

Analysis of Components Emitted during Photodegradation of Bionylon with Light-Induced Hydrolysis

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■ Abstract

As the issues of marine plastic waste become more serious, there is a need to develop plastics that exhibit sufficient performance in use but quickly decompose in the marine environment. The authors have developed a high-performance nylon resin from itaconic acid that starts to decompose in water once exposed to sunlight. The nylon has a pyrrolidone ring in the main chain and exhibits light-induced hydrophilicity, but the structural changes and mechanisms involved have not been clarified. Therefore, when components emitted from samples due to light irradiation were analyzed using high-sensitivity GC-

MS, it was confirmed that high CO₂ emission levels occurred. Presumably, the light-induced ring-opening of the pyrrolidone ring resulted from CO₂ liberation, generated secondary amines to make nylon hydrophilic.

1. Introduction

The total amount of plastic waste that has flowed into the oceans globally is estimated to be 150 million tons, with annual accumulation estimated to be at least 8 million tons per year.¹⁾ In fact, even a large number of projects for recovering marine debris could reduce the waste amount significantly and such large amounts of plastic waste have already had a tremendous impact on marine ecosystems. For example, about 700 species of fish, seabirds, marine mammals, sea turtles, and other organisms have been killed or injured by the effects of marine debris, of which 92 % are due to the accidental ingestion of plastic bags or other plastics.²⁾

The intake rates of plastic waste are estimated to be 32 % for green turtles³⁾ and 90 % for seabirds.⁴⁾ According to the World Economic Forum, known as the Davos Conference, 82 % of the marine plastic waste currently flowing into the sea is generated from Asian countries.⁵⁾ In 2050, with the production volume of plastics having quadrupled, a shocking forecast has been announced that the amount of marine plastic waste will exceed that of fish in the sea.⁶⁾ Furthermore, Japan has exported large amounts of plastic waste to Asian countries, mainly China, as a resource. In that way, it is possible that Japan has had an impact on the outflow of marine plastic waste from Asia. Plastic waste accumulation also causes enormous economic losses. For example, the annual loss from plastic waste in the Asia-Pacific region is estimated to be \$ 620 million in the tourism industry and \$ 360 million in the fishing and aquaculture industries.⁷⁾ Therefore, if the development of marine-degradable plastics solves that problem, it could potentially reduce the economic loss in the Asia-Pacific region in addition to contributing to global environmental problems.

Considering that background, Japan's enormous responsibility with respect to the issue, and its significant role as a leader in Asia, Japanese cleanup projects should be an urgent task. The fundamental solution is to distribute plastics that are degradable in marine environments. On the other hand, their decomposability increases the speed of degradation during use, which hinders practical applications. The way to escape that trade-off is to develop a plastic that has sufficient durability when used but that is degradable when exposed to the marine environment.

Therefore, the author teamed up with experts from eight different universities and public institutions to set up a project for developing plastics with photo-controlled degradability that focuses on both the strong sunlight irradiation in sea surface environments and the darkness of underwater and seabed environments as external stimuli in the marine environment. The purpose of the research is to develop biodegradable plastics that start hydrolysis when triggered by light. In August 2020, the idea was accepted as one of the R&D projects for achieving the Moonshot goal "Realization of sustainable resource circulation to recover the global environment by 2050," led by Japan's Cabinet Office and The New Energy and Industrial Technology Development Organization (NEDO). Accordingly, the team implemented a project entitled "Development of photo-switching ocean-degradable plastics with edibility." In this report, the author describes the light-induced hydrolysis process, which is the seed of this project, and using a gas chromatograph mass spectrometer (GC-MS) with the highest sensitivity in the world to evaluate the components emitted from the plastic samples when exposed to light.

