Development of Photo-Switching Ocean-Degradable Plastics with Edibility

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Tokyo University of Agriculture and Technology,
National Institute of Advanced Industrial Science and Technology(AIST),
Osaka Research Institute of Industrial Science and Technology(ORIST).

Ultimate goals

【Research ①-1】

Various bionylon blocks containing a pyrrolidone ring are obtained by reacting itaconic acid with various diamines. Compounds having a purity of 99% or more on a scale of 1 kg for a typical sample in any of the amino acid type, dicarboxylic acid type, diamine type, and terminal-modified type are prepared. In addition, we aim to produce polymers with a molecular weight of 50,000 or more and a purity of 99% or more from various bio-nylon blocks on a pilot scale of 10 kg for representative samples of various nylons, PETs, and polyurethanes.

【Research ①-2（red part in charge）】

Photocatalyts are developed that have no optical or mechanical effects on the plastic composites together with a humidity control material. The biodegradation of the composites is caused from the inside by making it easier for water and bacteria to enter inside by the two effects of oxidative decomposition activity and photoinduced superhydrophilicity just when the composite surface is damaged by physical, chemical, or biological stimuli before going out to the ocean. The mechanism will be clarified.

【Research ①-3】

Develop an additive system that, when added to photoswitchable degradable polymers, has stability equivalent to the dye fastness level 5 or higher in the absence of salt, and leads to rapid degradation in the presence of salt.

【Research ①-4】

Establish processing methods for both ON-type and OFF-type photo-switchable biodegradable polymers to provide high-performance products compared with conventional plastics.

