Development of Photo-switching Ocean-degradable Plastics with Edibility

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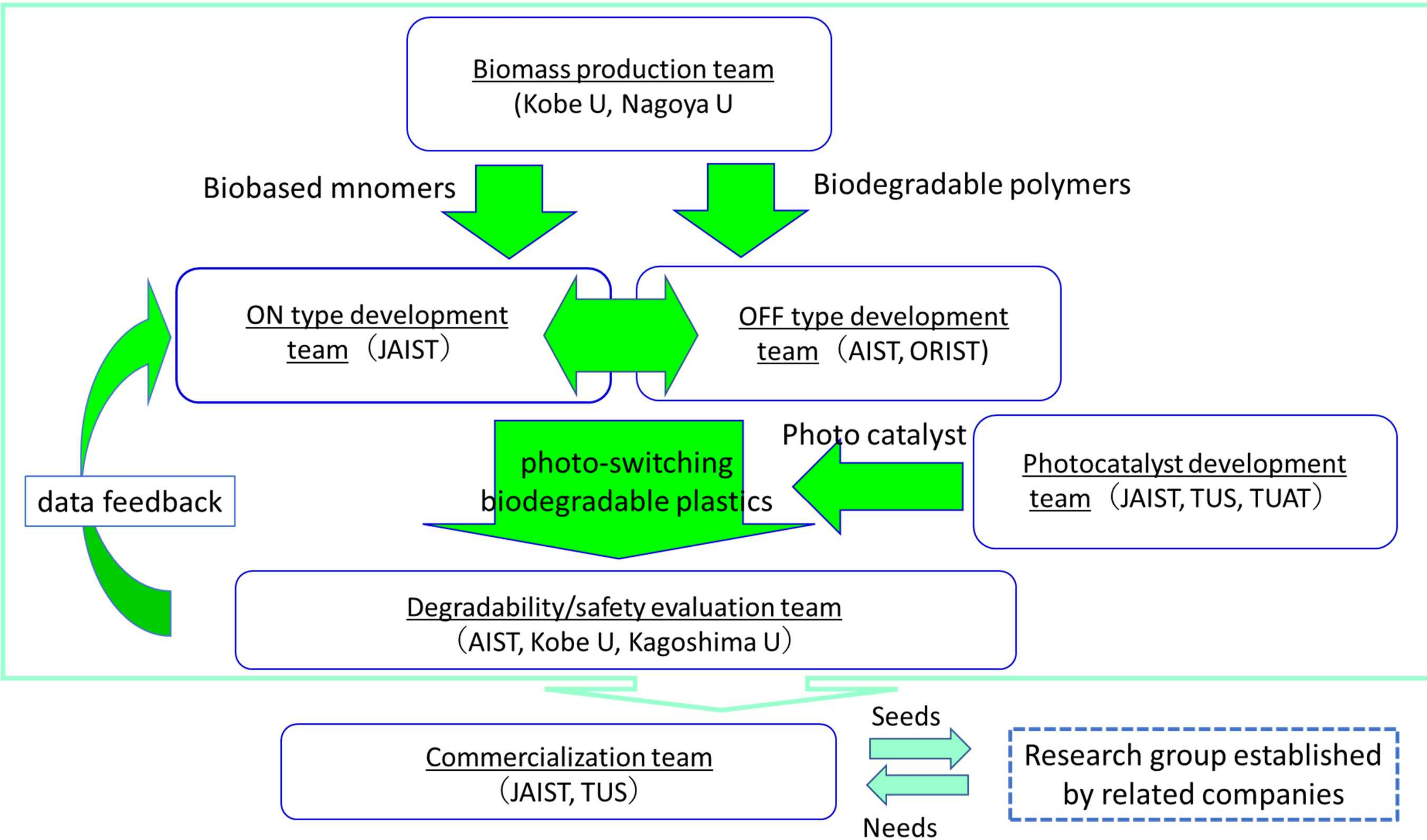
Implementing organizations :Japan Advanced Institute of Science and Technology, Kobe University, Nagoya University, Kagoshima University, Tokyo University of Science, Tokyo University of Agriculture and Technology, National Institute of Advanced Industrial Science and Technology(AIST), Osaka Research Institute of Industrial Science and Technology(ORIST).

Development of Photo-switching Ocean-degradable Plastics with Edibility

Term FY2020-2023

Ultimate goals Developing a photo-switching ocean-degradable plastics composited with a newly developed high-performance photocatalyst

Research system



Research and development items/contents (this year)

Development of switch type biodegradable resin

ON type biodegradable resin

Development of photocat. for ON type switch

↓

Development and molding of ON type biodegradable resin

← Composite

OFF type biodeg. resin

Development of reduced photocat. for OFF type switch

↓

Compounding, Antibacterial evaluation

↓

Safety and environmental impact assessment

Biodegradability evaluation

Real environment immersion biodegradability evaluation
Laboratory seawater biodegradability evaluation
Evaluation using nylon biodegrading bacteria and enzymes
Consideration of composting process

Safety evaluation

Evaluation using enzymes and fish
Evaluation by various marine organisms
Evaluation in simulated intestinal environment
Examination of changes in Intestine gene expression

ON type switch and OFF type switch

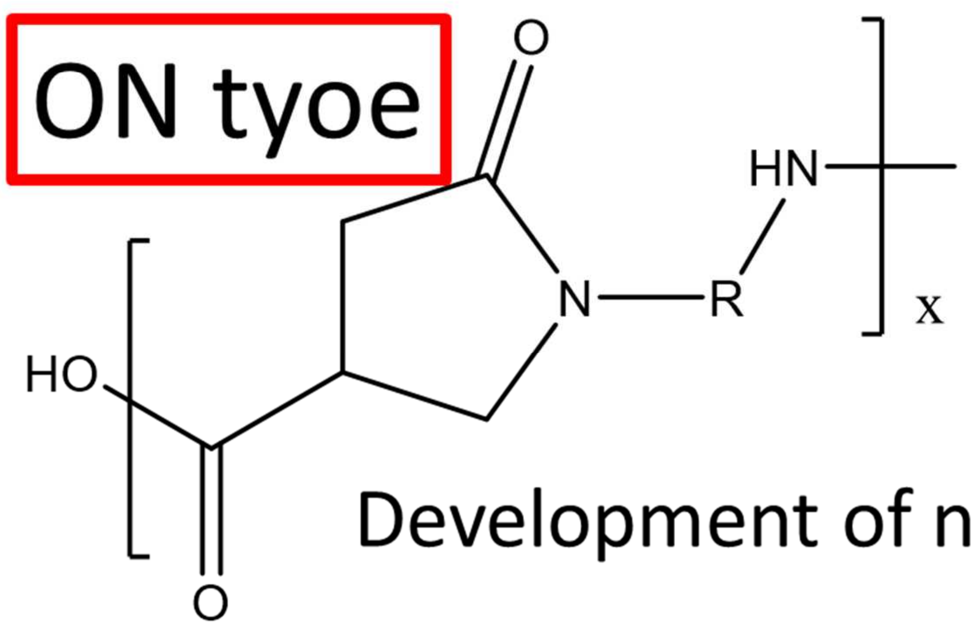
ON type switch	Biodegradation progresses under light exposure
OFF type switch	Biodegradation suppressed under light exposure

ON type switch	Converting a non-biodegradable structure to a biodegradable structure through chemical conversion。
OFF type switch	Limits microbial activity with photo-antibacterial power.

Requires strong light intensity

Low light intensity is sufficient

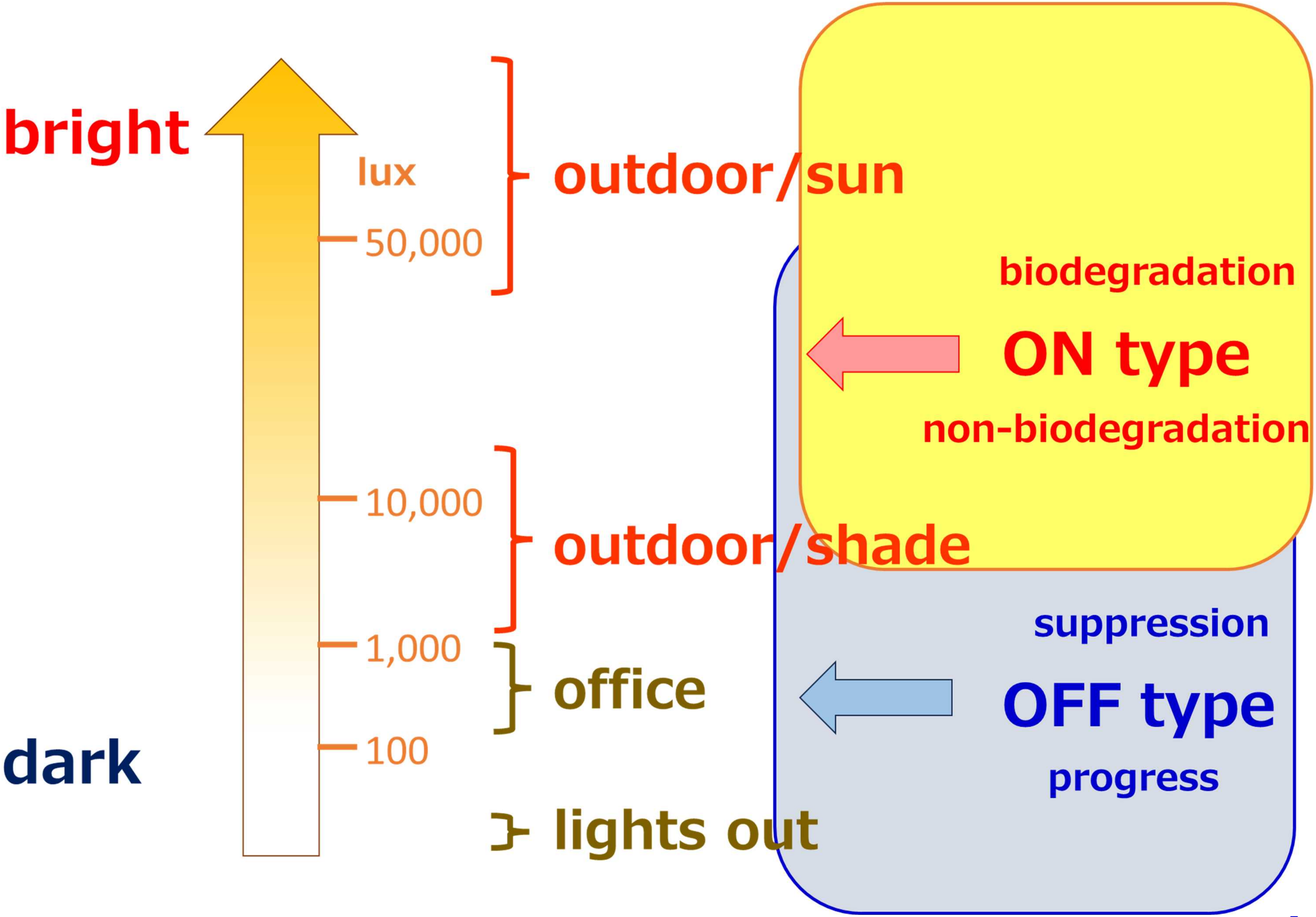
ON tyoe



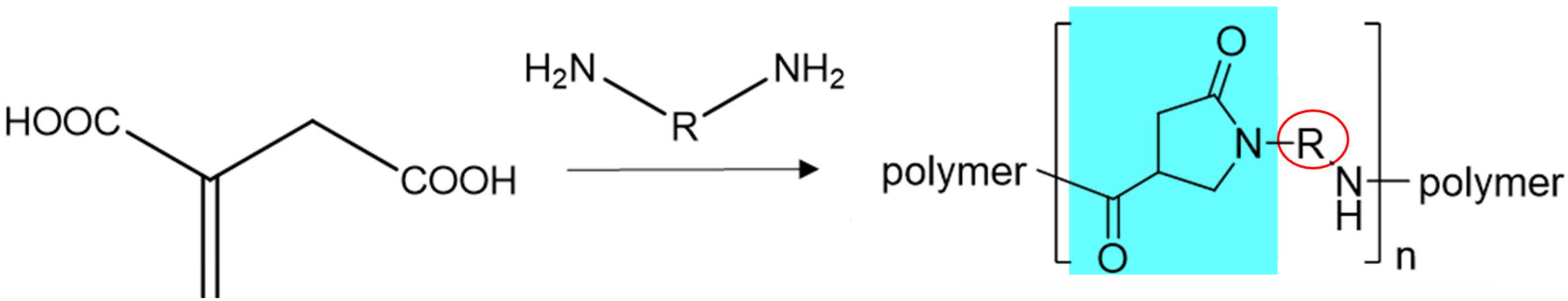
Development of new biodegradable materials

OFF type

Equipped with existing biodegradable materials


bright
lux
50,000
10,000
1,000
100
dark
outdoor/sun
outdoor/shade
office
lights out
biodegradation
ON type
non-biodegradation
suppression
OFF type
progress

Development of biodegradable resin with ON-type photo switch

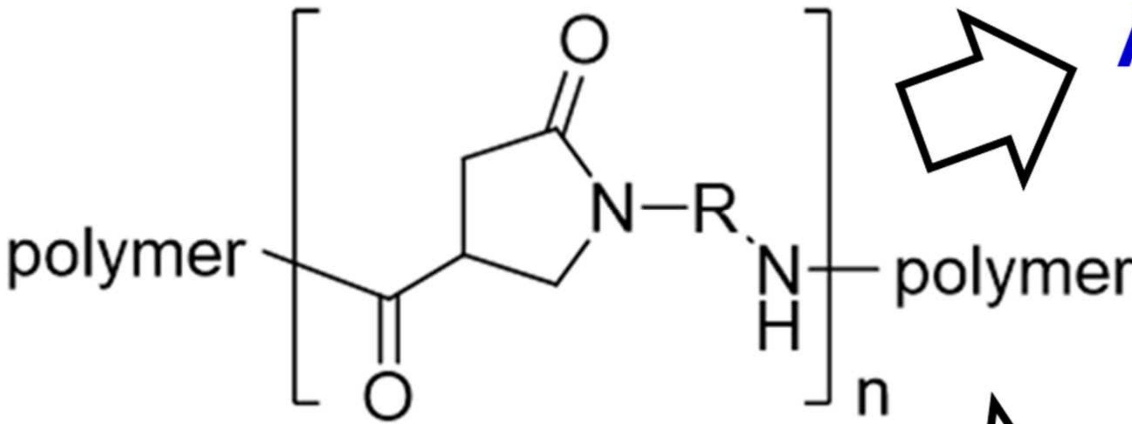


R= $-C_6H_{12}-$ **Ny6i**

= $-C_5H_{10}-$ **Ny5i** all biomass

Pentamethylene diamine ← Decarboxylation of lysine

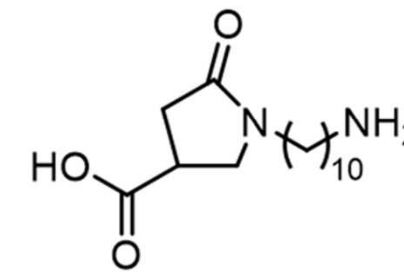
Various monomer synthesis as photo-switch core part and various ON type copolymers



Homopolymer (nylon 6i, nylon 5i, etc.)

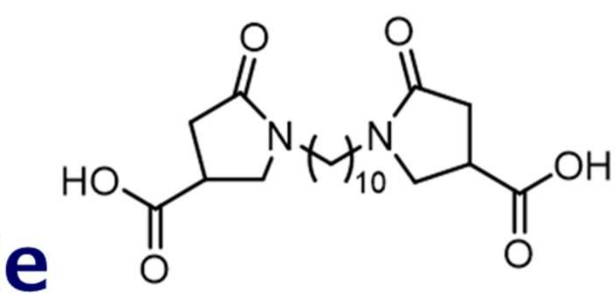
Aminocarboxylic acid type monomer

Polyamide, Copolyamide



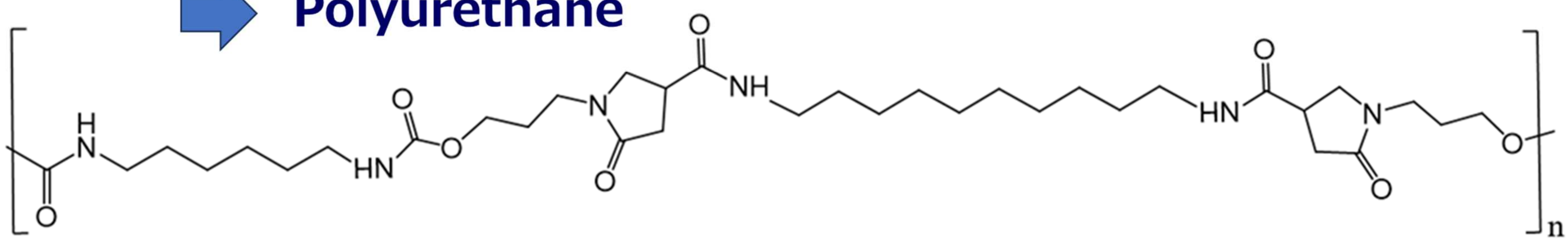
Dicarboxylic acid type monomer

Polyamide, Copolyesteramide



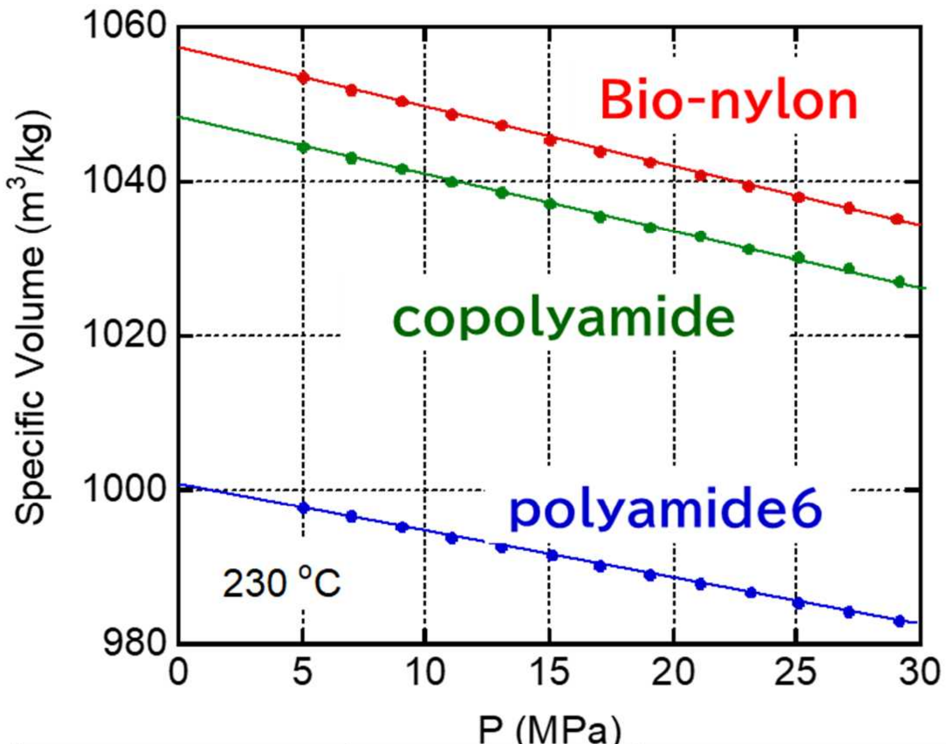
Diol type monomer

Polyurethane



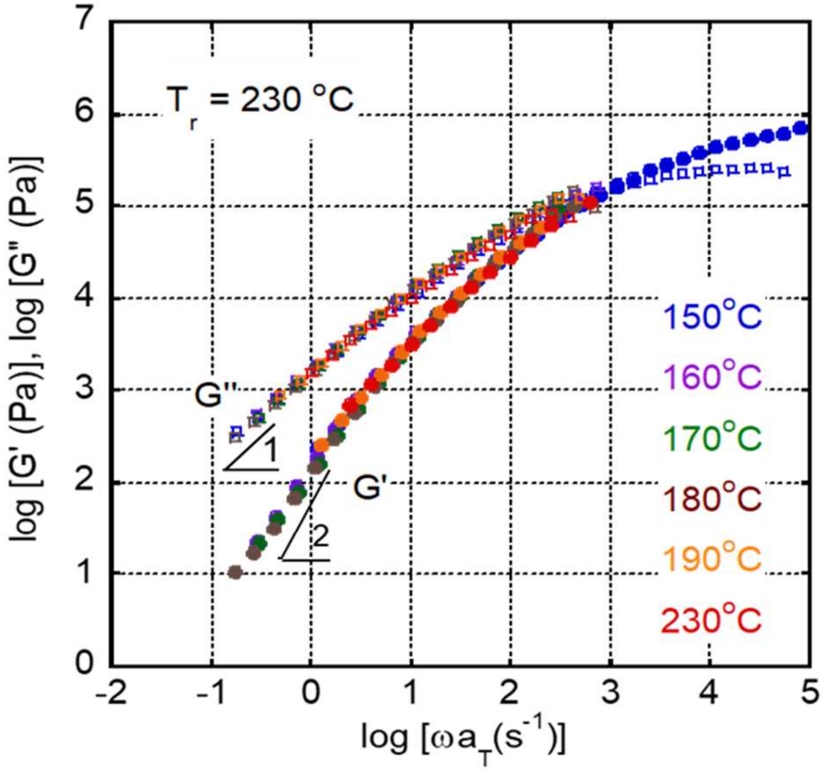
Molding processability of ON type optical switch polyamide

Pressure-Volume relation



	Melt density [kg/m³]	Bulk modulus [GPa]
Ny6i11(50)	946	1.40
Copolyamide	954	1.47
PA6	999	1.66

Oscillatory shear modulus



Viscoelastic properties of bio-nylon are similar to those of conventional nylons.