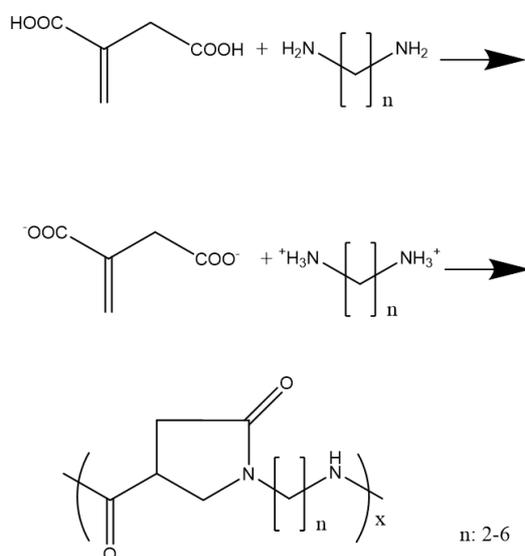


Fig. 1 Chemical Structure of Nylon Derived from Itaconic Acid

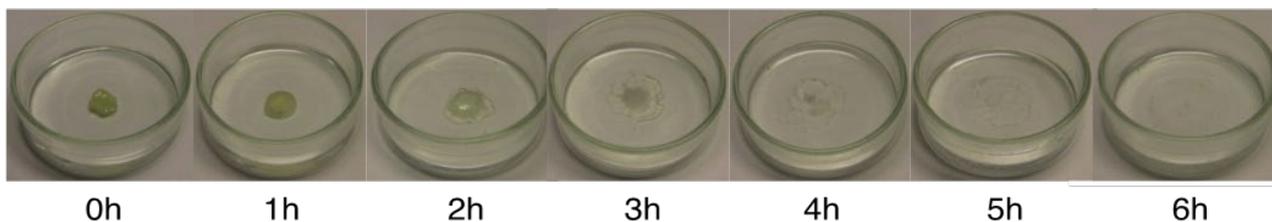


Fig. 2 Water-Solubilization of i-Nylon Resin by High-Pressure Hg Lamp Irradiation (UV-B)

3. Analysis of Components Emitted Due to Light Irradiation

i-Nylon from IA and hexamethylenediamine (6 carbon number) (Nylon 6i) shown in Fig. 3 were used. 200 mg of the sample was placed in a quartz cell with a screw cap, 1 ml of Milli-Q water was added, and then irradiated with a Xenon lamp (Hamamatsu Photonics LC8 Lighteningcure, wavelength 300 to 450 nm, and irradiation distance 10 cm) for 6 hours. The gas phase portion was collected with a gas-tight syringe and injected into the GC-

2. Light-Induced Hydrolysis

The sample used here is nylon derived from itaconic acid (IA), which has the characteristic that enhanced hydrolysis can be triggered using photoirradiation like a switch. IA is a biocompound obtained by thermal decomposition of citric acid, but IA is currently one of the compounds industrially produced by mass-bioprocessing (more than 30,000 tons per year). IA has been selected as a "12 Top Biobased Molecules" by the US Department of Energy and has long been used as a raw material for many chemical products, such as adhesives and rubber additives.⁸⁾ The global market for IA is worth 8.08 billion yen in 2016, with an average annual growth rate of 4.1 % from 2017 to 2025, indicating increasing needs.⁹⁾ Nevertheless, there were no academic papers published on nylon synthesis before our research. In fact, it was extremely difficult to synthesize nylon from IA due to side reactions, but we succeeded in synthesizing IA-derived nylon (i-Nylon: Fig. 1) with a clear structure by using the salt monomer method.^{10,11)} The glass transition temperature, T_g , of i-Nylon is 80 to 97 °C, which is higher than the T_g of conventional PA66 and PA6 nylons (57 °C and 53 °C).¹²⁾ This can be due to the two kinds of amides. One is a cyclic amide giving rigidity to the polymer backbone chain. The other is a normal amide giving hydrogen bonding. In terms of mechanical properties, the strength at failure ranged from 65 to 90 MPa and the Young's modulus from 430 to 2800 MPa. These values are also higher than those of PA66 nylon (failure strength: 65 to 68 MPa, Young's modulus: 590 to 1700 MPa)^{13,14)} and PA6 nylon (failure strength: 41 to 60 MPa, Young's modulus: 440 to 1400 MPa).^{14,15)} In addition, i-Nylon showed alkali hydrolysis and decomposition in soil, and gradually disintegrated in water under irradiation with ultraviolet rays, eventually disappearing (Fig. 2).^{8,9)} Based on such phenomena, i-Nylon resin exhibits remarkable disintegration as well as degradation characteristics. On the other hand, all organic substances have the property of being decomposed by light irradiation, as clarified in research on photooxidation-degradable plastics that was actively carried out in the latter half of the 20th century. Ocean-degradable plastics of aliphatic polyesters are no exception and the contribution of photodegradation cannot be ignored. As long as we propose a methodology using "photo-switches" in our samples, it is necessary to evaluate the contribution of photolysis carefully. Therefore, the following research was carried out in order to clarify how the process of direct decomposition by light occurs in IA-derived nylon.