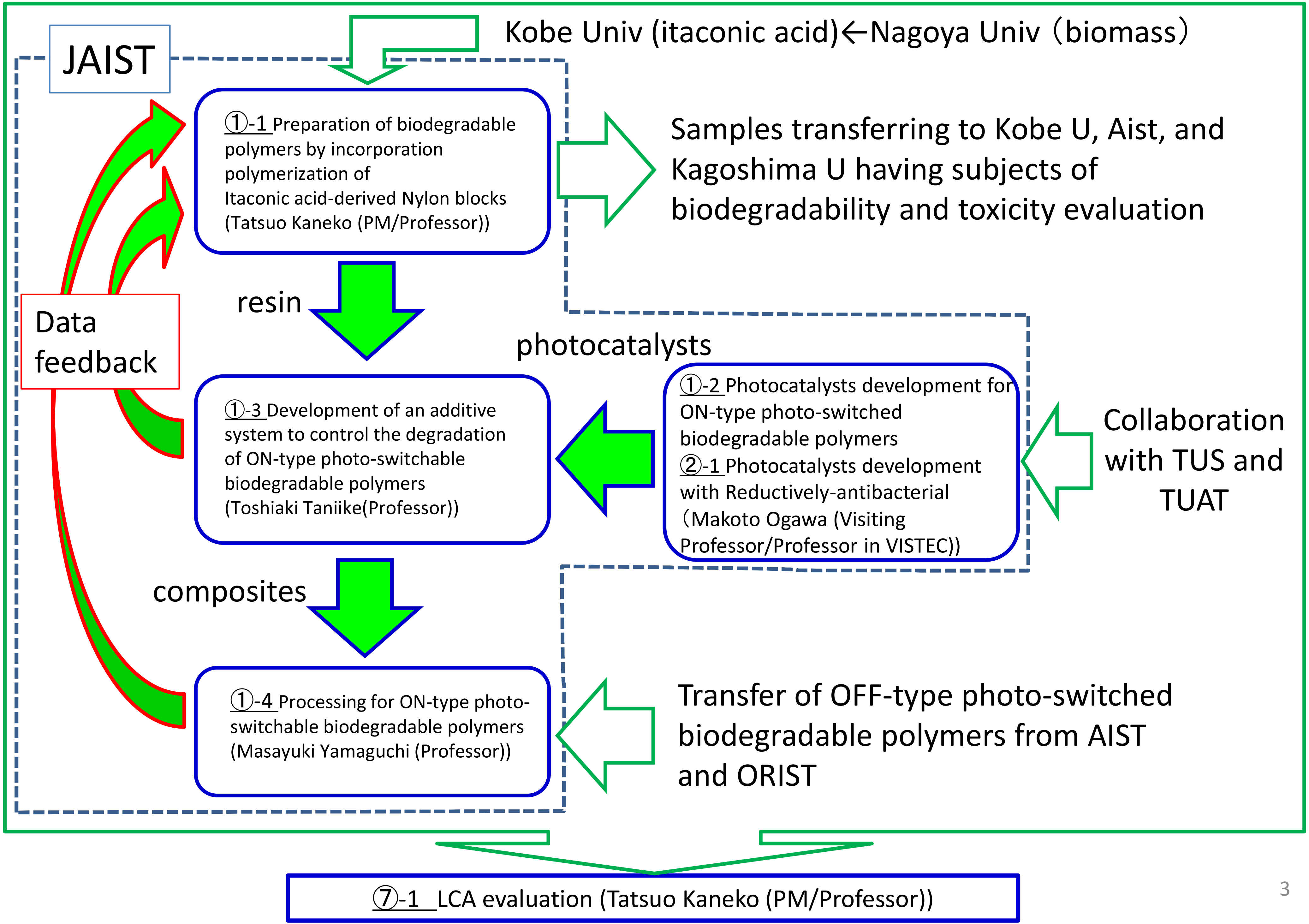
【Research ②-2（red part in charge）】

Antibacterial photocatalysts are developed that prevents biodegrading bacteria from growing on the resin surface during use, and after use, the antibacterial activity is lost in dark places such as