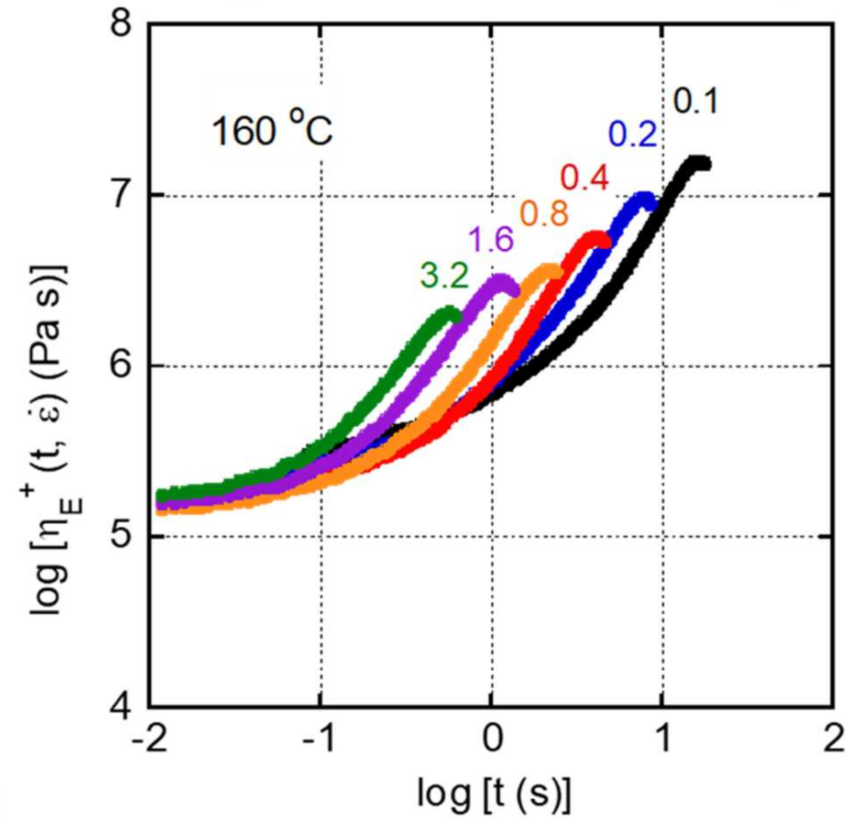
Entangement molecular weight

$M_e = 2700$

PA6 $M_e = 2490$

PA66 $M_e = 2000$

Elongational viscosity



Strain hardening, i.e., viscosity increase with time, is detected

Spinning

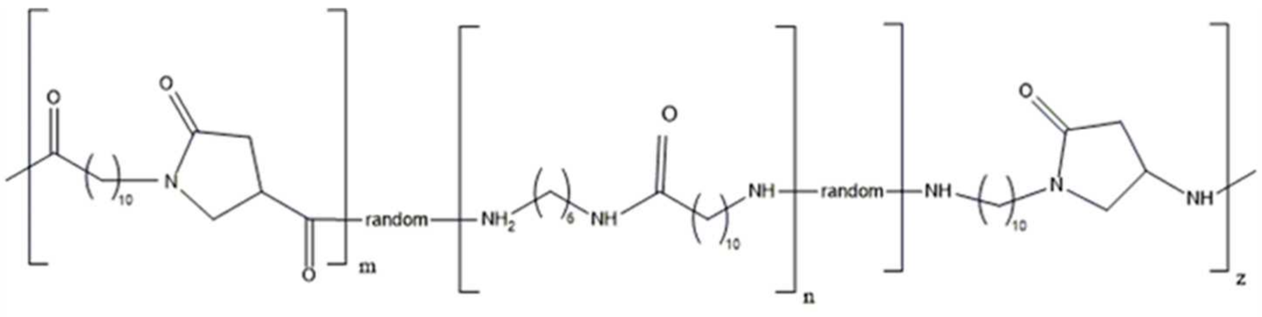
・Melt spinning is available (diameter 15-50 mm)

・It is possible to obtain a sheath-core fiber.

Film, foaming, and blow-molding

・A small addition of reactive modifier provides strain-hardening in elongational viscosity, leading to good processability.

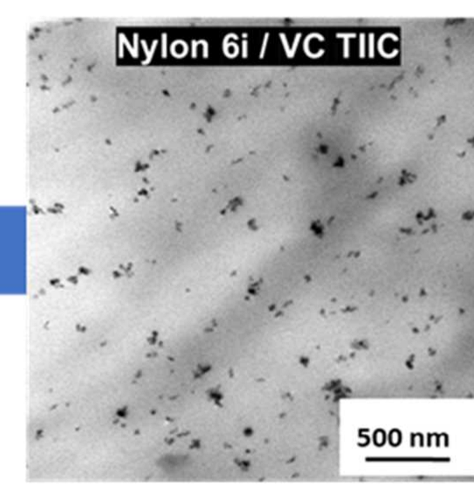
Photodegradation



Nylon 6i-11-50%
+
Photocatalyst (0.5 wt%)

Melt compounding
(140°C)

Film pressing
(130°C)

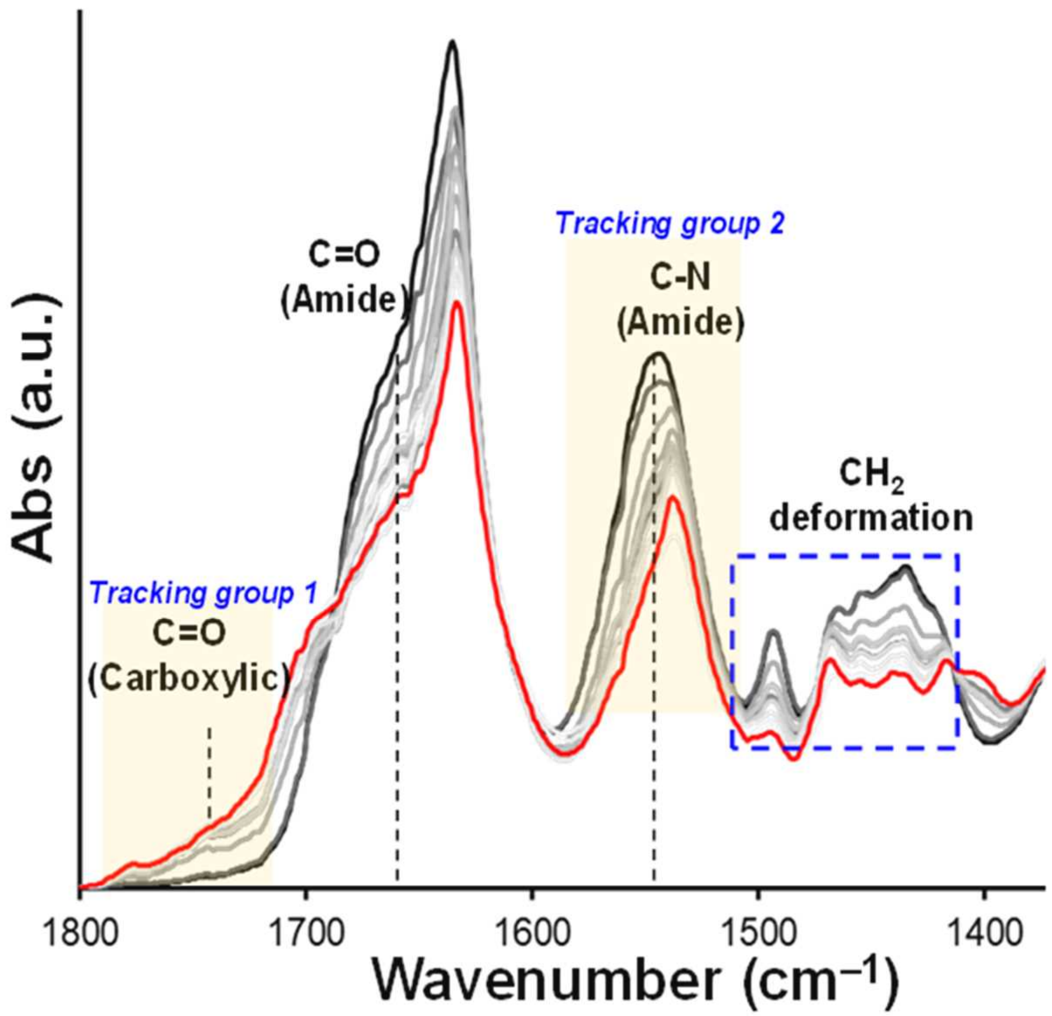


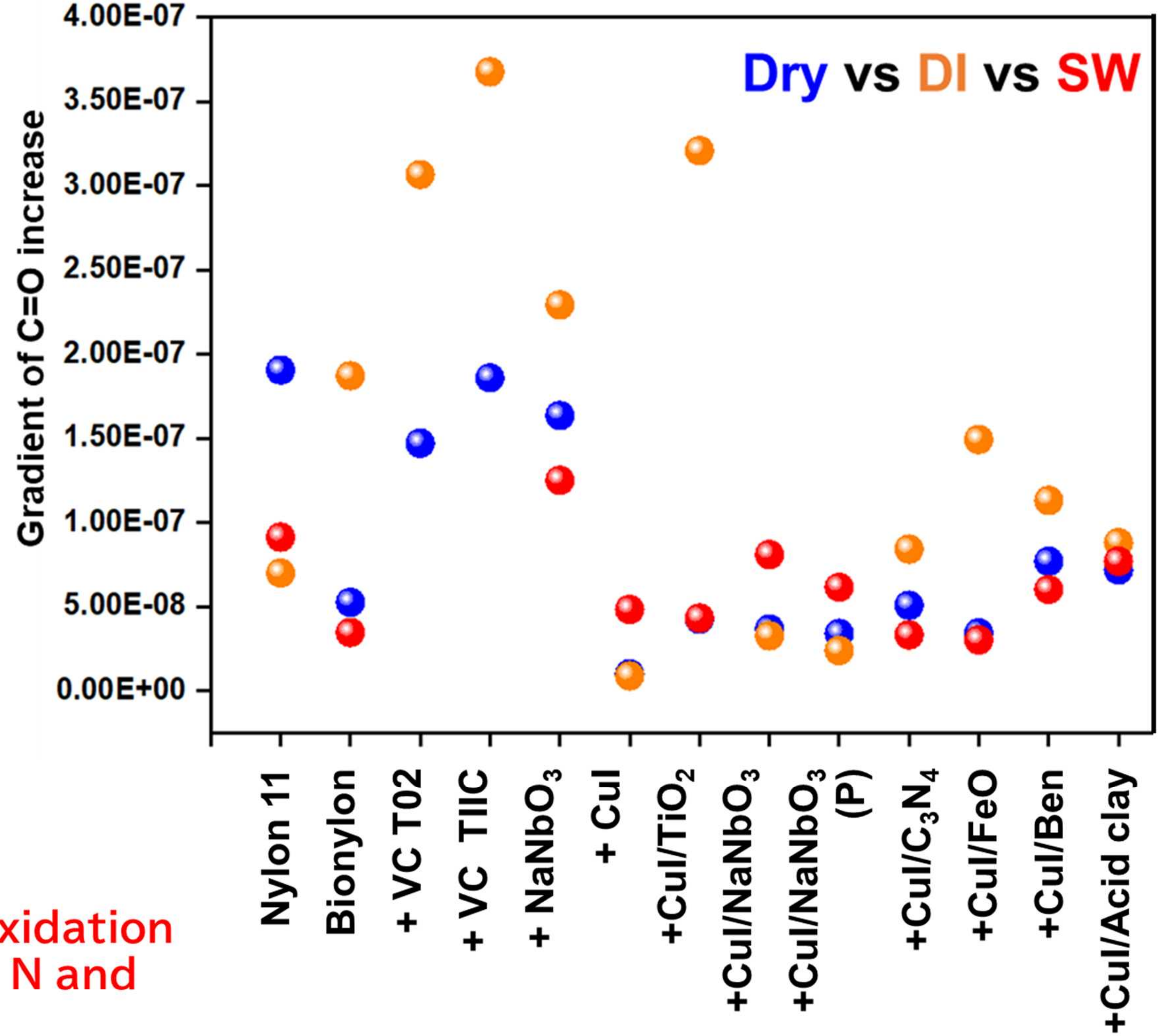
Uniform dispersion and film appearance

Xenon lamp
(550 W/m², 35 °C)

Aging in dry air, pure water, and sea water
(~12 weeks)

