Research and development of marine biodegradable plastics with degradation initiation switch function

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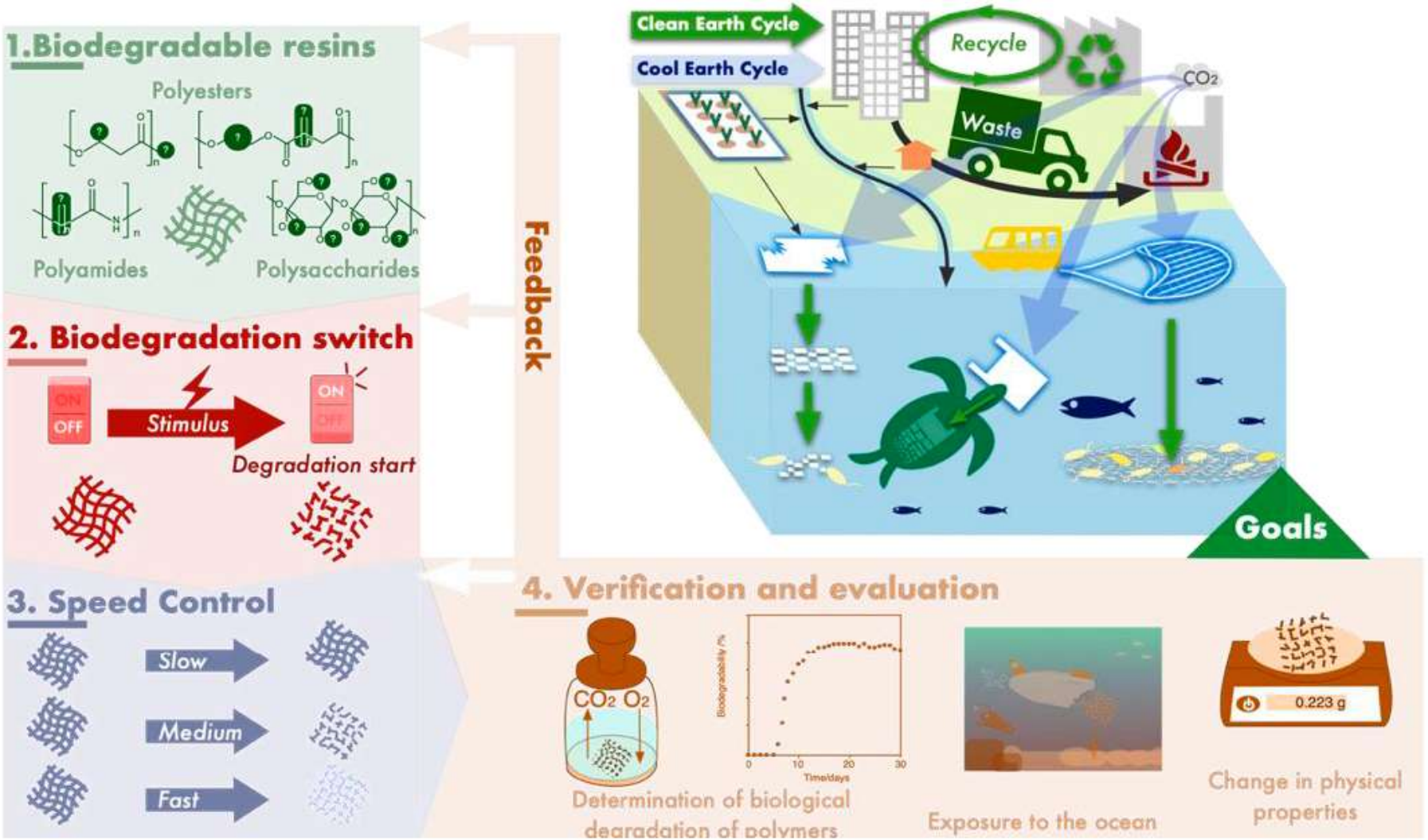
Institute of Physical and Chemical Research (RIKEN),
Japan Agency for Marine-Earth Science and Technology (JAMSTEC)