underwater, seabed, compost, etc. Then the antibacterial mechanism in composites are clarified.

【Research ⑦-1】

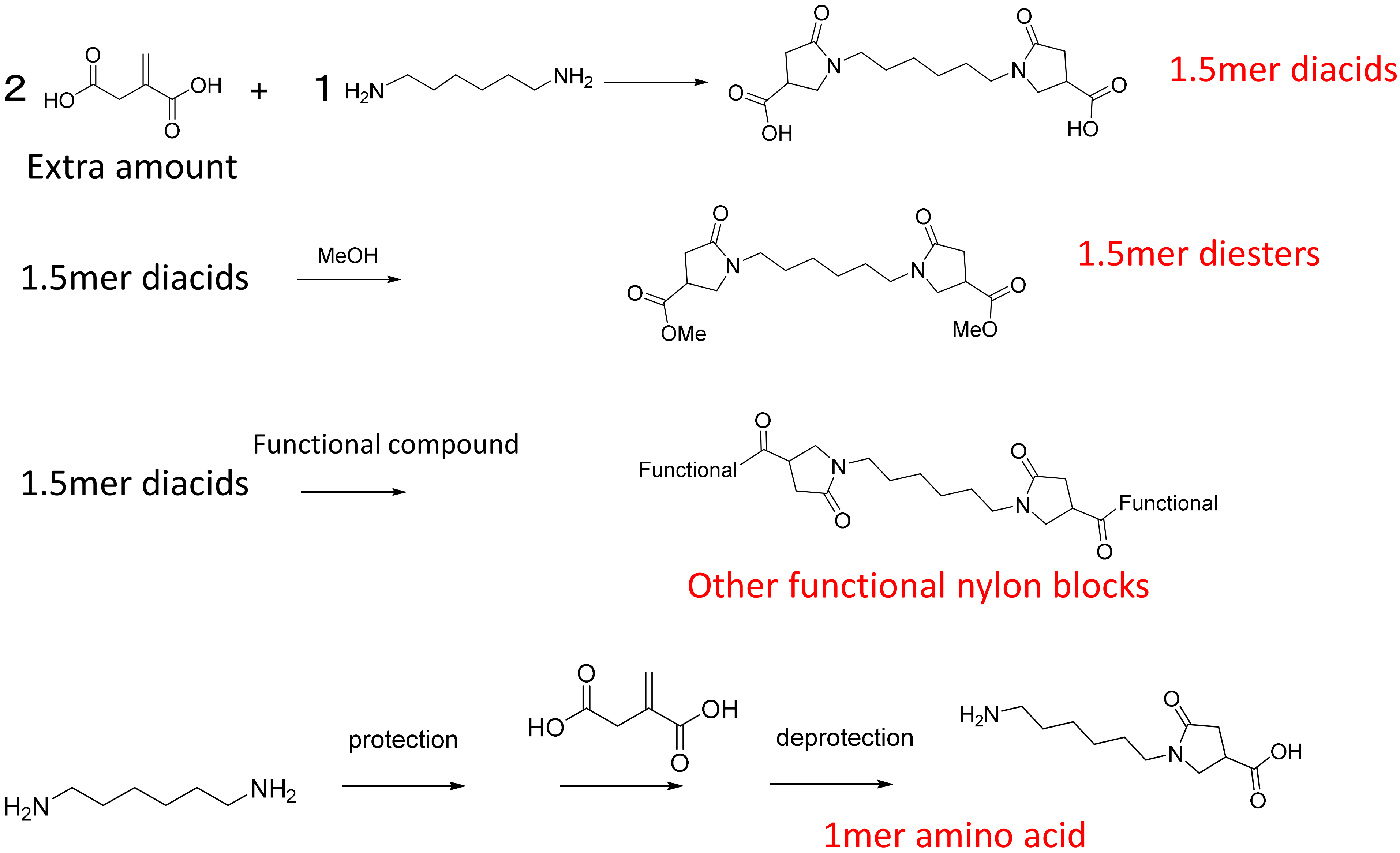
Worldwide GHG emission reduction contribution when our marine degradable plastic produced by low carbon mass production process become popular.