Photo-Degradation

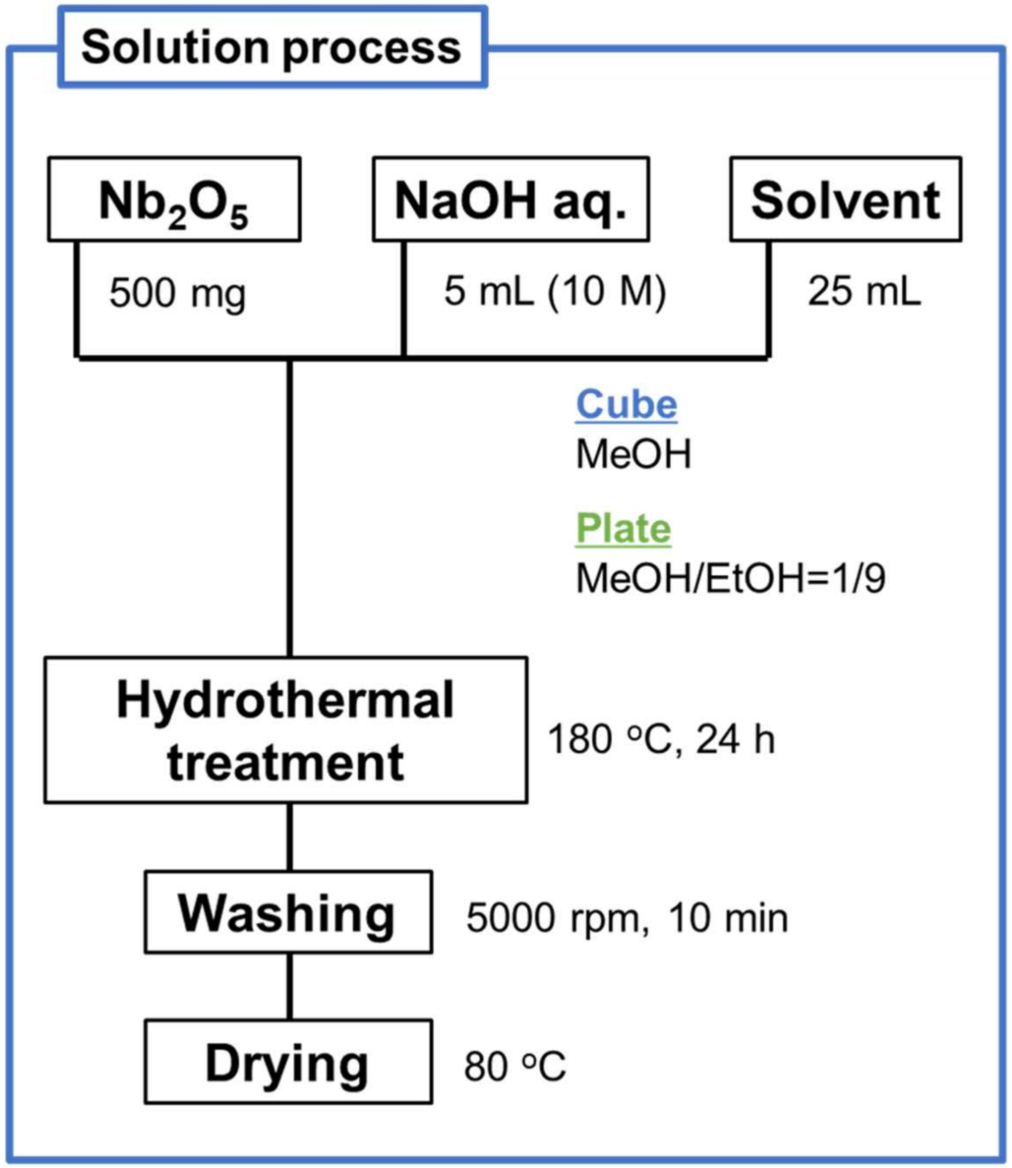


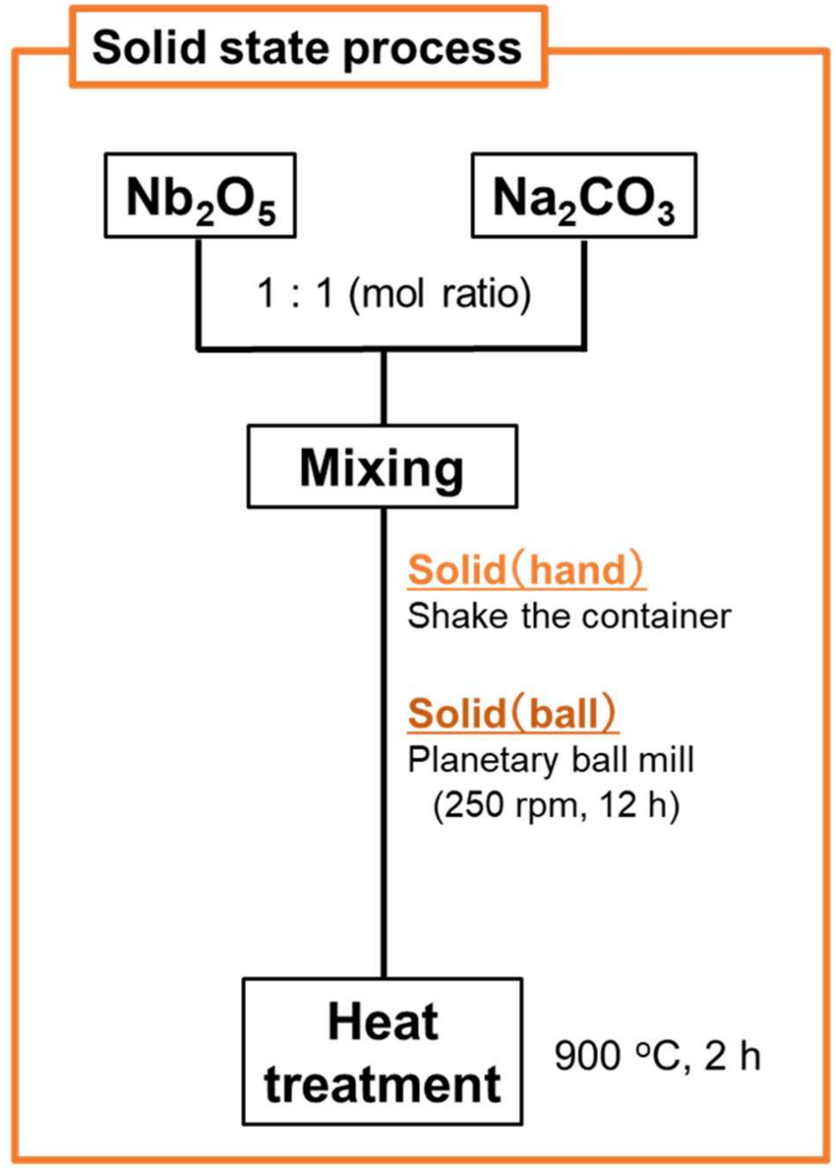


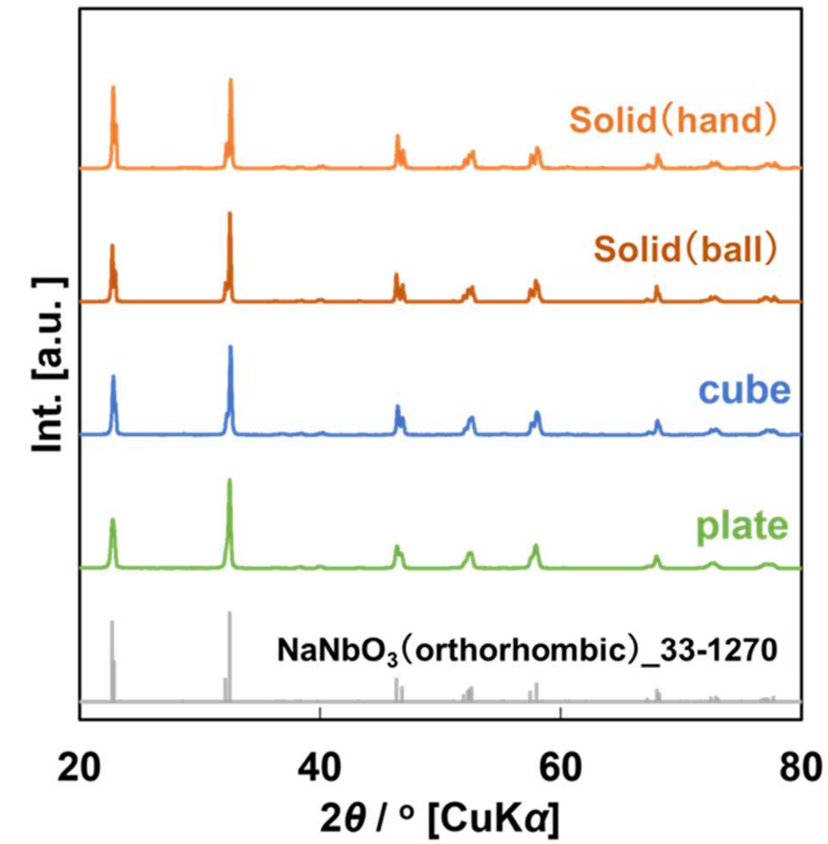
- Bio-nylon degraded via th oxidation of CH_2 next to pyrrolidone N and amide scission.

- Bio-nylon degraded via the oxidation of CH_2 next to pyrrolidone N and amide scission.
- The pyrrolidone groups selectively promoted degradation in pure water.
- The TiO_2 addition accelerated the photodegradation by 2-3 times.
- The addition of CuI largely suppressed the degradation, while the degradability in water could be recovered by TiO_2.

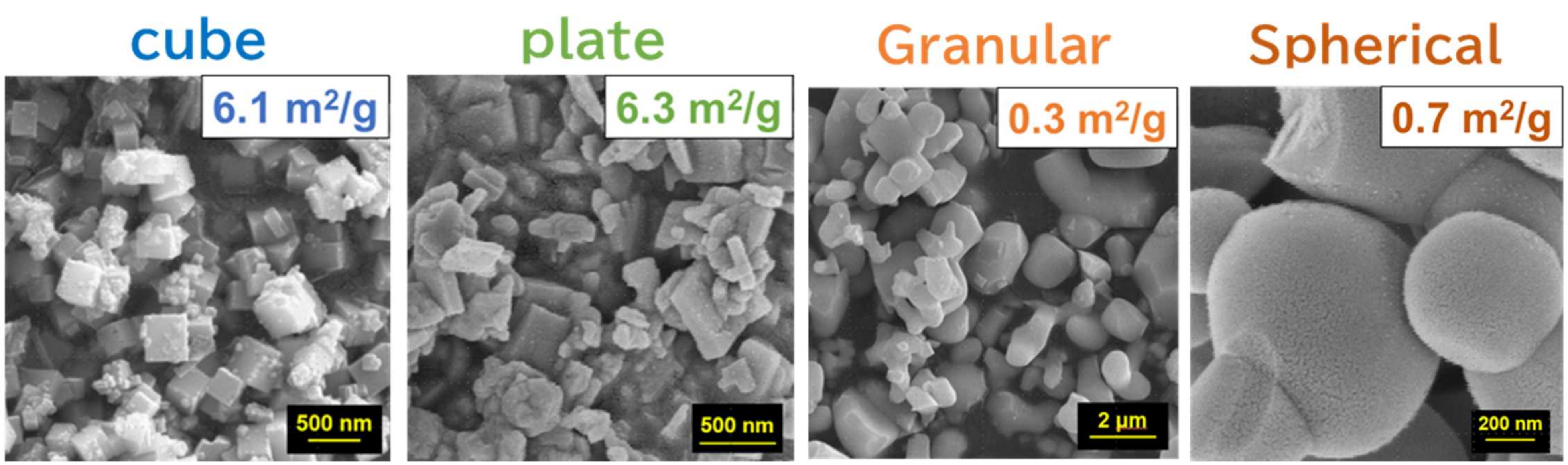
Photocatalyst for ON type resin($NaNbO_3$)





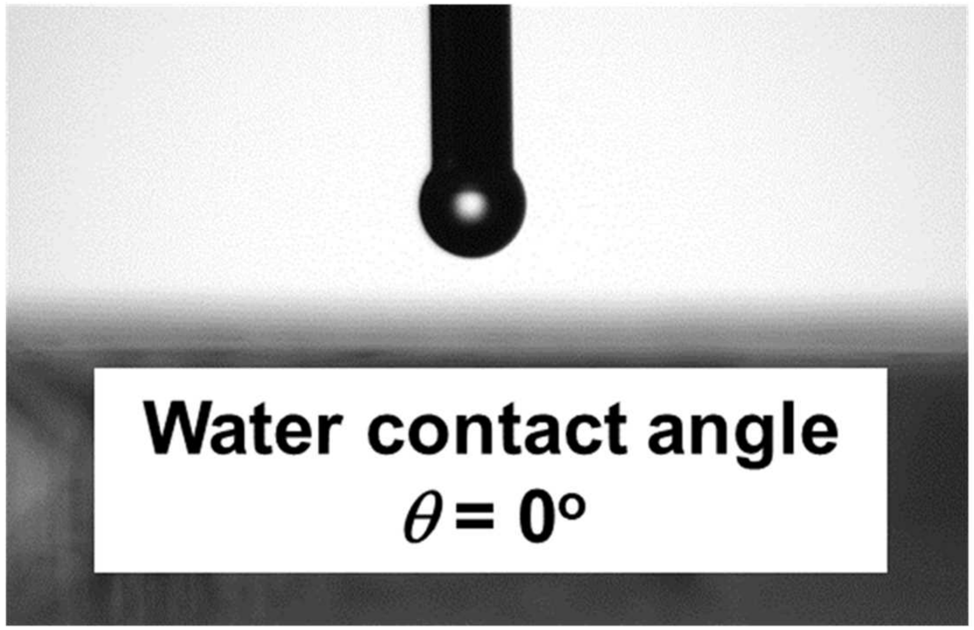


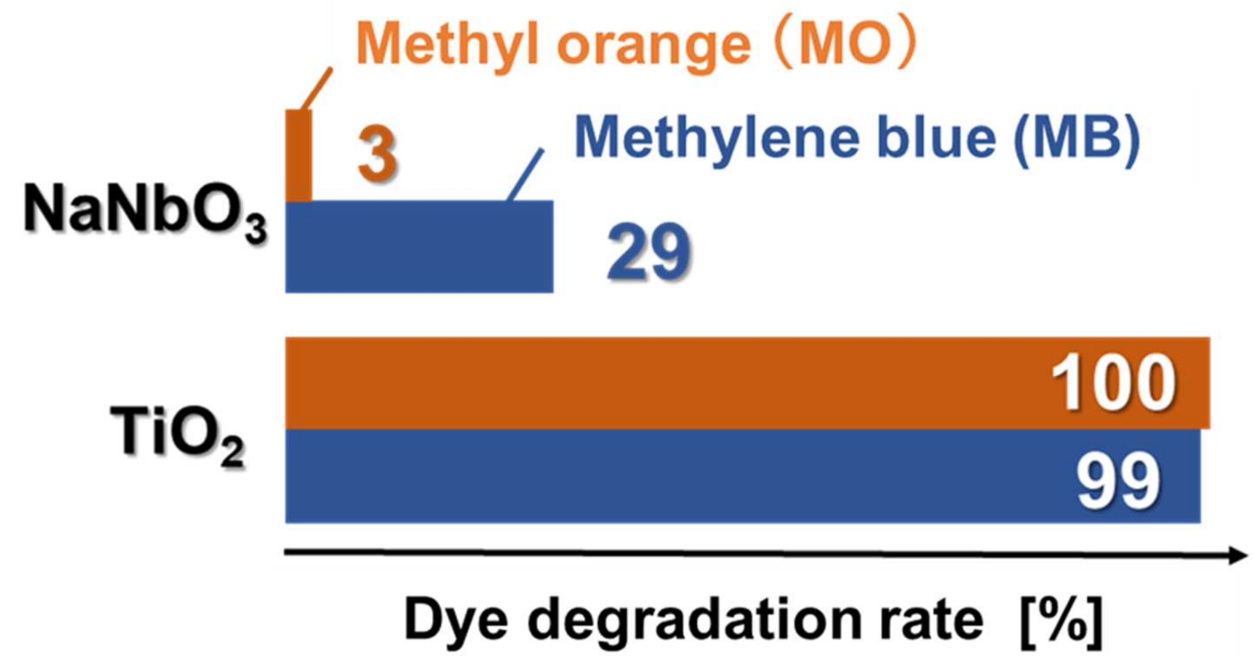
The same $NaNbO_3$ can be prepared.



・Various shapes and particle sizes can be made

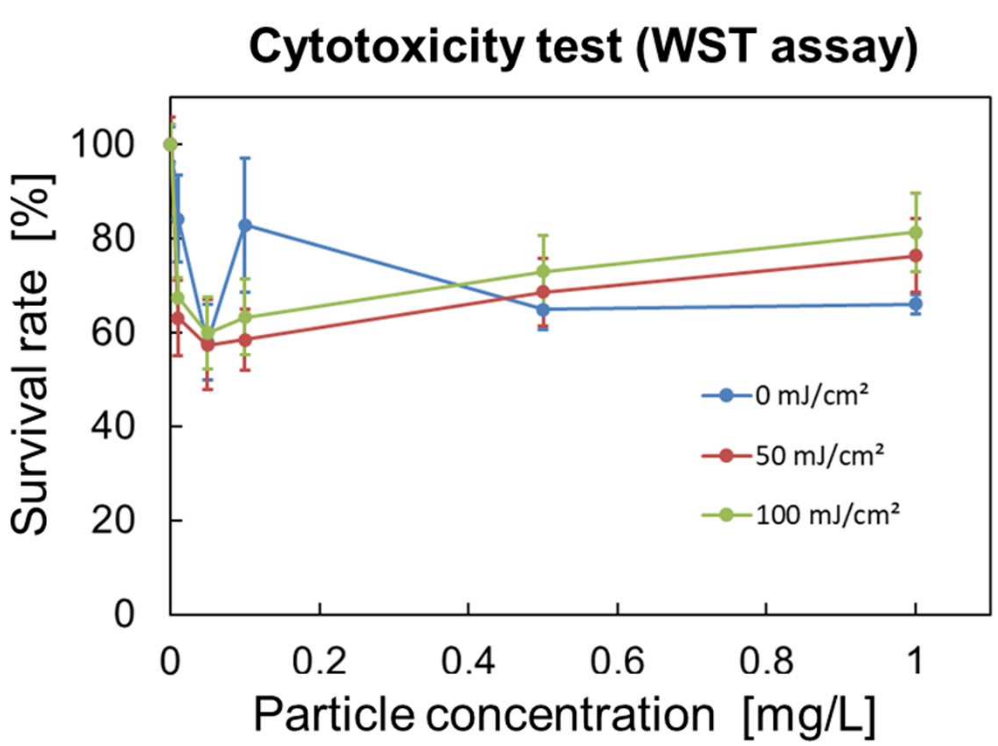
Evaluation of photocatalyst for ON type resin($NaNbO_3$)





The same NaNbO3 can be prepared

NaNbO3 has lower degradation activity than TiO2.



$NaNbO_3$ has little or no cytotoxic under light irradiation.

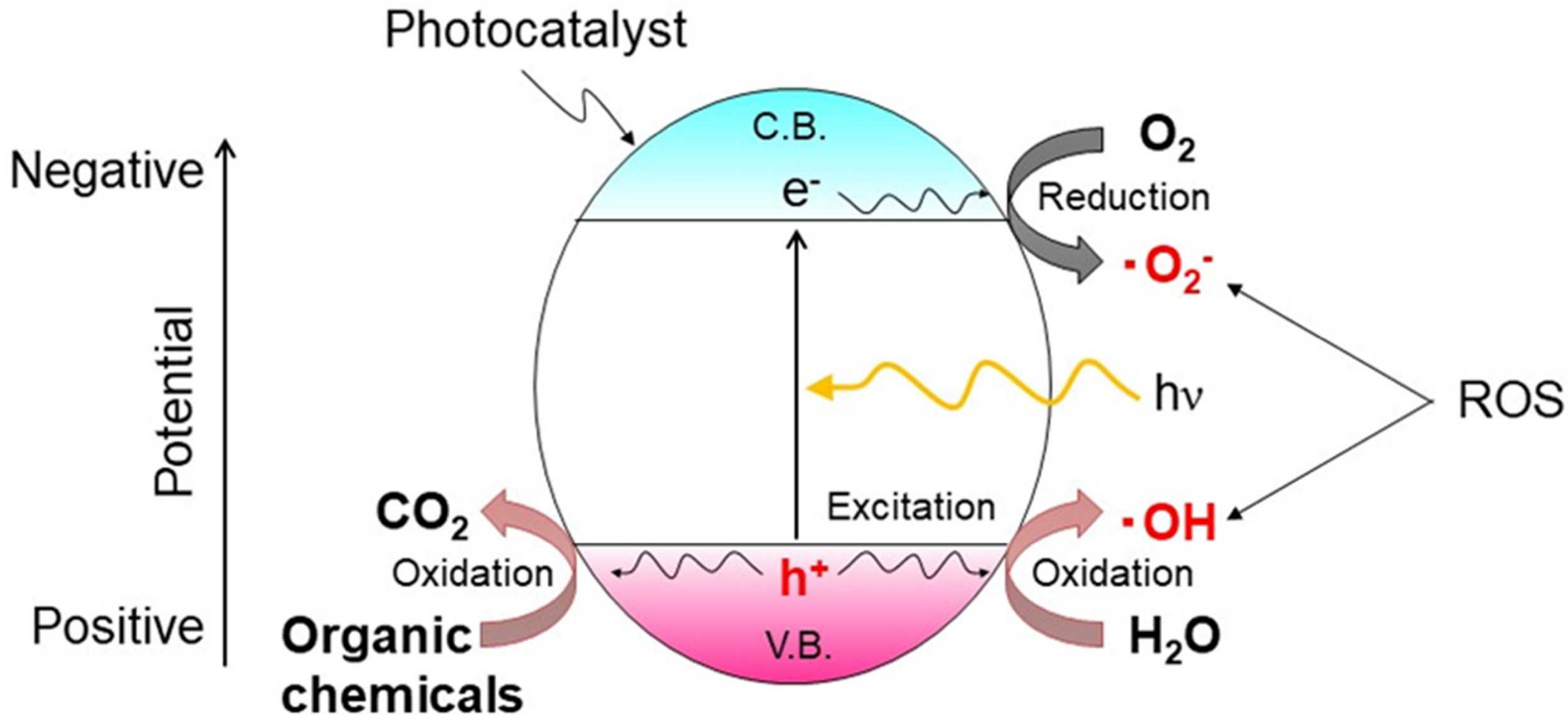
$NaNbO_3$ has little or no antimicrobial performance under light irradiation.

NaNbO3 has almost no cytotoxicity under light irradiation conditions.

Photocatalyst for OFF type

What kind of photocatalyst is required?

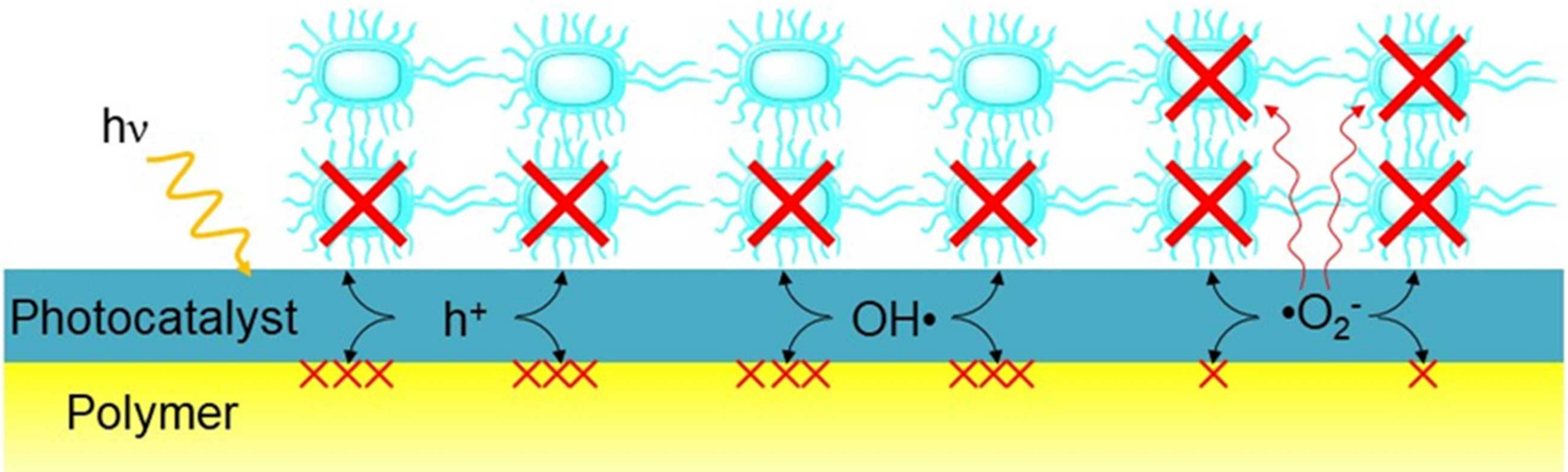
(1) Under visible light, (2) without decomposing polymer,
(3) sterilizable photocatalyst



Three types of h^+, $OH\cdot$, and $O_2^-\cdot$ affect
for sterilization and polymer decomposition.