MS system manufactured by Shimadzu Corporation (GCMS-QP2020 NX), used in combination with the NIST Mass Spectral Library, 2020 version. Analytical conditions include a PLOT column (Rtx-Q-BOND [0.32 mm I.D., 30 m long, 10 μm thick]) for analysis of carbon dioxide and low-mass hydrocarbons. A capillary column (Rtx-5MS [0.25 mm I.D., 30 m long, 0.25 μm thick]) was used for analysis of larger masses. A sample without light irradiation was used as a control.



Fig. 3 Appearance of Nylon 6i Resin Used as Specimens. (Left: Without Photo-Irradiation. Right: With Xe-Lamp Irradiation for 6 Hours.)



GCMS-QP2020 NX

Table 1 Instrument Configurations and Analytical Conditions

GC-MS:	GCMS-QP2020 NX
Column:	SH-Q-BOND (30 m × 0.32 mm, 10 μm) (Code No., 221-75764-30, Shimadzu) SH-I Guard Column (0.32 mm, 1.5 m MS side)
GC	
Inlet Temp.:	250 °C
Injection Mode:	Split
Split Ratio:	30
Carrier Gas:	He
Carrier Gas Control:	Constant linear velocity (52.8 cm/s)
GC Oven Program:	35 °C (1 min) → (15 °C/min) → 270 °C (10 min)
Injection Volume:	500 μL
Injection Method:	Manual injection with a gas-tight syringe
MS	
Ion Source Temp.:	200 °C
Interface Temp.:	250 °C
Measurement Mode:	Scan
Event Time:	0.3 s
Mass Range (m/z):	20 to 300

The measurements resulted in the chromatograms shown in Fig. 4. They show that some volatile components were detected from the sample irradiated with light. The details are summarized in Table 1. Carbon dioxide was the most abundant vaporized component, followed by acetaldehyde, ethylene, propene, ethane, butane, and others, detected in that order. Similarly, evaluating the large-mass components with a capillary column resulted in detecting components such as pentene, benzene, and octene.

The above results indicate that photodecomposition accompanied by the elimination of these components occurs when Nylon 6i is irradiated with light. In particular, it showed the quantity of carbon dioxide detected was two orders of magnitude higher than other components and that photooxidation decomposition occurred. The detection of an aliphatic hydrocarbon with 6 or fewer carbon atoms is considered to indicate emission from both IA and hexylene moieties.