JAIST research system（relationship with other affiliations)



Researches ①-1

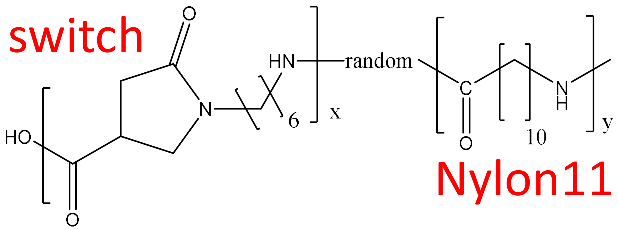
① Various bionylon oligomers have been prepared as an ON-type switch.



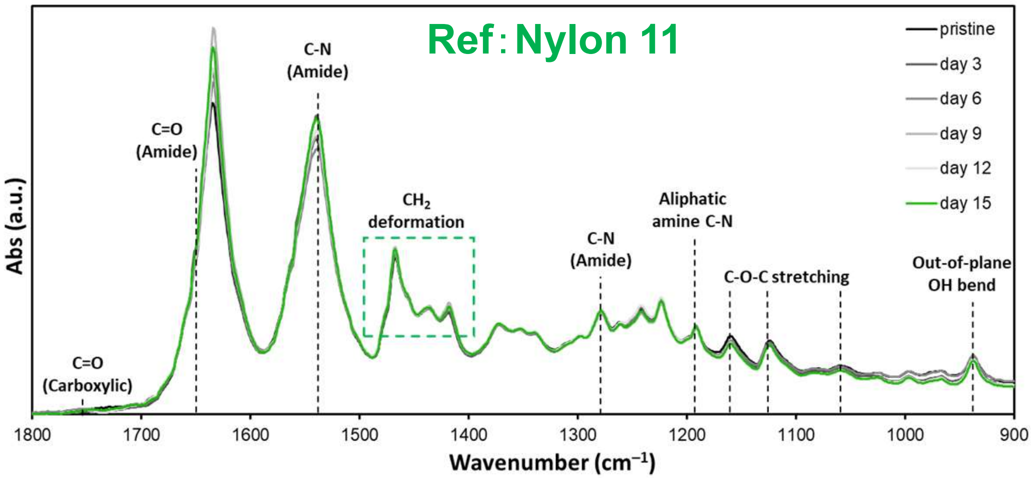
Researches ①-2、①-3、②-2

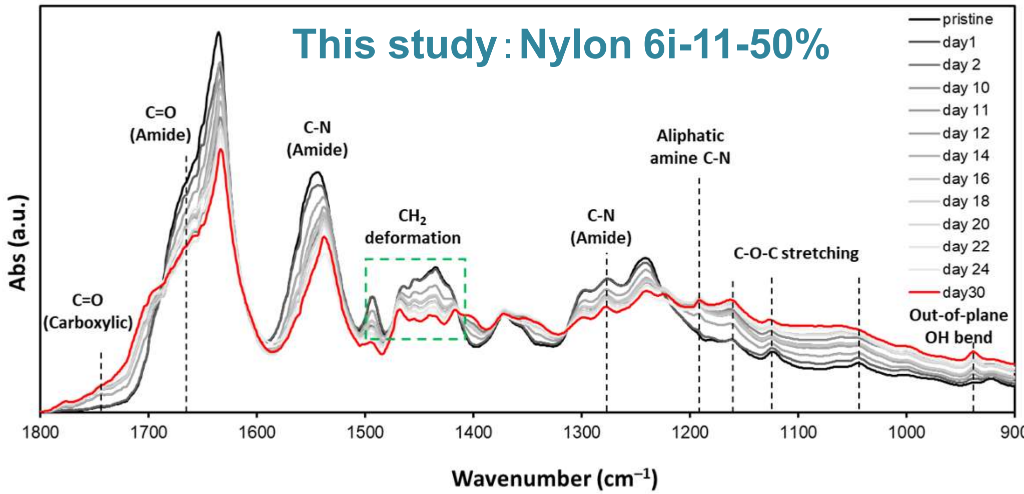
② The ON type switch greatly accelerated the degradation under sunlight and water.

ON-type switch



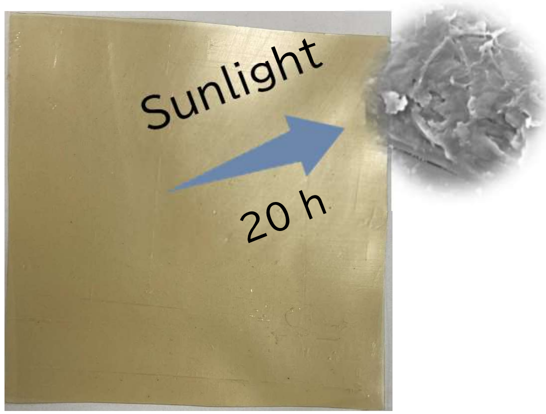
Degraded into a gel-like product in copresence of sunlight and sea water





③ Compounding of photocatalysts led to further accelerated degradation.

Nylon 6i-11-50%-CuI



Nylon 6i-11-50%-CuI/TiO_2 (0.5 wt%)

Nylon 6i-11-50%-CuI/Develop photocatalyst (0.5 wt%)

・Clays were appropriate as humidity control materials
・Carbon nitrides were appropriate as antibacterial photocatalysts (explained by TUAT)

Sunlight: Sun tester (Xenon lamp), r.t.