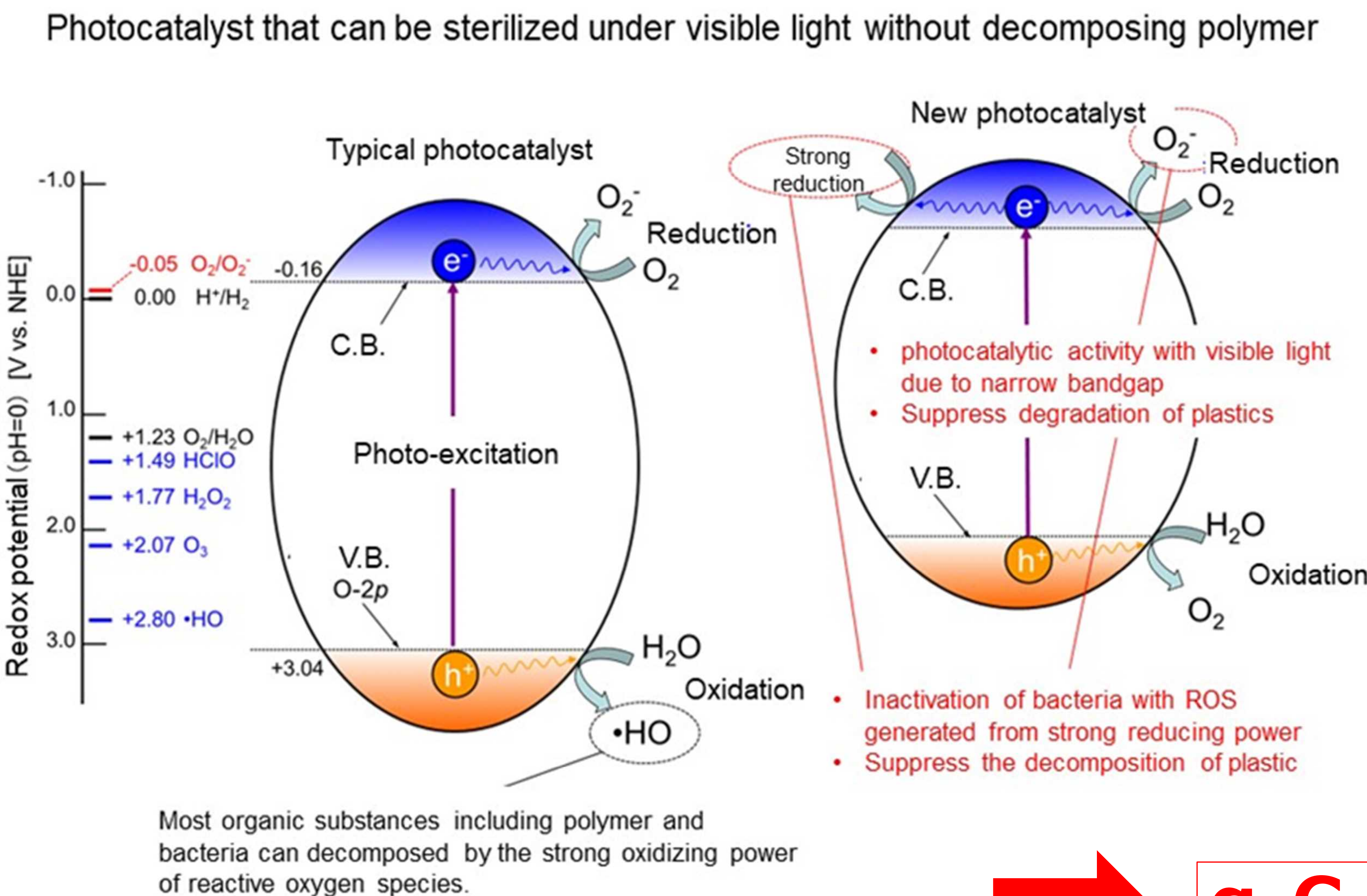
Comparison of ROS

ROS	Life time	Diffusion length	Redox potential (vs. NHE)
h^+	<1 ns	In photocatayst	Depends on photocatalyst
OH•	70 ns	20 nm	+2.8 V
$•O_2^-$	5 s	100 μm	+0.16 V



- Sterilization by $•O_2^-$ is preferable

Photocatalyst that suppresses photodegradation

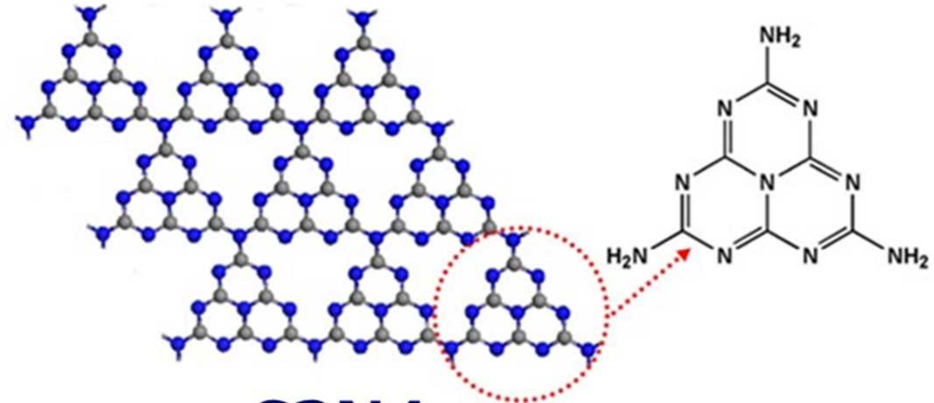


$g\text{-}C_3N_4$

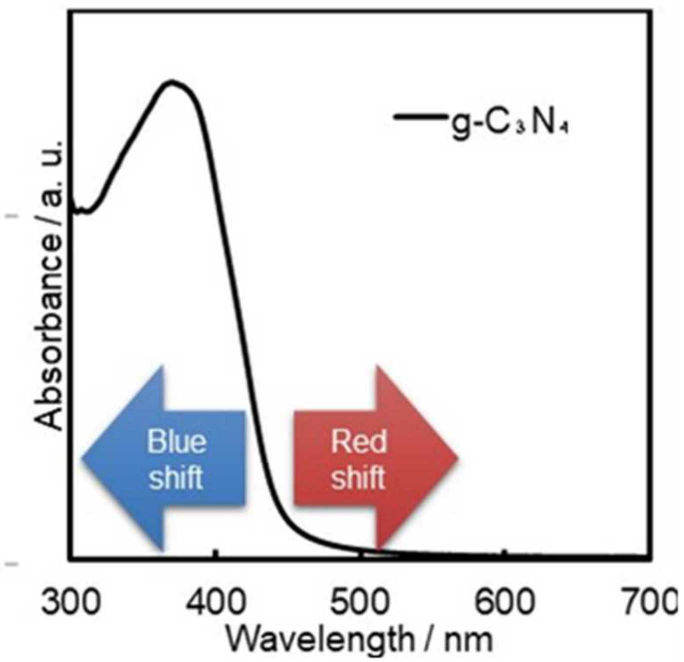
Synthesis of g-C3N4 and its antibacterial properties

Selection of raw materials ➡ Firing … Can be made separately

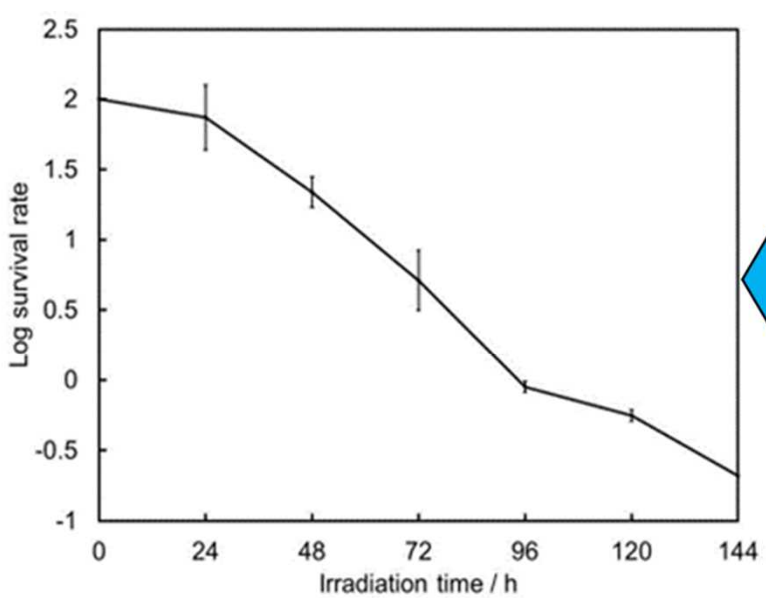
Blue shift **Red shift**

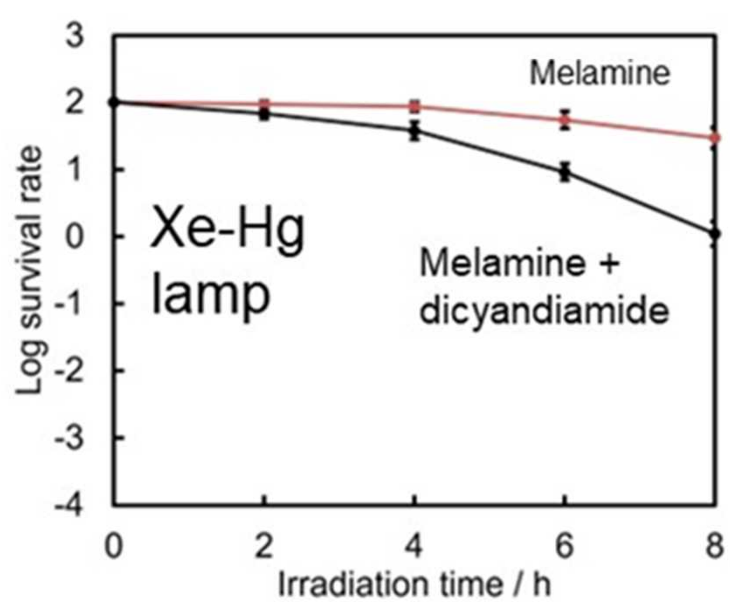


gC3N4



	Blue shift	Red shift
Adv.	High activation by improving oxidization ability (less amount of sample necessary)	Works in environments where short wavelength light is not present (Can be used in a wide range of environments)
Disadv.	Inactivated in the absence of short wavelength light	Low activation due to decreased oxidation ability
Method	Delamination by thermal oxidation treatment	Doping





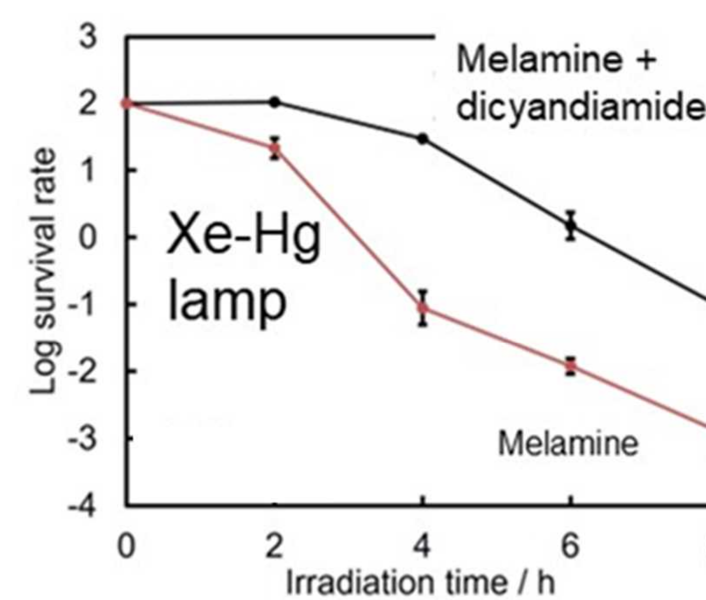
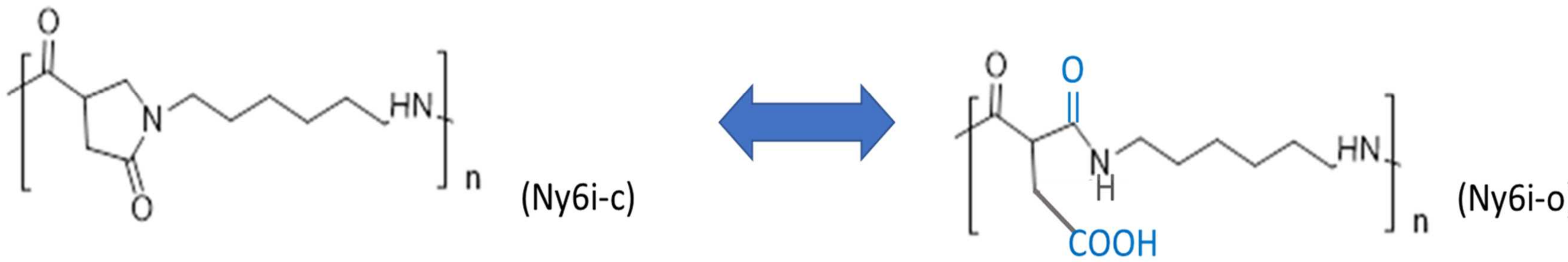
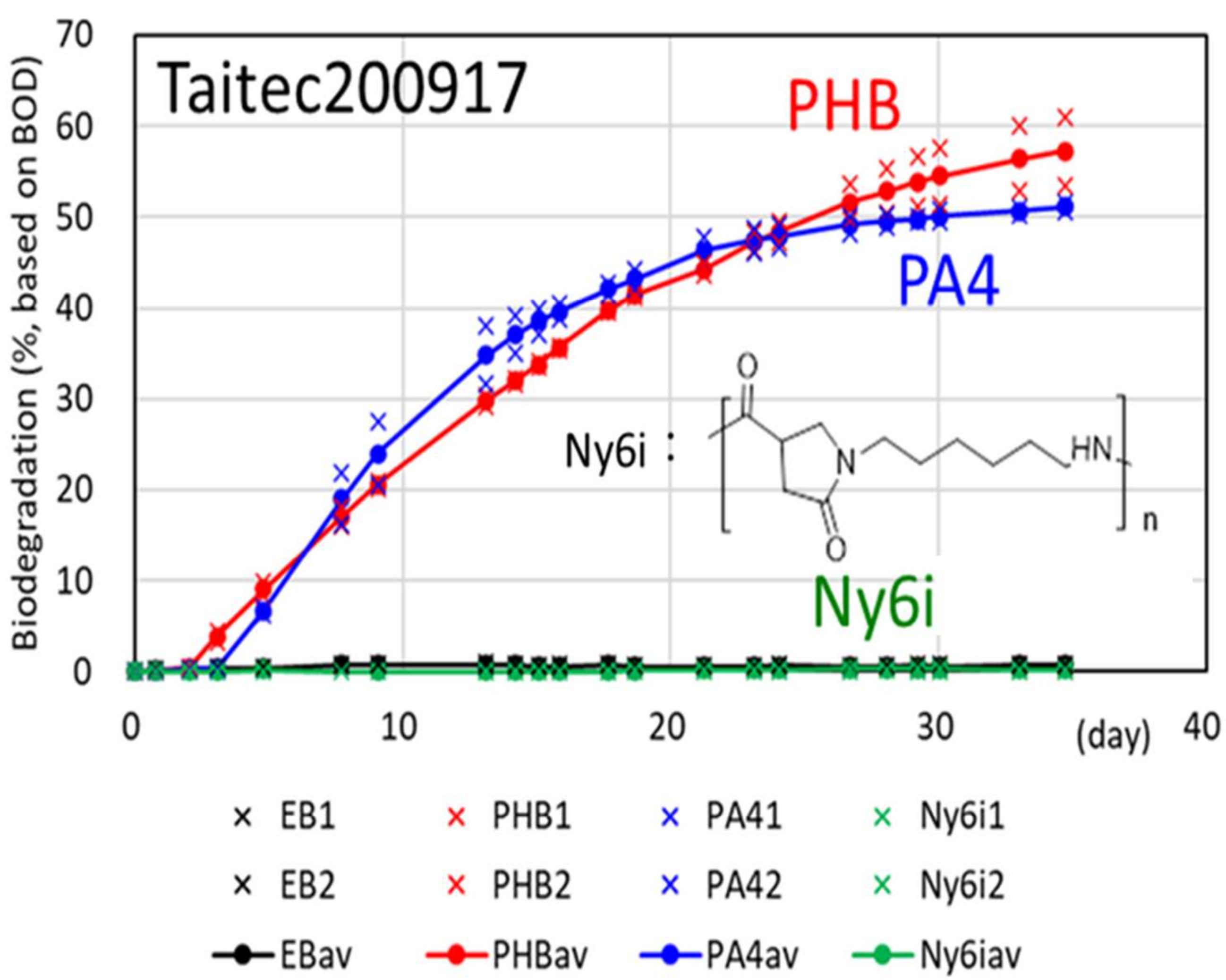


Photo switch operability and biodegradability…ON type

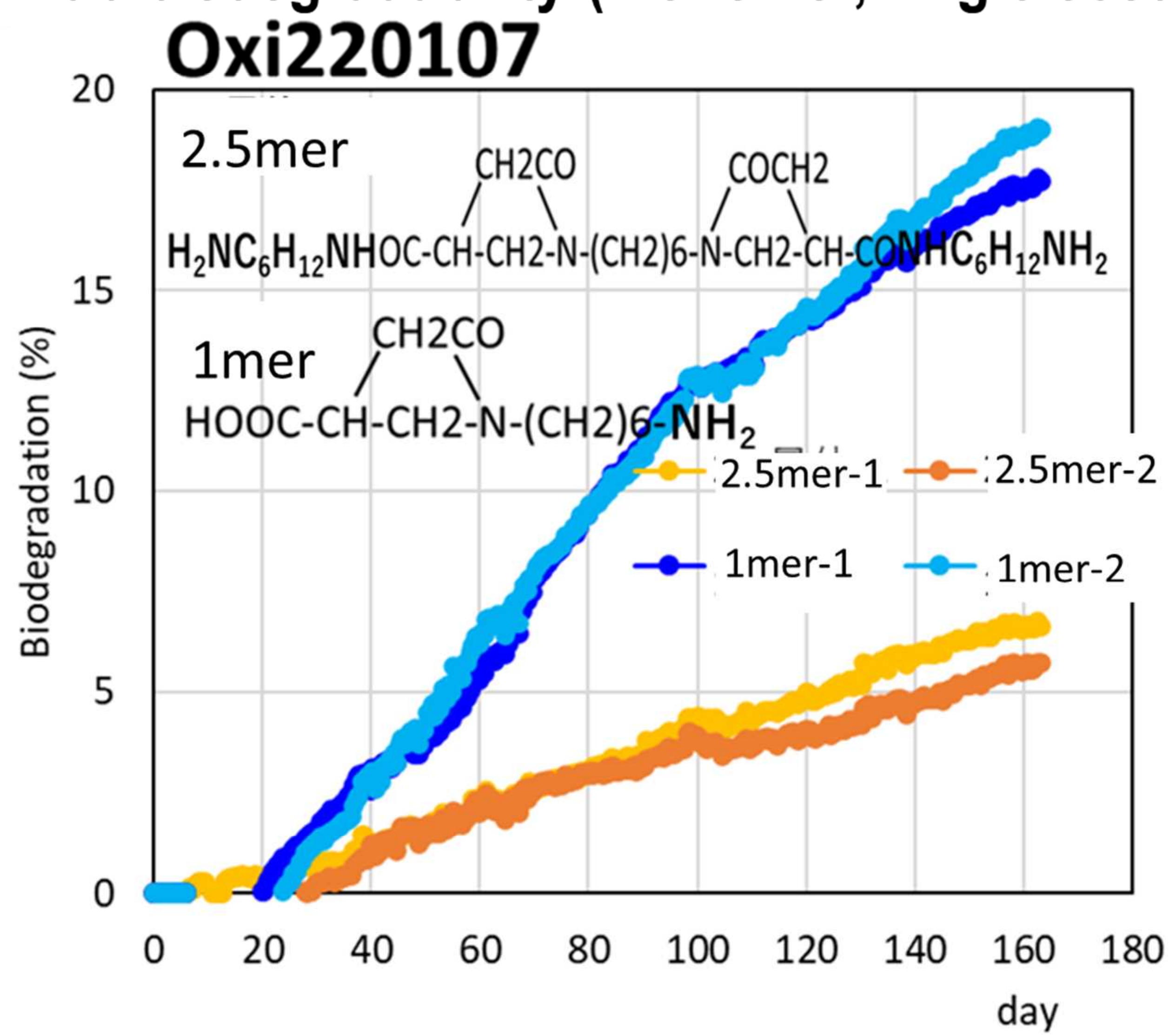
Ny6i：



Lab biodegradability (polymer, ring closed)