Development items & Targets



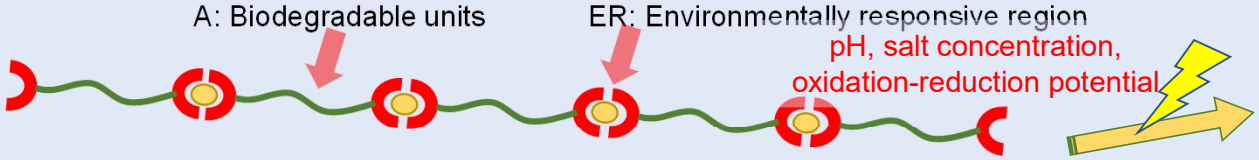
＜Targets by 2029 (from RIKEN)＞

- Materialization of 1 or more new bio-based marine biodegradable plastics that exhibit biodegradabilities of 90% in 6 months in seawater at 30 °C after the switching function responded to salt concentration is expressed.
- Materialization of 1 or more new bio-based marine biodegradable plastics that exhibit biodegradabilities of 10% in 6 months in seawater at 4 °C after the switching function responded to temperature or pressure is expressed.
- Verification of the biodegradabilities of developed plastics with switching functions under the marine environment.

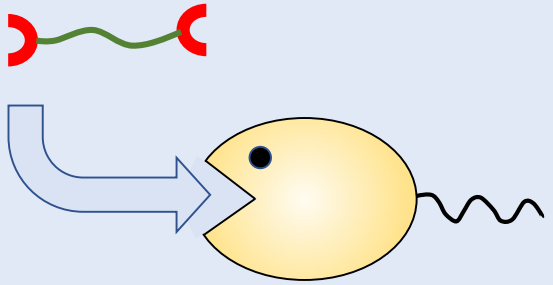
Concepts of switching functions inducing marine biodegradation

Type 1 （Respond to chemical stimulus）

Chemical environmental changes lead to recovering the biodegradability of the biodegradable polymers whose biodegradability has been made lost.



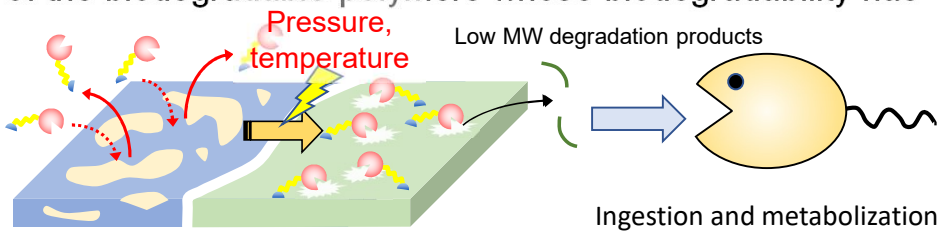
Environmental factor (EF)	(ER)	Controlling factor
pH (inflow into marine)	Ester bonds	Reduction of MW, Exposure of degradable surface
Salt conc. (inflow into marine)	Coordinate bonds	Reduction of MW, Exposure of degradable surface
Salt conc. (inflow into marine)	Supramolecular	Reduction of MW, Exposure of degradable surface
Salt conc. & pH (inflow into marine)	Ionic binds	Reduction of MW, Exposure of degradable surface
Oxid-red. potential (inflow into marine)	Disulfide bonds	Reduction of MW, Exposure of degradable surface



Type 2 （Respond to physical stimulus）

Physical environmental changes lead to recovering the biodegradability of the biodegradable polymers whose biodegradability has been made lost by regulation of the phase structure.