④ To find stabilizers to reduce crosslinking reaction for ON-type photo-switchable Nylon11

Sample　Nylon6i,11-75%

Stabilizers KI and CuI (1% for each)

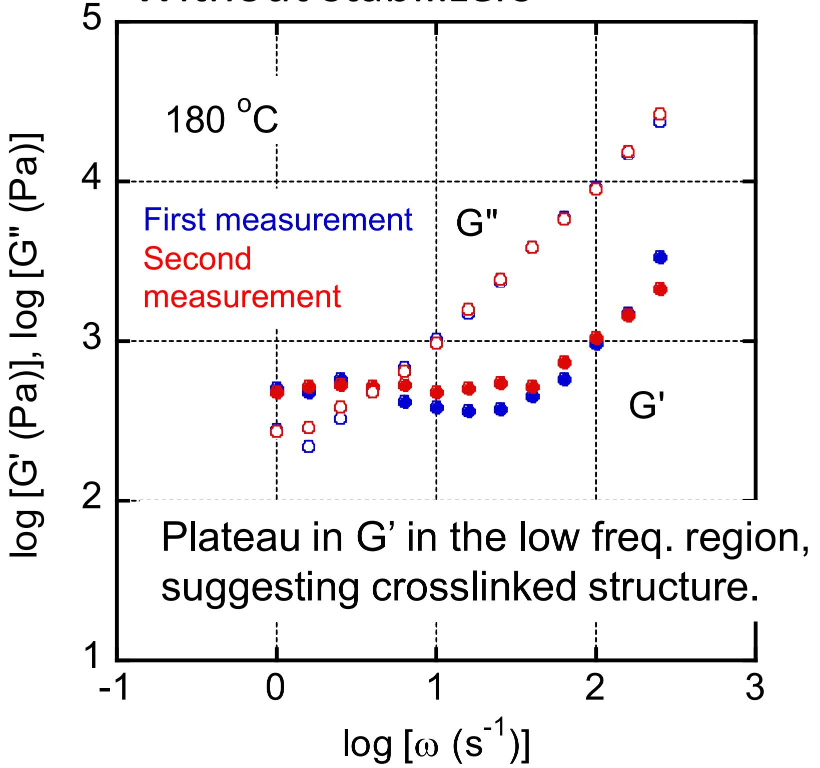
Blend procedure

Dry up the polymer at 50℃ under vacuum.

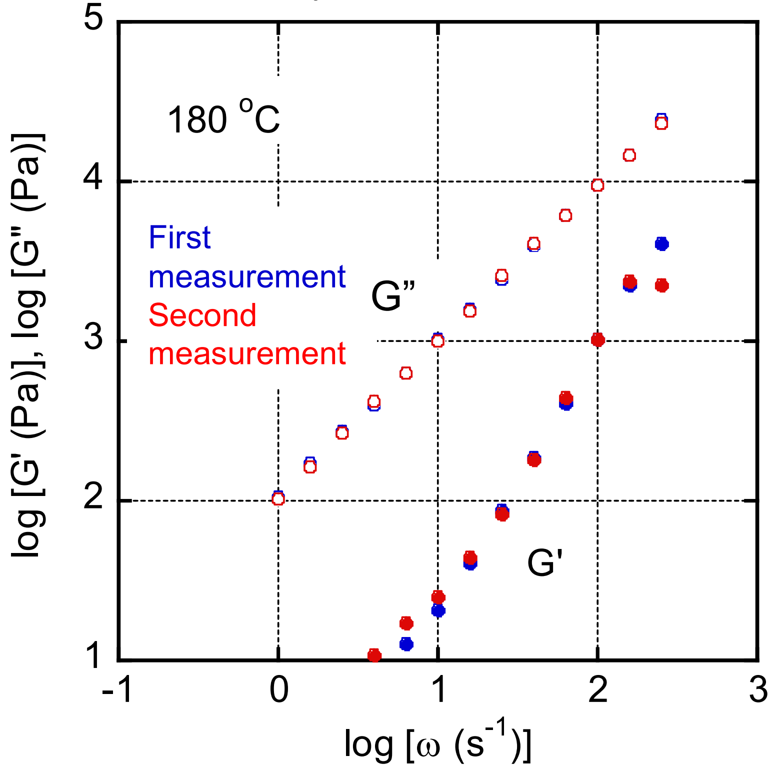
Melt-mixing in a 30 cc mixer for 5min at 180℃ with 60rpm as a blade rotation speed.

