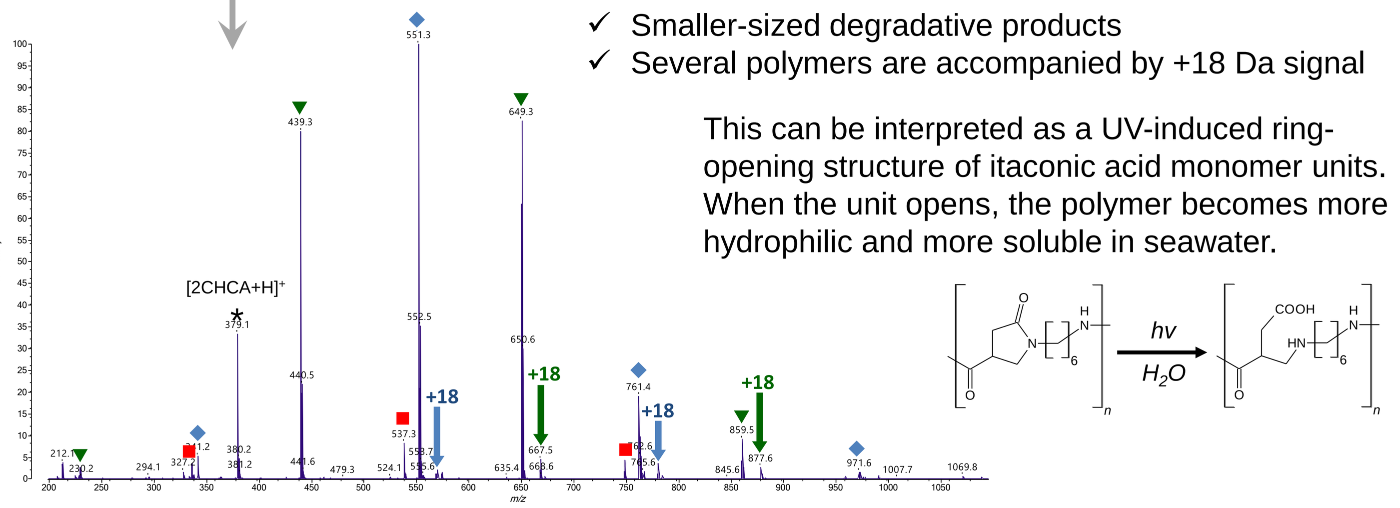
Estimated fragment structures



3-4. Degradation by UV light irradiation

To accelerate degradation, UV irradiation was performed before sunlight/seawater degradation. Interestingly, the UV-irradiated bio-nylon before the sunlight/seawater degradation showed smaller-sized polymers compared to the non-irradiated bio-nylon. This may indicate that the degradation characteristics of this degradative bio-nylon depend on UV wavelength or irradiation intensity.





✓ Smaller-sized degradative products
✓ Several polymers are accompanied by +18 Da signal

This can be interpreted as a UV-induced ring-opening structure of itaconic acid monomer units. When the unit opens, the polymer becomes more hydrophilic and more soluble in seawater.

4. Conclusions

- Polymer profiling by benchtop MALDI-TOFMS is useful for the evaluation of degradation characteristics of bioplastics.
- Elucidation of decomposed bio-nylon can be supported by MS^n measurements by MALDI-DITMS.
- Since polyamide-based polymers can be readily ionized as protonated form, the high level of salt contents in seawater does not prevent MALDI-MS analysis. This offers the wide application of MALDI-MS for analyzing degraded bioplastic polymers dissolved in seawater.

5. Acknowledgements

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