Environmental factor (EF)	Controlling factor
Pressure (settling to deep sea)	Changes in phase structure
Temperature (settling to deep sea)	Changes in phase structure

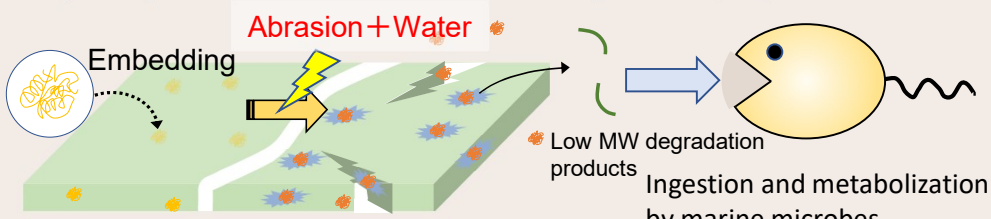


Controlling the adsorption of enzymes via phase transition of polymeric materials

Type 3 （Respond to multiple stimulus）

Abrasion of material lead to inducing the acceleration of biodegradation by enzymes or microbes embedding in the polymers.

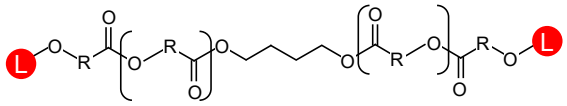
Environmental factor (EF)	Decomposition promoter	Controlling factor
Abrasion (time-of-use)	Depolymerase	Reduction of MW
Abrasion (time-of-use)	Microbes	Reduction of MW



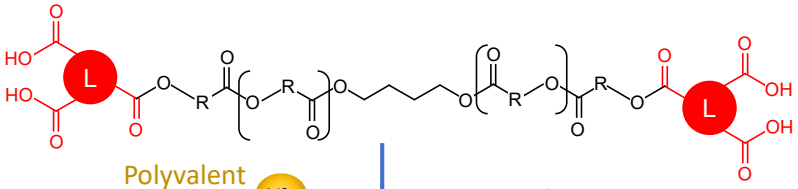
Activation of enzymes or microbes via water invasion through the abrasion of material