Sample set (10min) → First measurement (90s) → Second measurement (90s)　Total time 13min

Without stabilizers



With CuI/KI



Addition of CuI/KI greatly reduced crosslink reaction.

⑤ Establish the appropriate spinning condition for ON-type photo-switchable Nylon11.

Temp (℃)	90	100	110	120	130	140	150	160	170	180
Resin Force (N)	5000 <	5000 <	5000 <	2700	1500	900	850	700	600	550

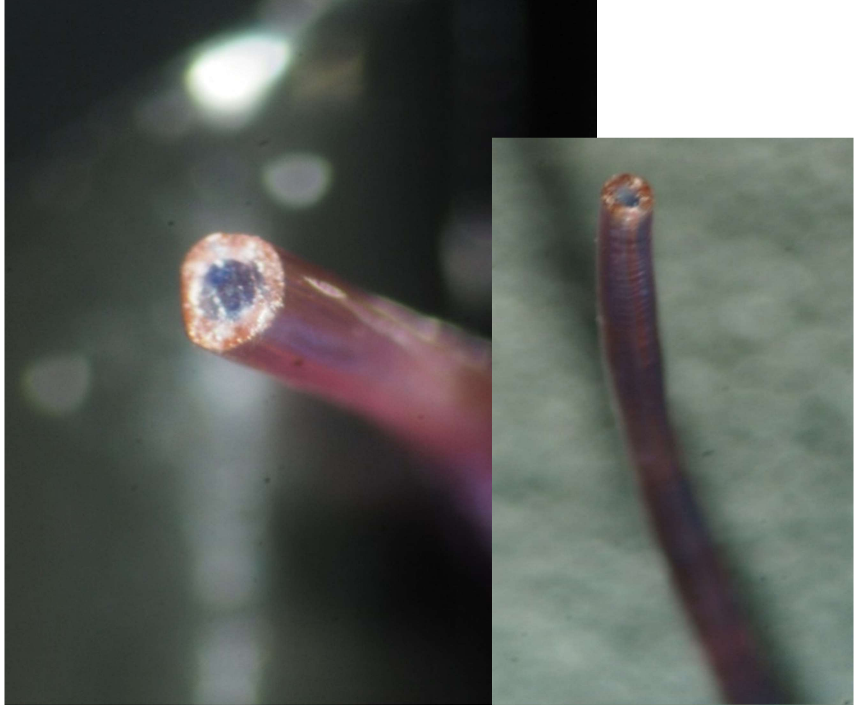
Longer than 10 m

⑥ Develop the novel spinning system to produce core sheath fiber with a small amount of polymer (using polystyrene as a model polymer).

Twin-capillary rheometer

Joint portion

Exit of orifice



Core-sheath fiber

Research ⑦-1

LCA was conducted as two themes, product LCA in a narrow sense and calculation of wide range GHG emission reduction contribution.

	Concept	Subjects	Results
Theme1 Product LCA	LCA of a new product such as clothes used our new material is conducted in detail. In this term, GHG emission in the raw material procurement stage (sorghum cultivation, itaconic acid production, nylon synthesis, catalyst synthesis, kneading and spinning) is calculated collecting laboratory data.	Nylon thread kneaded catalysts (Final product)	①First calculation was conducted collecting laboratory data and important points for GHG emission reduction were elucidated. ②Laboratory data was collected again reflecting points. ③Second calculation was conducted and further important points were considered.
Theme2 GHG emission reduction contribution	GHG emission reduction contribution of our new material through preventing emission of marine plastic waste is quantified as far as possible. GHG emission reduction contribution is defined as GHG emission by preventing emission of marine plastic waste without our new material.	Clothes, PET bottle, cover fertilizer	①Present condition of marine plastic waste was investigated. ②Subject plastic products were selected. ③The waste emission schemes of subjects were investigated.