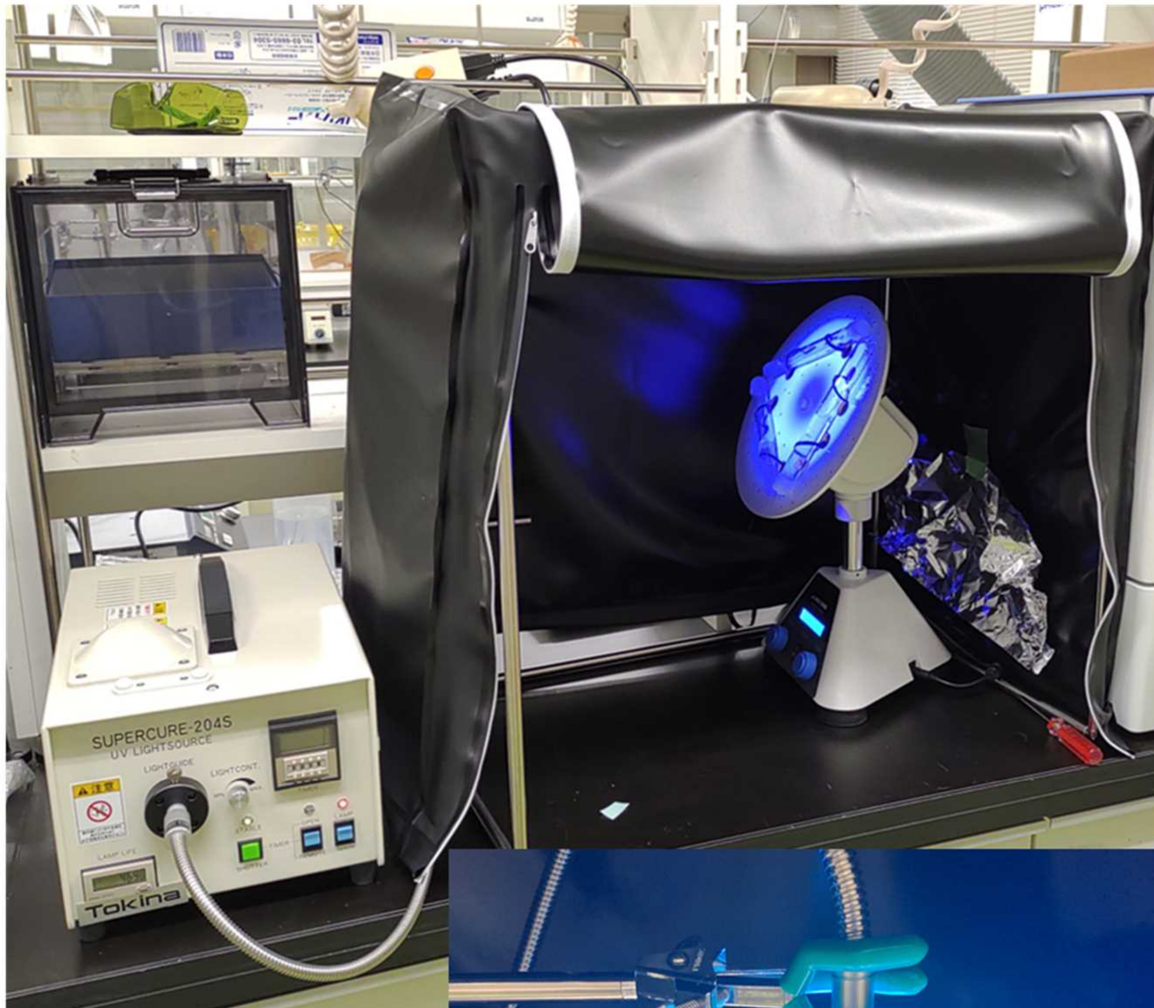


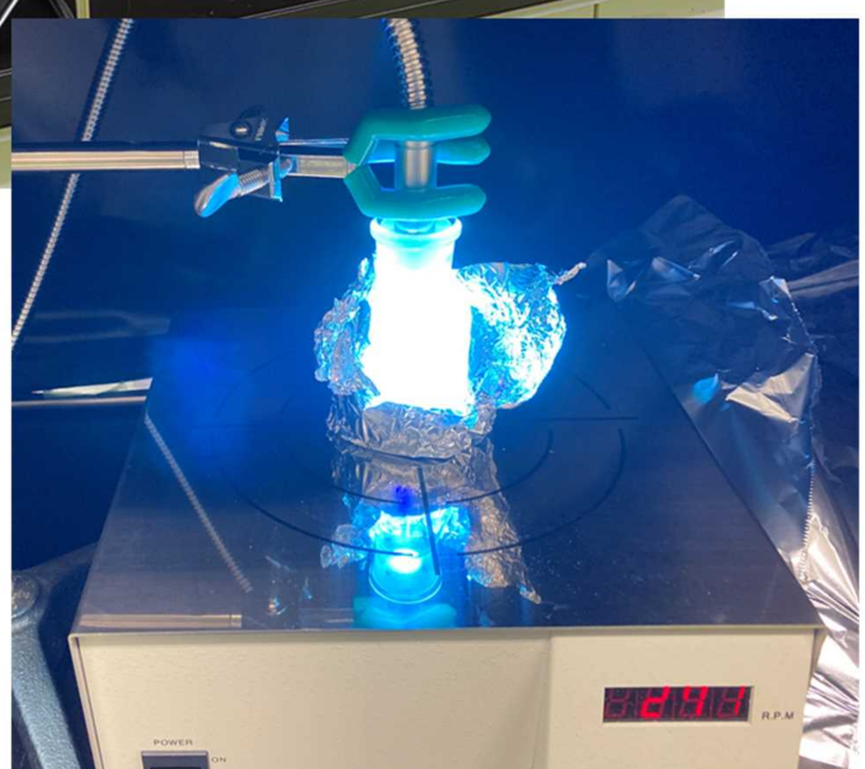
Lab biodegradability (monomer, ring closed)

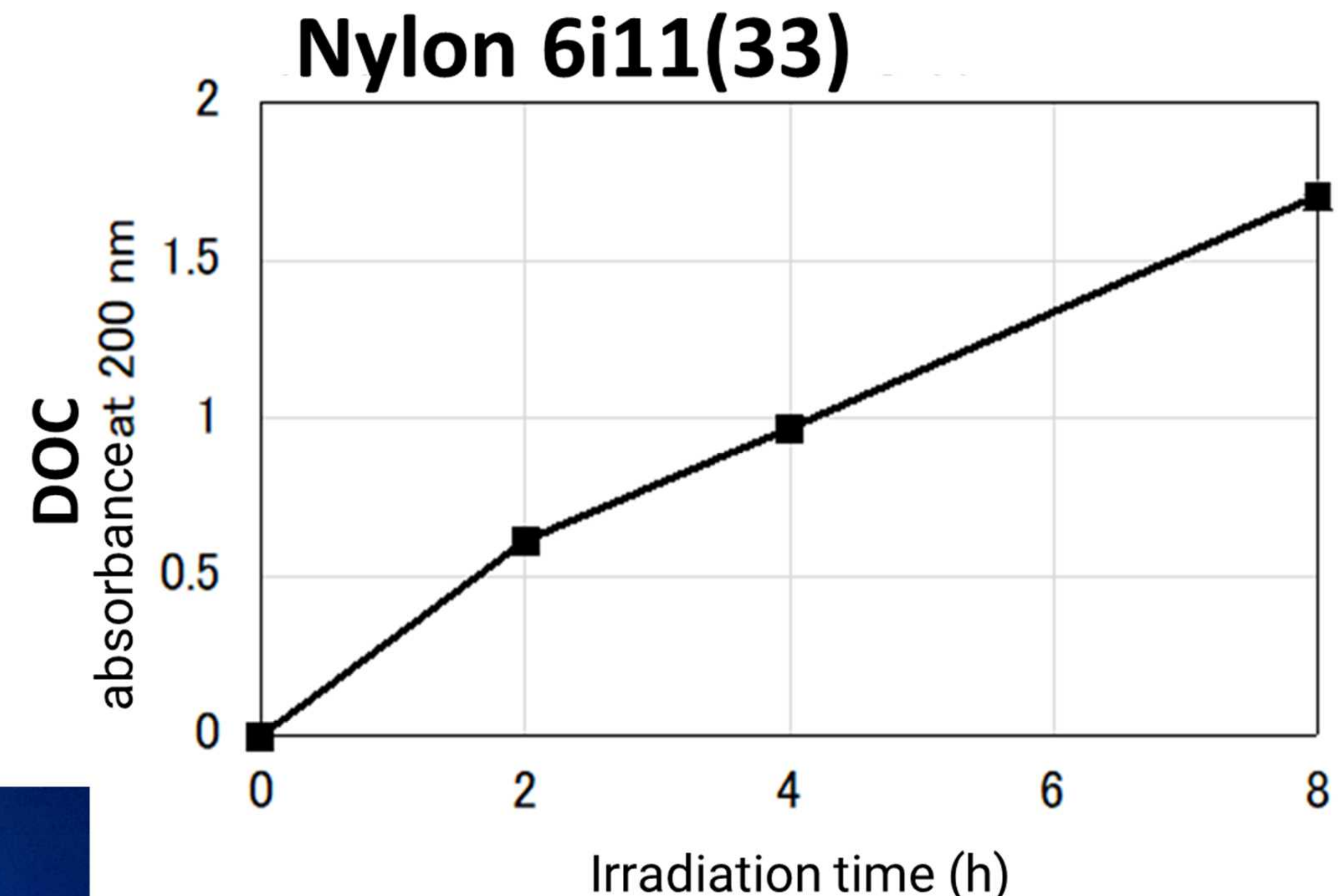


Optical switch operability and biodegradability…ON type

Preparation of ring-opened samples and biodegradation test

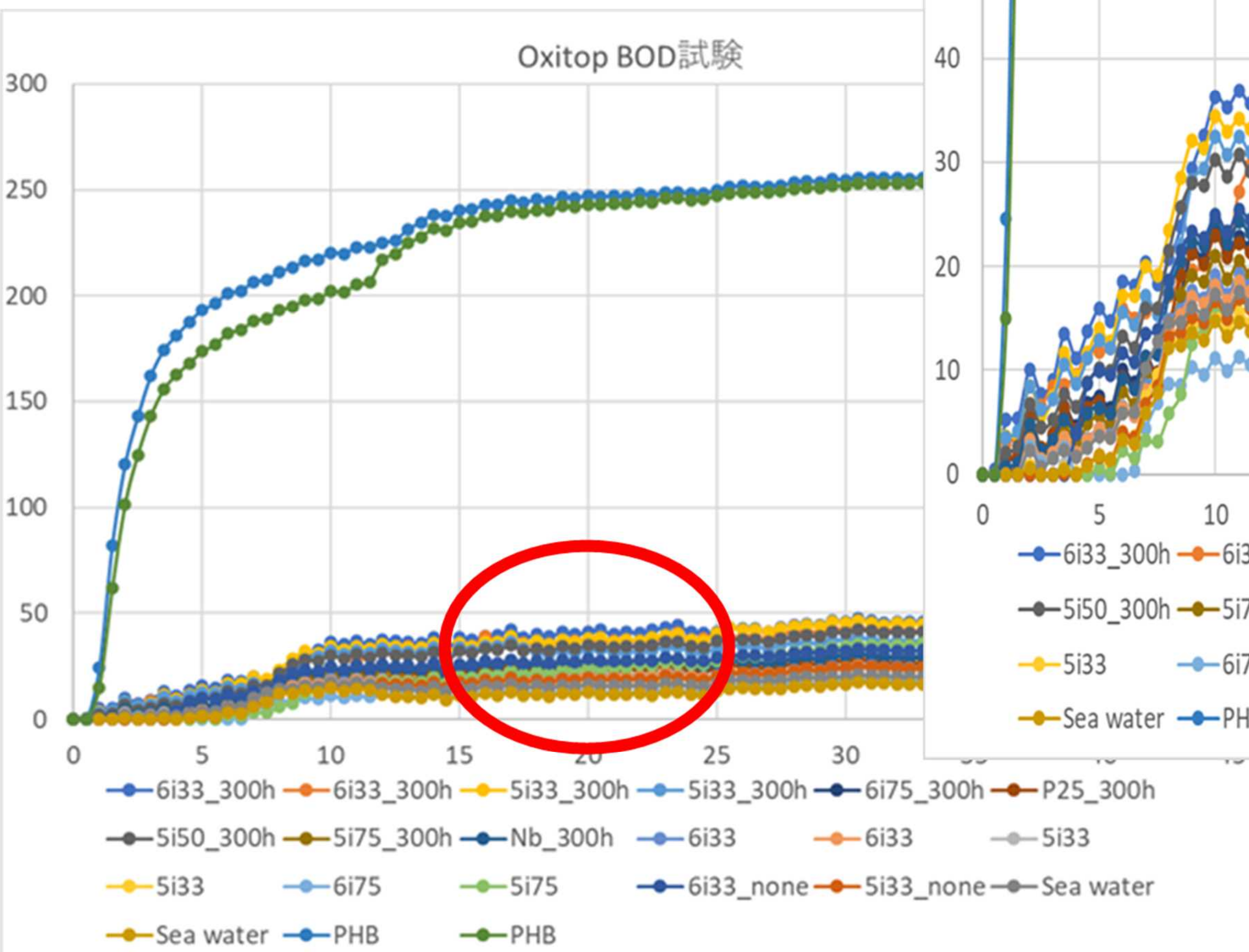


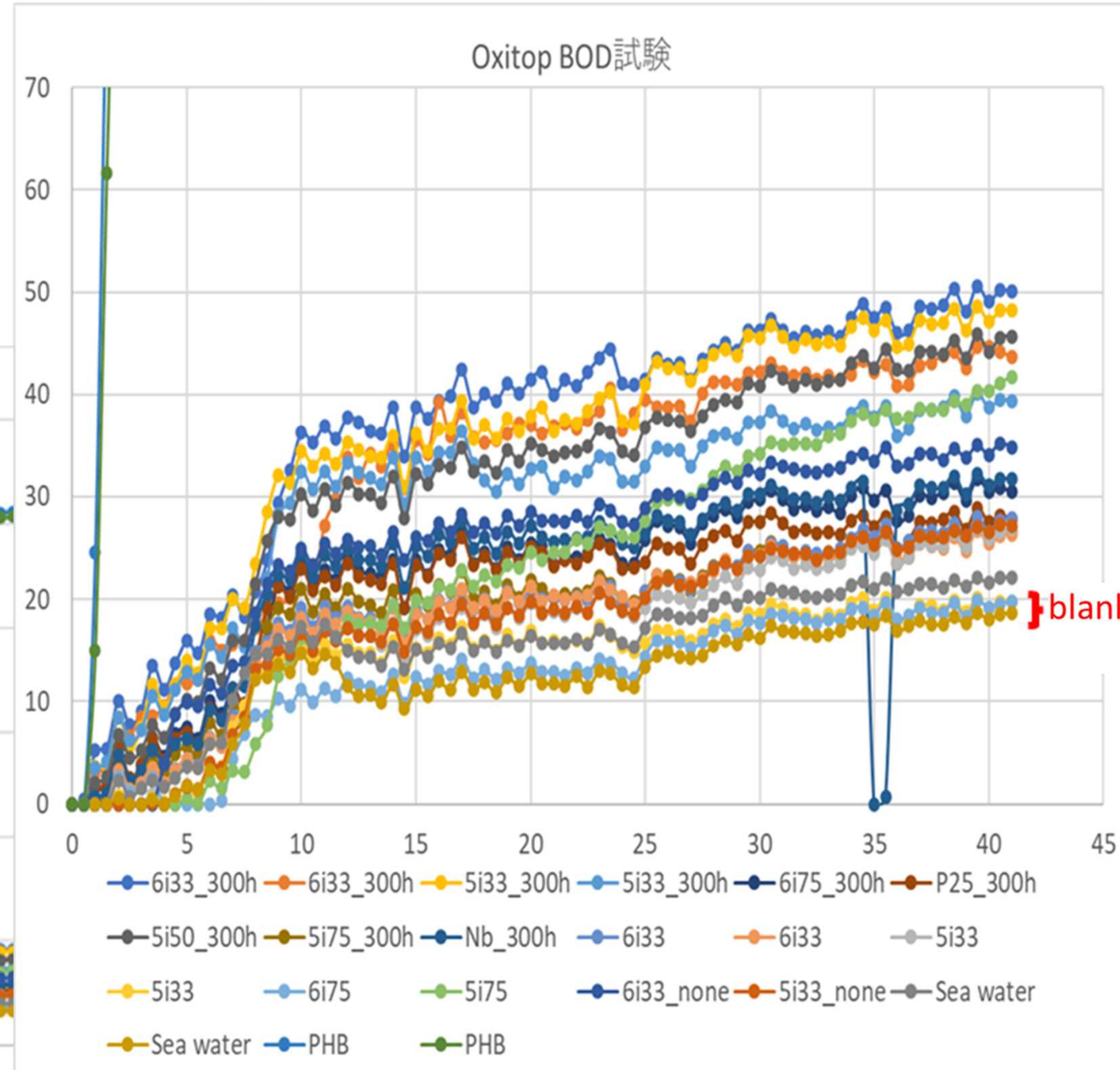




Optical switch operability and biodegradability...ON type

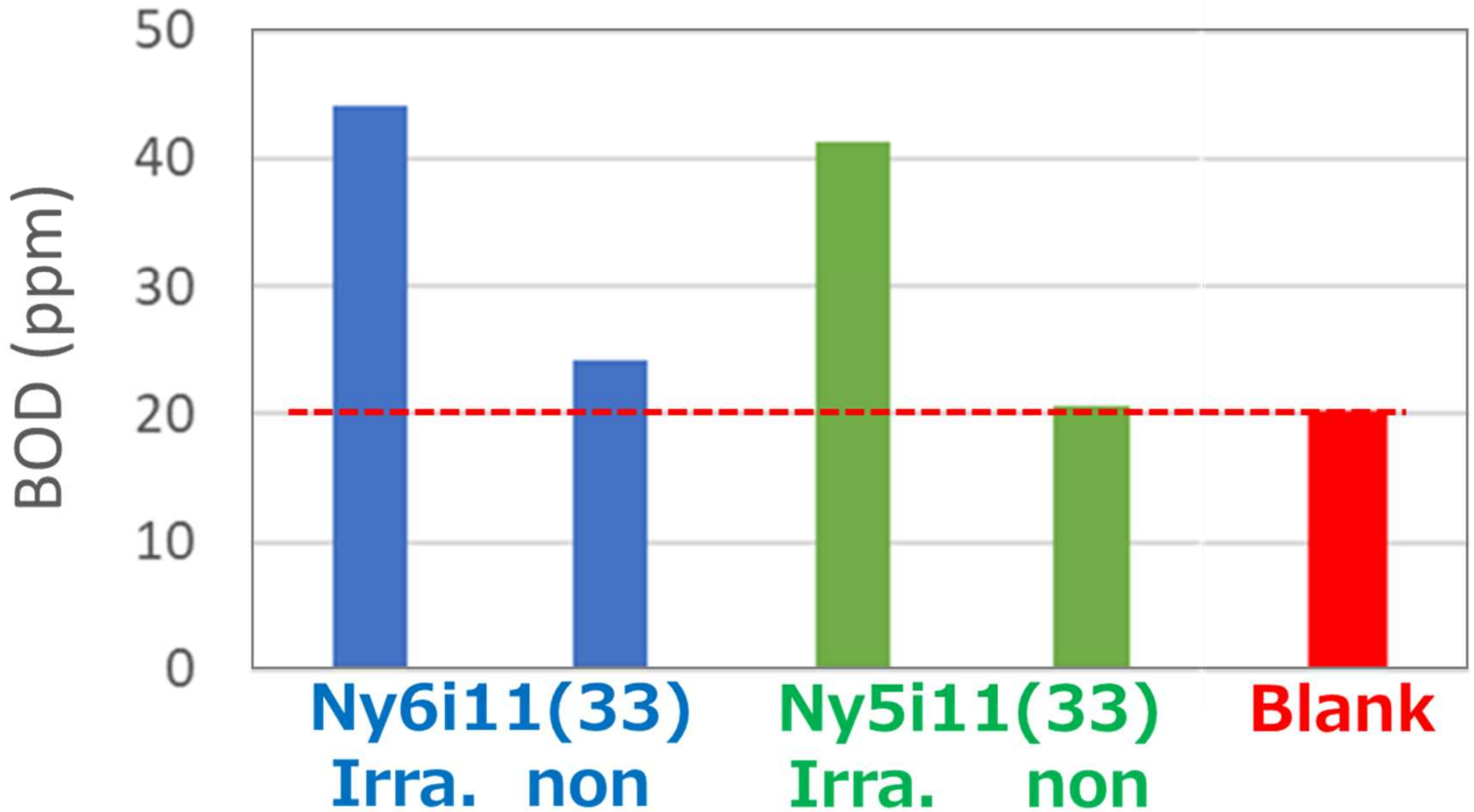
Preparation of ring-opened samples and biodegradation test