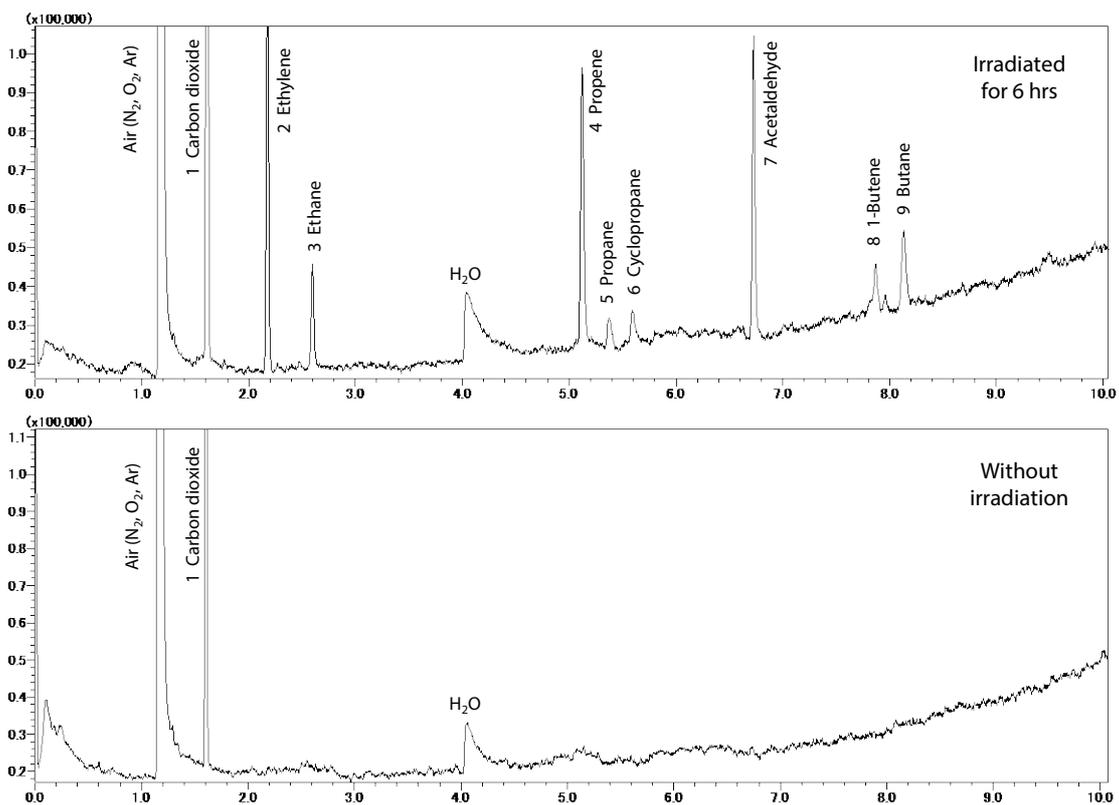


Fig. 4 TIC Chromatograms of Nylon 6i (PLOT Column)

Table 2 Top Compounds in Similarity Search Results

ID	Compound	Similarity Score	Molecular Formula	m/z	Area	
					Without Irradiation	Irradiated for 6 Hrs
1	Carbon dioxide ^(*)	99	CO ₂	44	384778	3384080
2	Ethylene	99	C ₂ H ₄	28		43828
3	Ethane	98	C ₂ H ₆	28		23271
4	Propene	96	C ₃ H ₆	41		32695
5	Propane	92	C ₃ H ₈	29		3904
6	Cyclopropane	92	C ₃ H ₆	42		4024
7	Acetaldehyde	97	C ₂ H ₄ O	29		62871
8	1-Butene	94	C ₄ H ₈	41		9159
9	Butane	93	C ₄ H ₁₀	43		18331

(*) 1st hit compound is not CO₂, but elution time indicated in literature corresponds with that of CO₂ (Carbon dioxide(CO₂): GCMS Application Data Sheet No. 56 GC-MS)

Benzene was also detected, but that is thought to be due to the reactions with emitted or other substances. It was also considered that the reason why the nitrogen-containing component was not detected despite the decomposition of nylon was due to lack of vaporization caused by highly polar products dissolving in water.

It is considered that the photooxidation decomposition includes reactions generally occurring when polyethylene decomposition emits carbon dioxide and oxygen that react with the amide bond, causing breakage of the backbone chain. Another structural change in the form shown in Fig. 5 can be assumed from the carbonyl elimination from the pyrrolidone ring. As a result, the highly hydrophilic secondary amine is incorporated into the backbone chain, to increase the hydrophilicity by photo-irradiation.

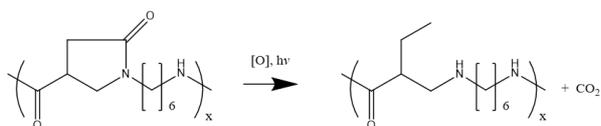


Fig. 5 Ring-Opening Reaction Assumed in Photooxidation of Pyrrolidone Ring in i-Nylon

4. Conclusion

By using IA produced by microorganisms, nylon has been developed that exhibits high heat-resistance, high strength, and light-induced hydrolyzability. Furthermore, GC-MS analysis identified the components emitted due to photoirradiation and clarified the mechanisms involved in photodecomposition and light-induced water solubilization. If i-Nylon is applied to fishing lines in the future, fishing lines dumped in the ocean are expected to be ideally degradable plastics that gradually disintegrate to dissolve in sea water and biodegrade under ultraviolet rays of sunlight.

Acknowledgments

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