Theme1 : Result example

Second calculation result

Process	GHG emission per 1 kg of final product[kg]			
	①Material	②Energy	③Waste	Total
Spinning	0.00	132.63	5.94	138.58
Kneading	0.22	518.18	0.99	519.39
NaNbO3 synthesis	1.30	14.33	0.03	15.66
C_3N_4 synthesis	11.13	42.58	0.00	53.71
Nylon synthesis	72.49	2.68	0.14	75.30
Itaconic acid production (Fermentation)	242.94	12,437.59	2.00	12,682.53
Itaconic acid production (Enzyme saccharification)	108.34	1,555.05	0.00	1,663.39
Itaconic acid production (Biomass pre-treatment)	3,581.05	3,182.90	3.99	6,767.94
Sorghum cultivation				0.00
Total				21,916.49

GHG emission per 1 kg of final product was reduced to one-hundredth of first calculation result because of efforts such as yield improvement.

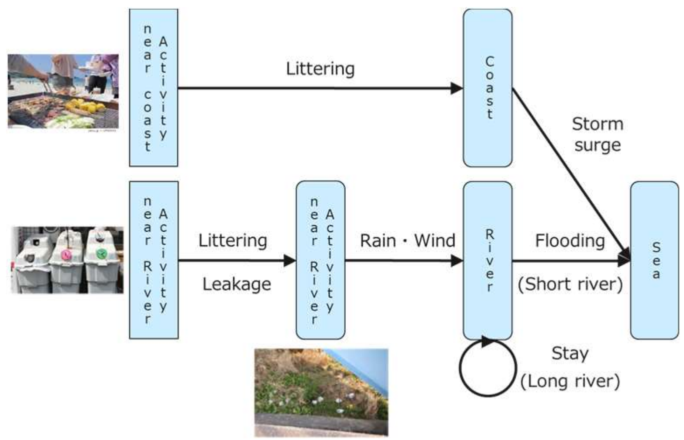
GHG emission reduction points

Process	Points
Spinning	Yield improvement, reconsideration of scale up coefficient
Kneading	Scale up coefficient
NaNbO3 synthesis	Reduction of catalyst amount by catalyst activity improvement
C_3N_4 synthesis	Reduction of catalyst amount by catalyst activity improvement
Nylon synthesis	Reconsideration of solvent with high GHG emission basic unit
Itaconic acid production	Fermentation yield improvement by genetic modification of bacteria, examination of electric energy amount using watt monitor
Sorghum cultivation	Data collecting

GHG emission reduction points were further yield improvement, reduction of catalyst amount by catalyst activity improvement and so on.

Theme2 : Result example

Waste emission schemes of PET bottle



Using these results, the scenario of preventing emission of marine plastic waste without our new material will be formulated.

Progress

Research ①-1: A method for synthesizing dicarboxylic acid-type, diamine-type and amino acid-type nylon blocks having a well-defined structure from itaconic acid was established. Incorporation into polyesters and polyamides were made.

Research ②-2: Clay mineral such as montmorillonite was selected as humidity control material and composited with itaconic acid-derived Nylons. Mechanical strength, elastic modulus, and elongation were improved by compositing.

Research ①−3: Established the degradation test method and proved for the first time that the ON-type switch built in Nylon 11 greatly accelerates the degradation under light irradiation in (salty) water.

Research ①-4: CuI is confirmed to prevent cross-linking of nylon 11 composites with nylon blocks showing ON-type optical switch, and it was found that 150-180 ℃ is the optimum processing temperature. A system for producing core-sheath fibers was constructed.

Research ②-2: Carbon nitride such as g-C_3N_4 was found to be suitable as a photocatalyst with antibacterial properties.

Research ⑦-1: GHG emission in the raw material procurement stage was calculated collecting laboratory data. GHG emission reduction contribution of our new material through preventing emission of marine plastic waste was quantified by considering GHG emission by preventing emission of marine plastic waste without our new material.

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