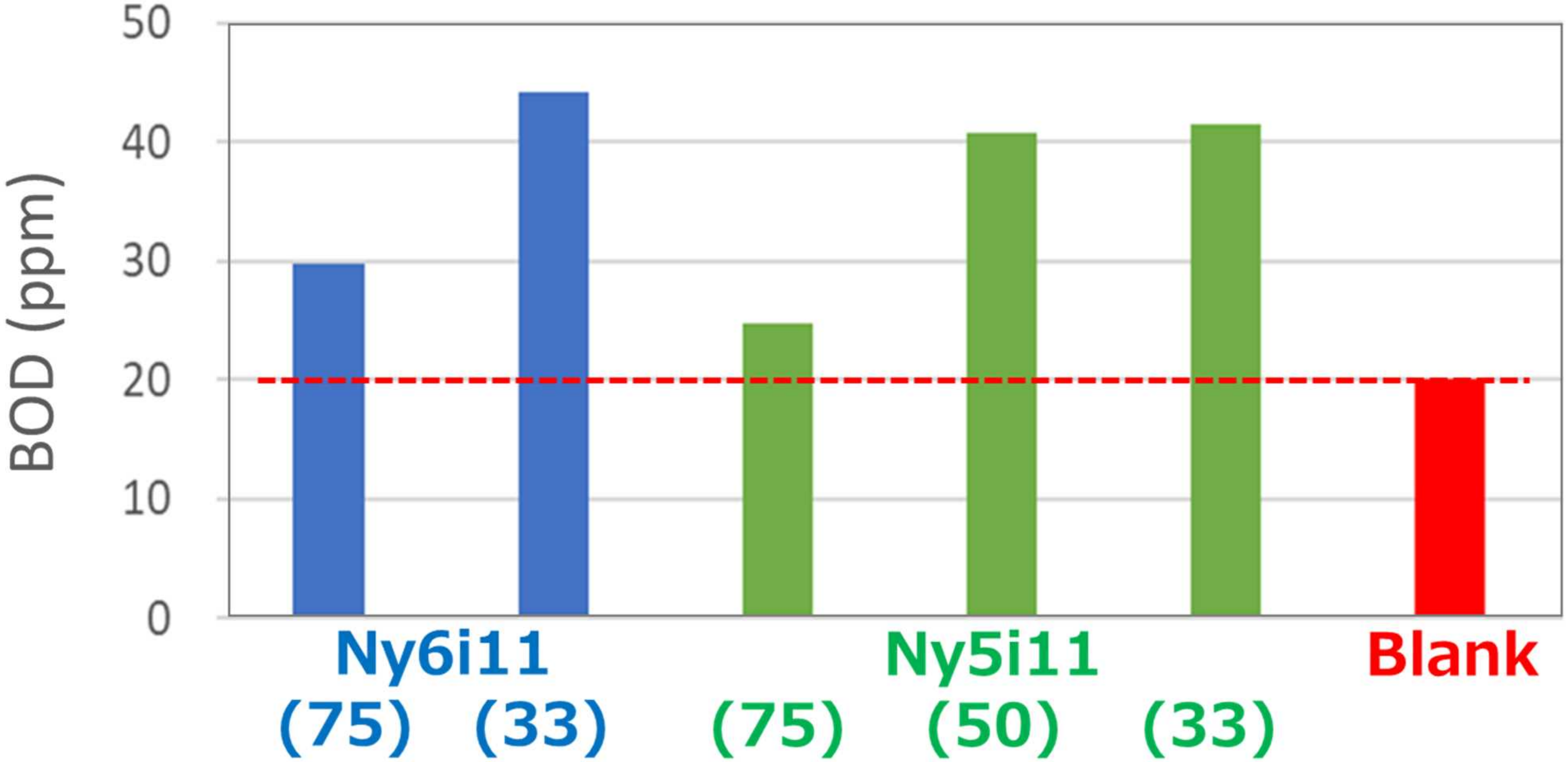


Optical switch operability and biodegradability...ON type

Preparation of ring-opened samples and biodegradation test

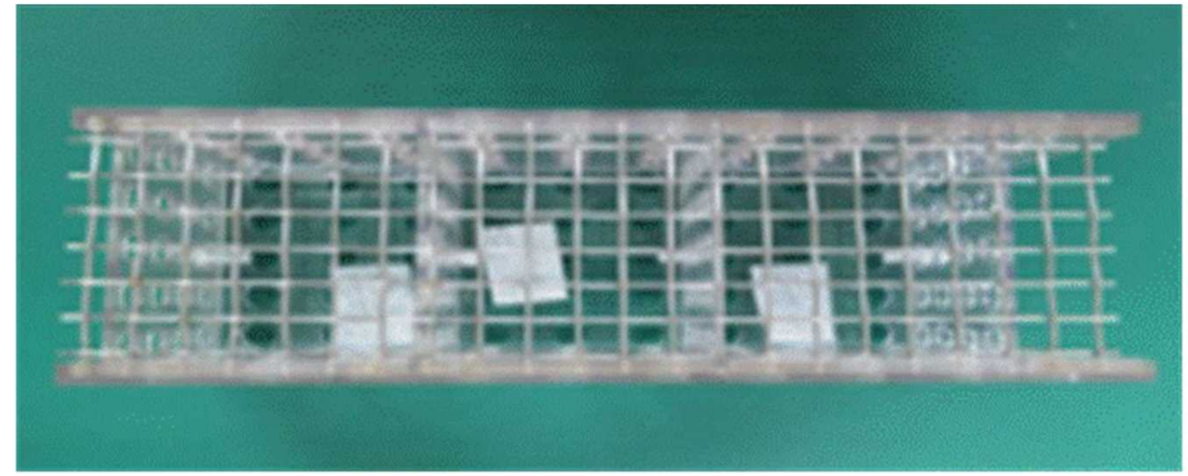


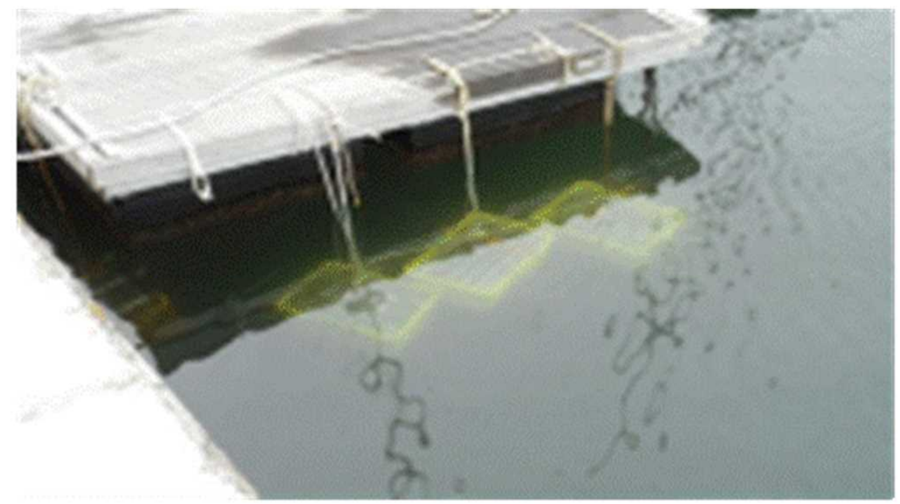
In the light-irradiated samples, biodegradation of water-soluble components progressed for both Ny6i11(33) and Ny5i11(33).

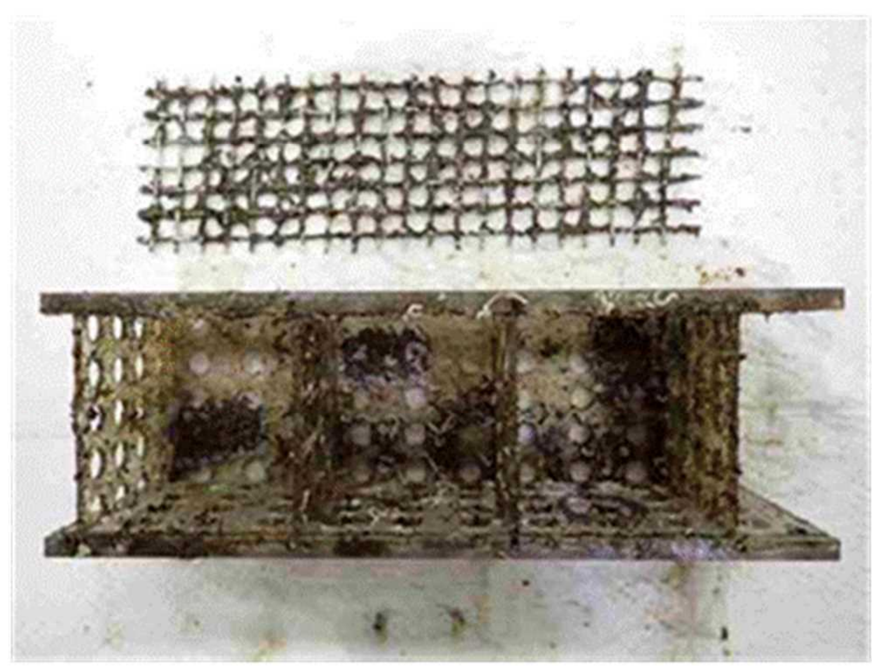


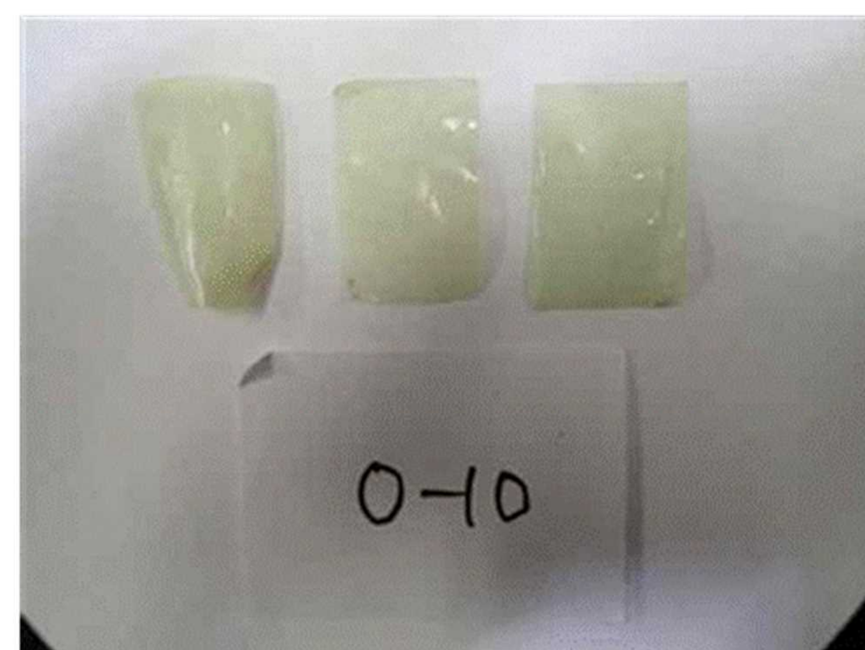
When the second monomer component (Ny11) increases, the BOD value decreases and the progress of biodegradation becomes slower.

Marine immersion test

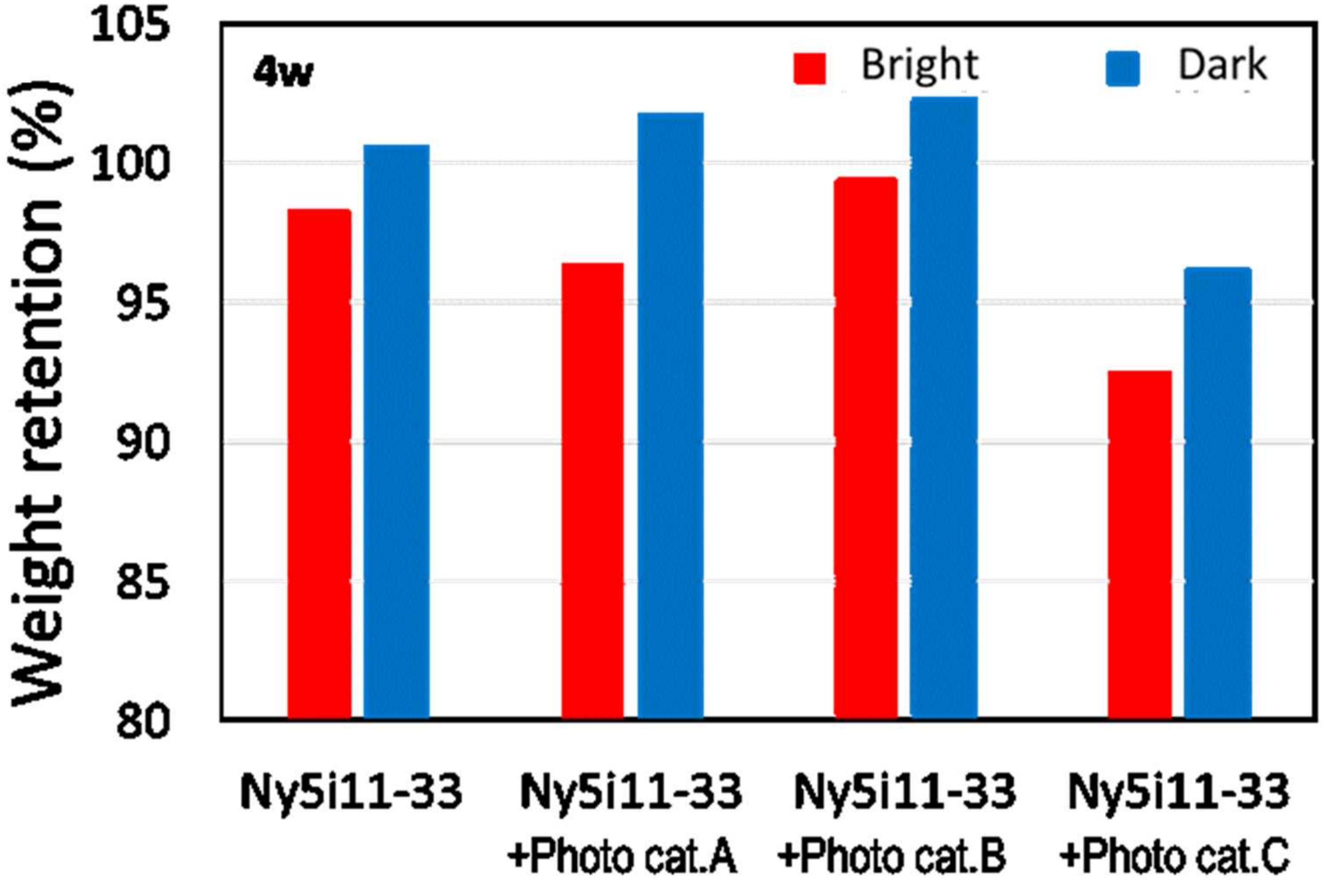




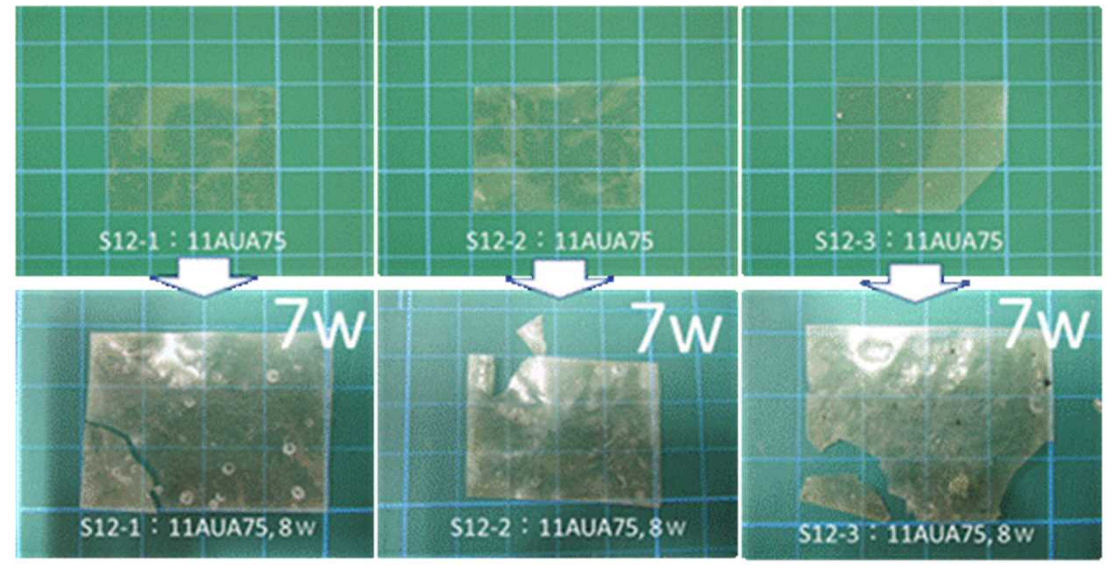


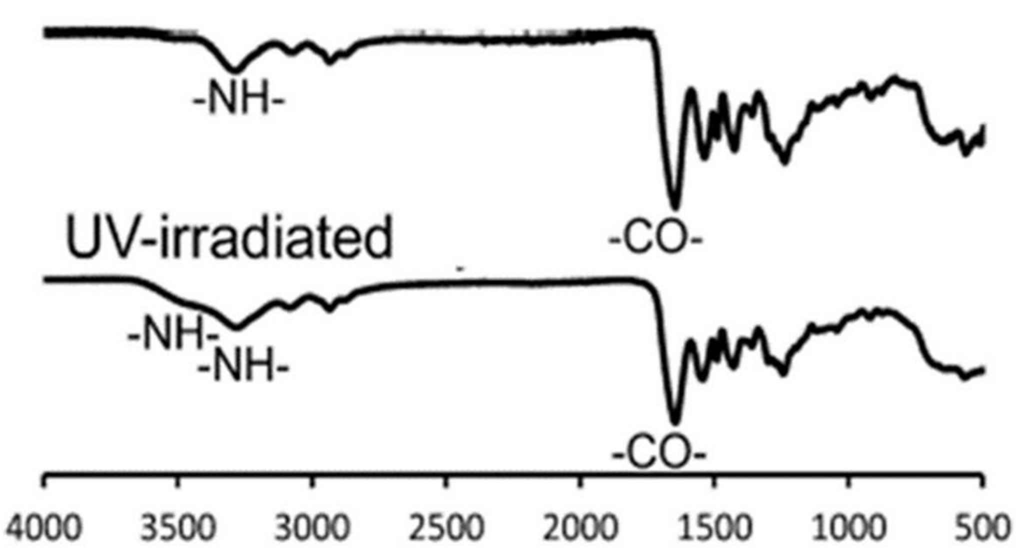


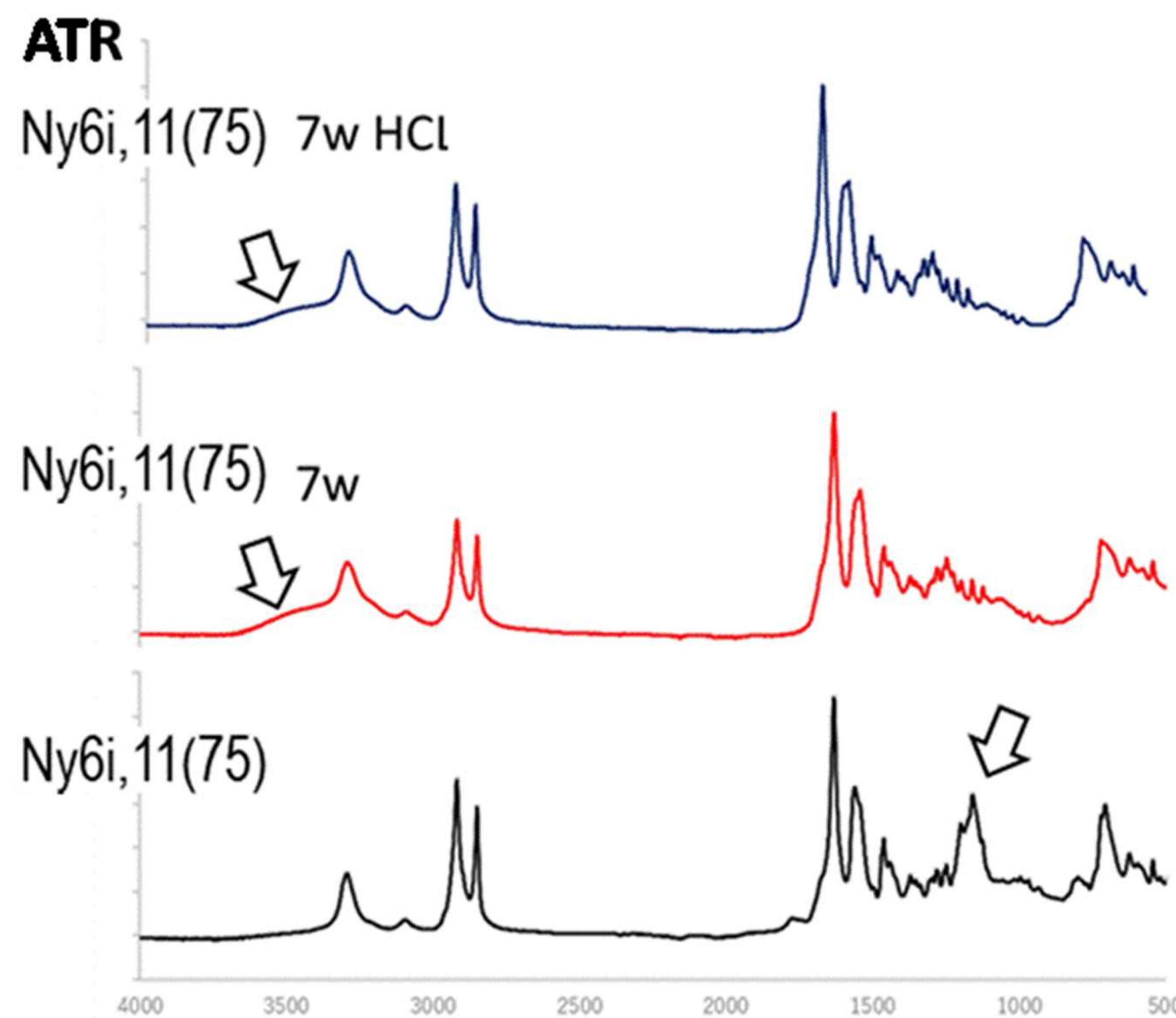
Marine immersion test



Ny6i11(75)



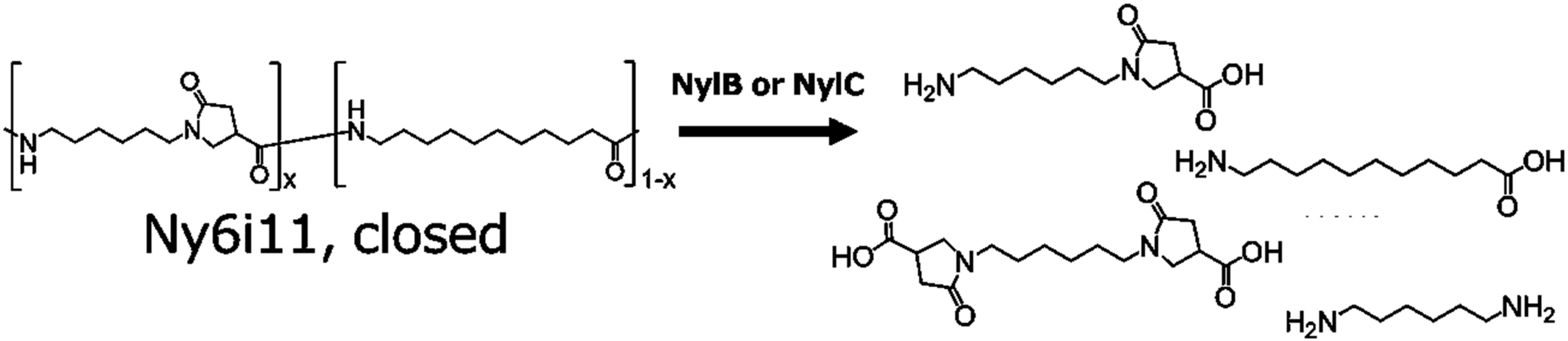




Enzymatic hydrolysis of ON-type resin and biodegrading bacteria

Deg. Enzyme for Ny6...NylA, NylB, NylC

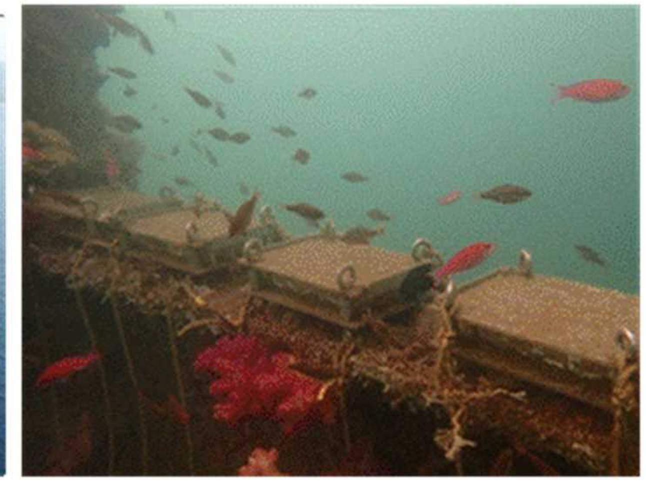
Arthrobacter sp. KI72
Kocuria sp. KY2
Agromyces sp. KY5R

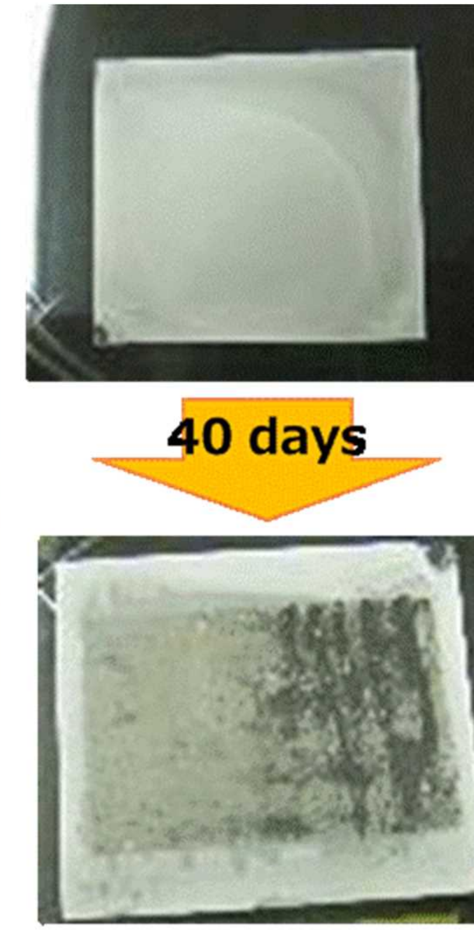


Ny6i11, closed

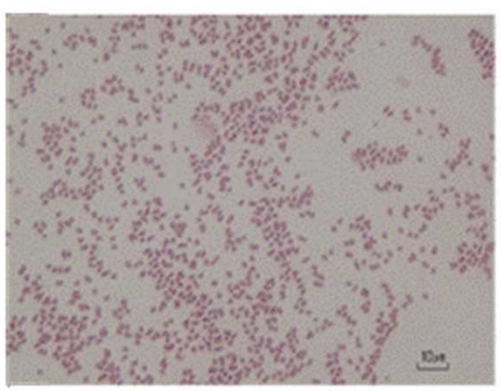
Photo-switching Nylon		x	M_w	Pretreat.	Monomerization (%)
H-Nylon6i		1	67,000	−	50
				+	−
Nylon6i-11(50%)		0.5	61,100	−	3
				+	64
Nylon6i-11(75%)		0.25	120,800	−	0.1
				+	26

Isolation of iNylon degradation bacterium

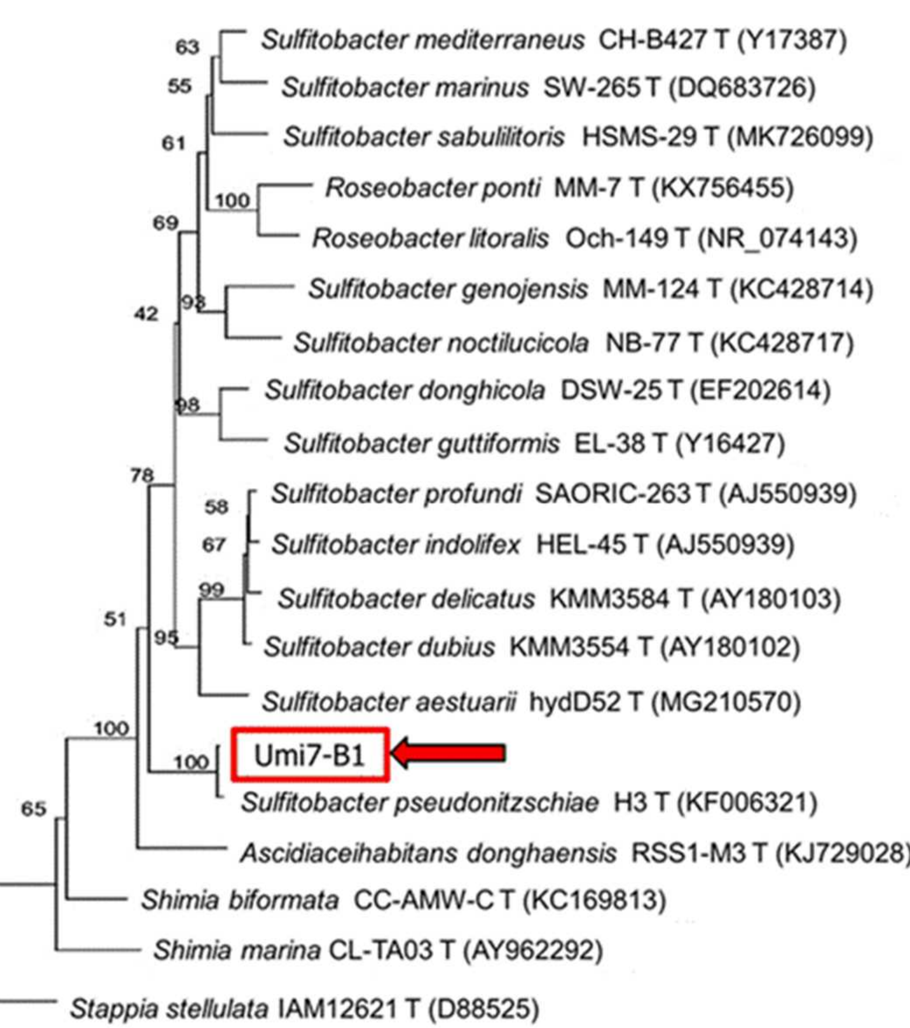


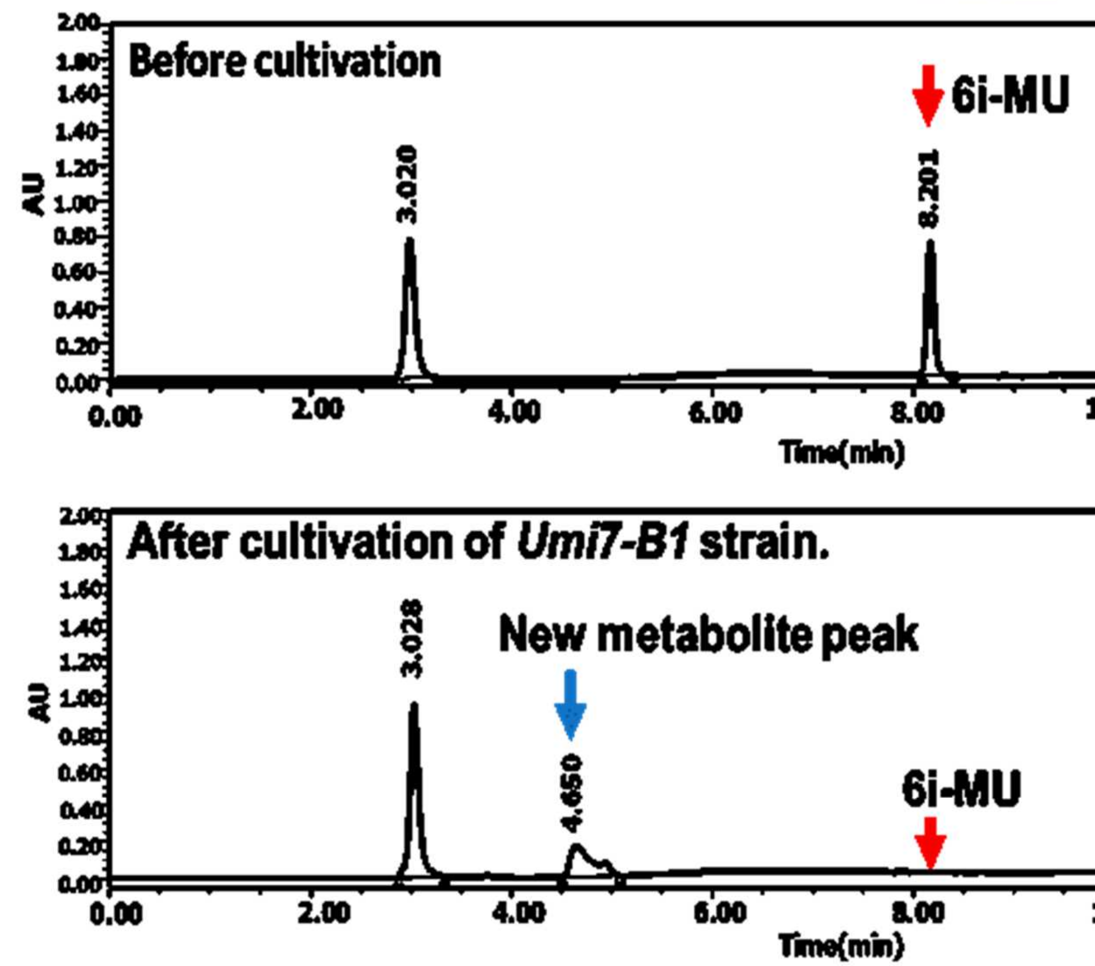


Isolated colony



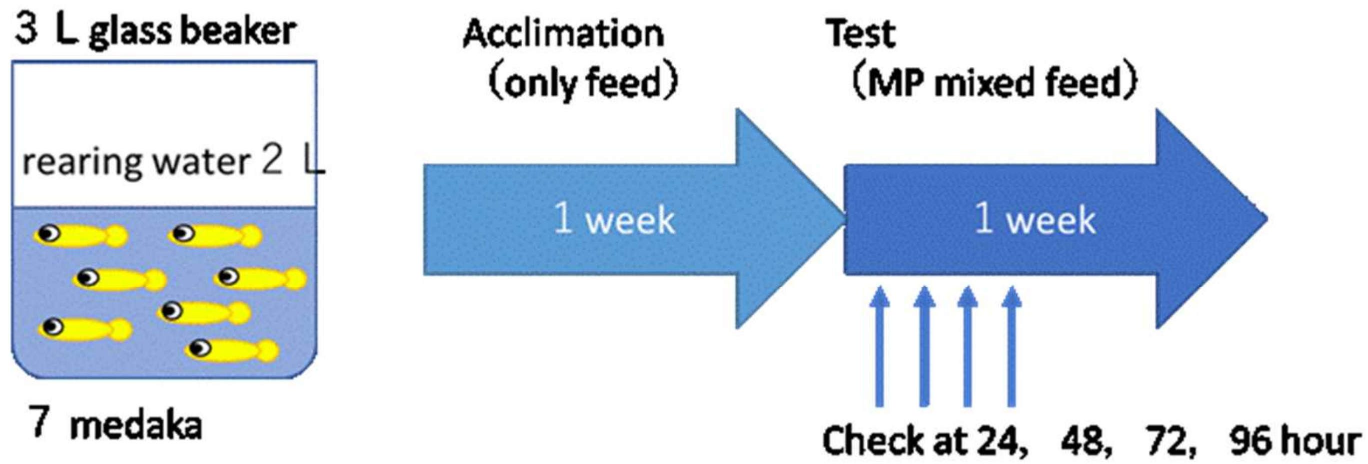
Gram-staining





Safety test: Oral ingestion acute toxicity study by medaka

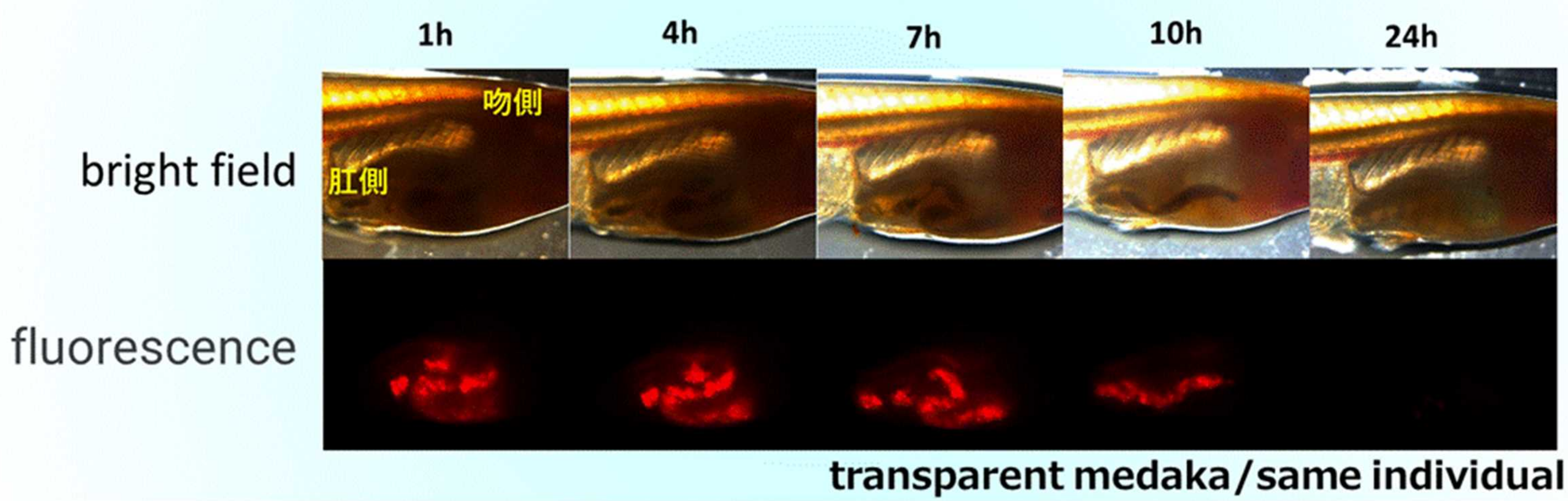
Compliant with OECD TG203



Appropriate feeding rate :
2～3% of body weight (about 250mg)
≒ 7.3mg/medaka/day → 360mg/week
360 mg of feed mixed with 180 mg of MP →MP :
3.7mg/medaka/day

Kind of MP	acute toxicity
Ny6	No
Ny6-L	No
Ny6i(0.5%TiO_2)	No
Ny6i(1%TiO_2)	No
Ny6i(1.5-mer)	No
Ny6i 75%	No
Ny6i 11 50%	No
Ny6i 11 50% CuI $NaNbO_3$	No
Ny6i11-33	No
Ny5i11-33	No
Ny5i11-50	No
Ny5i11-75	No

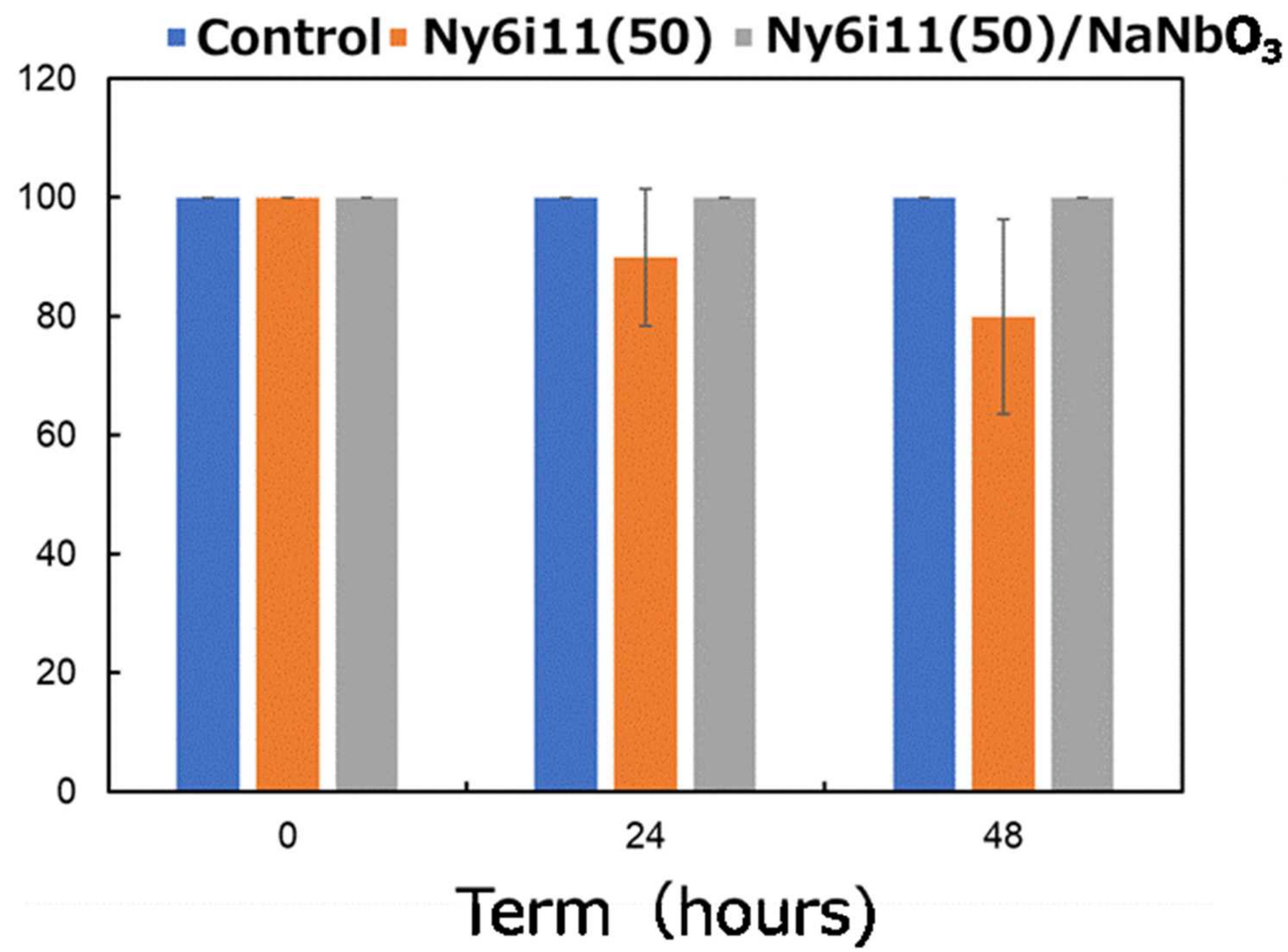
<Monitoring until the plastic powder is discharged after consumption>



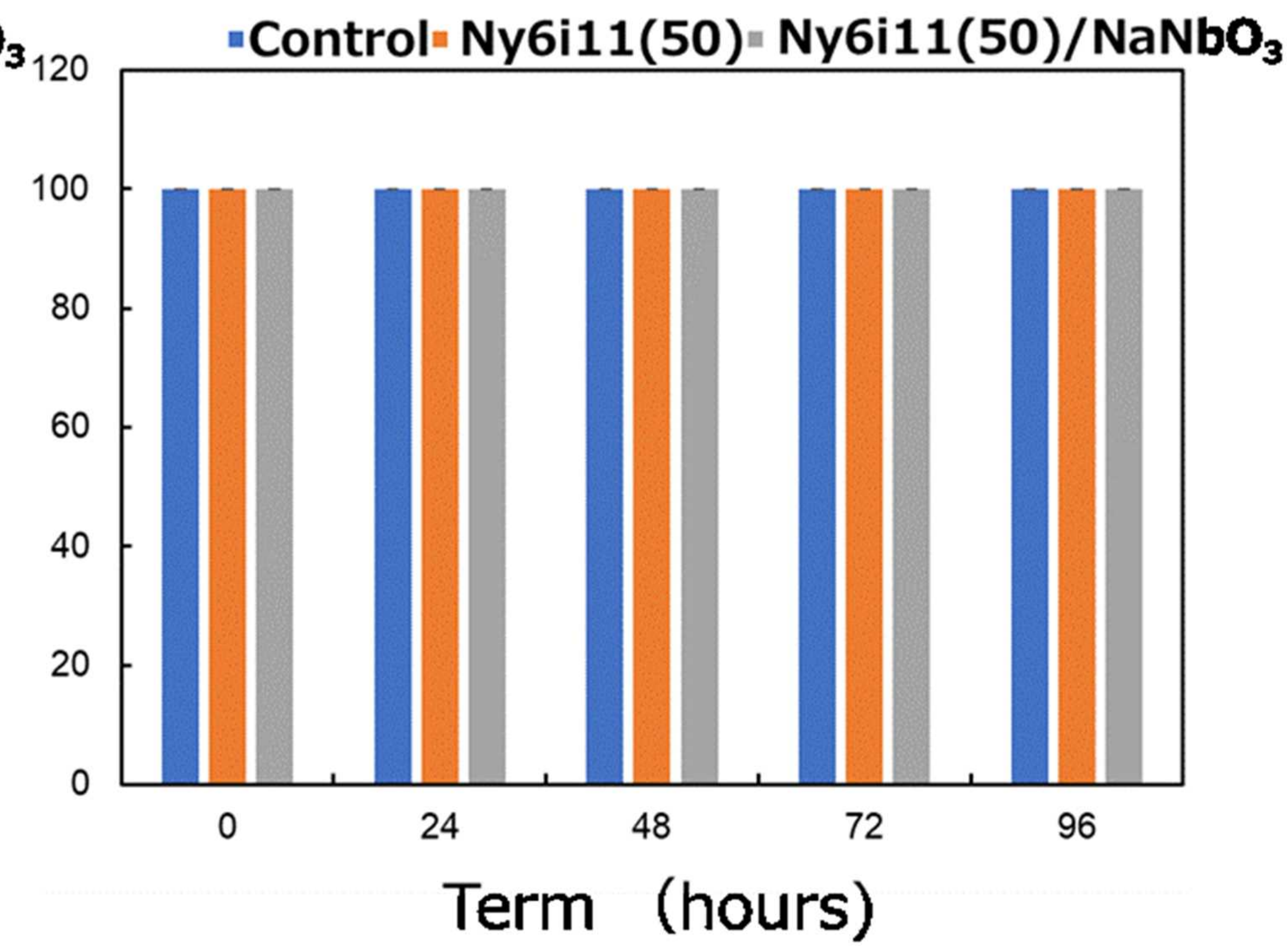
➡Excreted within 24 hours after oral vaccination

Safety test: Daphnia magna & zebrafish/ Acute toxicity test

Daphnia magna



Zebrafish



n=4, (Steel's test; $p < 0.05$)

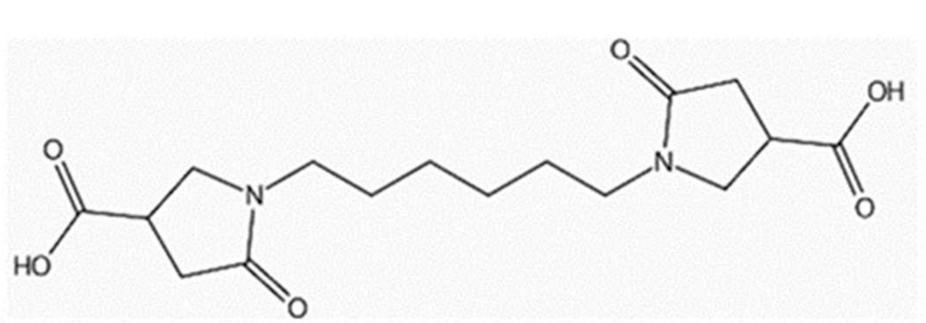
Acute toxicity of particulate Ny6i11(50), Ny6i11(50)+NaNbO3) to freshwater crustaceans (Daphnia magna) and freshwater fish (zebrafish) was not observed.

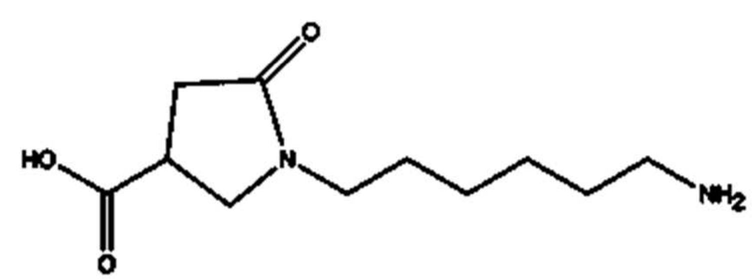
Safety test: PNEC

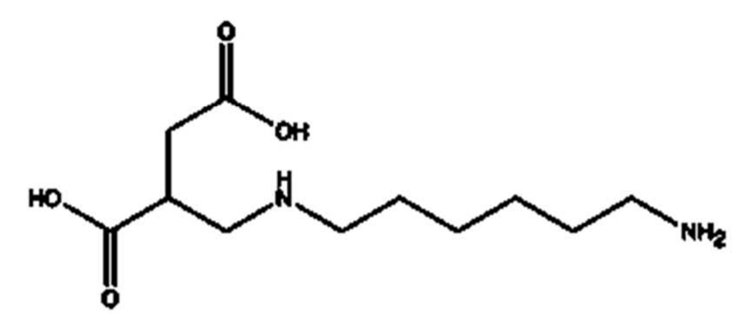
Acute toxicity to various aquatic organisms (EC50, LC50)

test organisms	Closed ring		Open ring
	Dicarboxilic type 1.5 dimer	Amino acid type monomer*	amino acid type monomer*
Marine luminescent bacteria	> 1,000	>10,000	>10,000
Marine microalgae	> 1,000	7,200	7,100
Brine shrimp	> 1,000	>10,000	>10,000
Marine rotifer	> 1,000	>10,000	>10,000
Freshwater microalgae	> 1,000	3,800	4,400
Freshwater crustacean	820	>10,000	7,600
Freshwater rotifer	370	>10,000	6,300

*including salt







PNEC 370 µg/L **3,800 µg/L** **4,400 µg/L**

Safety test: Effects on marine mammals

Examining the effect of Nylon 6iL on intestinal flora

Pacific white-sided dolphin
(*Lagenorhynchus obliquidens*)
×3 animals

Spotted seal (*Phoca largha*)
×3 animals

Provided from Kaiyukan

Animal species	ID	Sex	Age	Origin	Fecal Characteristics	Health Condition
Pacific white-sided dolphin (*Lagenorhynchus obliquidens*)	LO-1	M	35 years old	Wild (Kinosaki)	Healthy	Healthy
	LO-2	F	12 years old	Wild (Nanao-city)	Healthy	Healthy
	LO-3	M	23 years old	Wild (Ishikawa-Pref.)	Healthy	Healthy
Spotted seal (*Phoca largha*)	PL-1	M	28 years old	Kiyukan	Healthy	Healthy
	PL-2	M	27 years old	Kiyukan	Healthy	Healthy
	PL-3	M	35 years old	Wild	Healthy	Renal failure (Mild)

Marine-KUHIMM

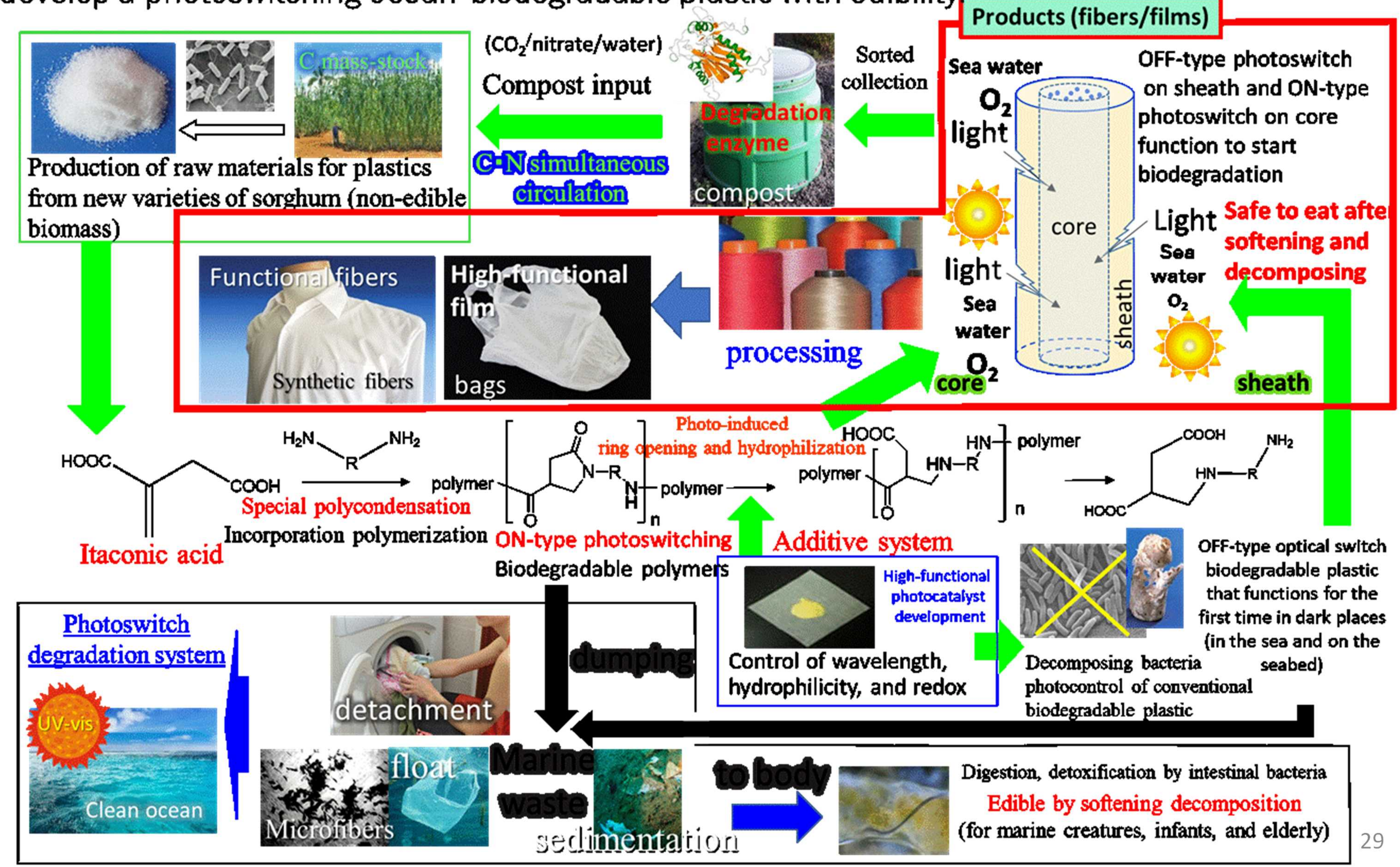
Nylon 6i-11 (75%AUA)
Nylon 6i-L

Changes in bacterial flora structure in PL (n=3)
Time course of similarity after addition to the bacterial flora structure immediately before addition (24 hours after culture start) in PL (n=3)
Time course of major metabolites (acetic acid, propionic acid, butyric acid) (n=3)

The addition of Nylon 6i-11 and Nylon 6i-L had almost no effect on the intestinal flora of marine mammals.

Final goal (2029) and Image of social implementation

【Final goal (2029)】 Using itaconic acid produced from a new cultivar of sorghum and a biodegradable polymer, a newly developed high-performance photocatalyst is composited to develop a photoswitching ocean-biodegradable plastic with edibility.



Thank you for your kind attention