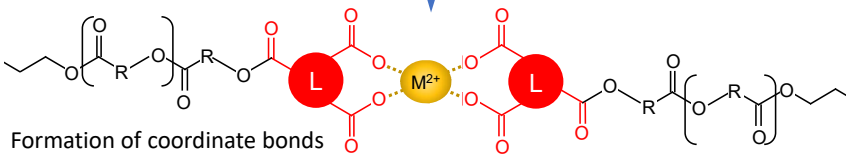
1. Biodegradable resins

Introduction of switching function responded to salt concentration

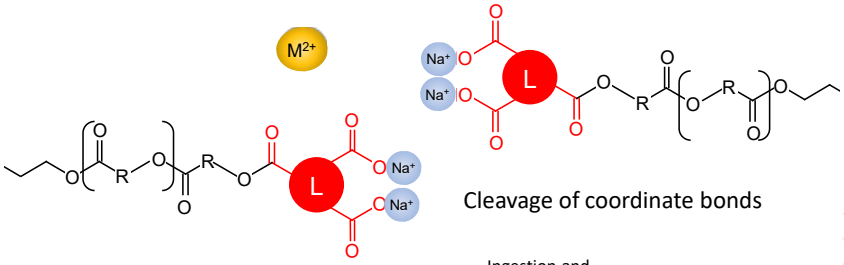


Polyesters introduced the ligands with dicarboxylic acid group

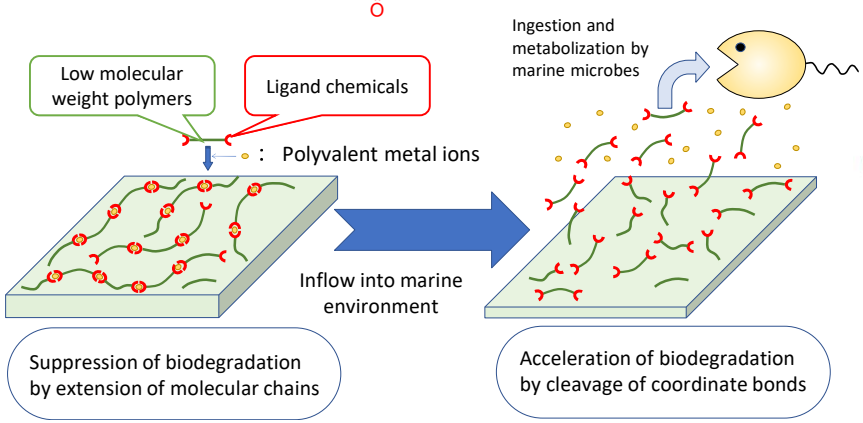


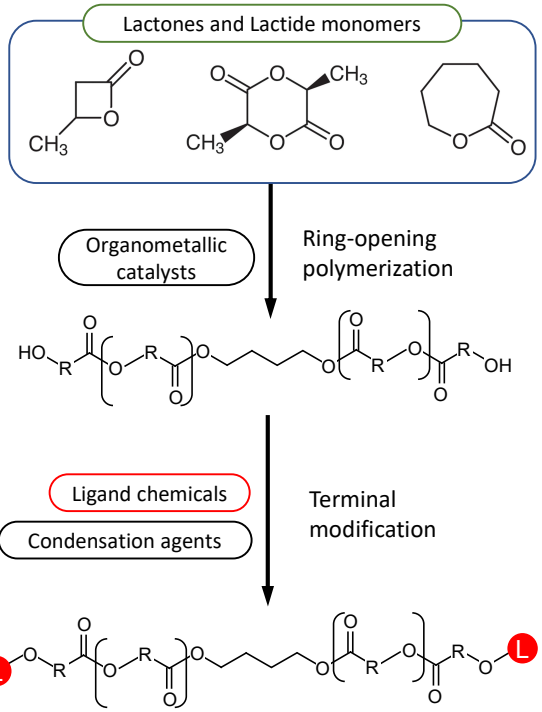


Formation of coordinate bonds

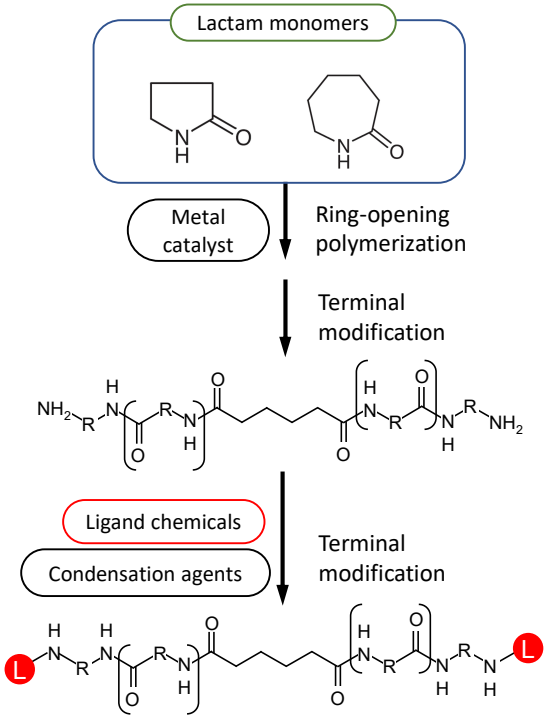


Cleavage of coordinate bonds



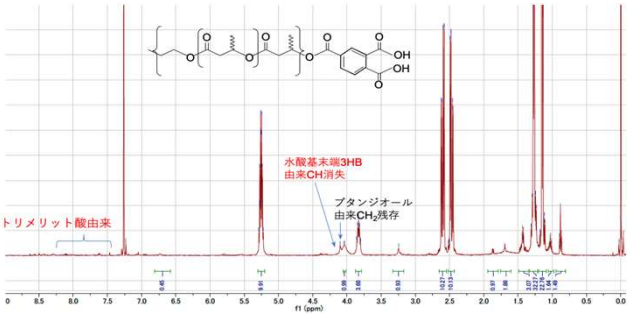


Polyesters with the terminal ligands

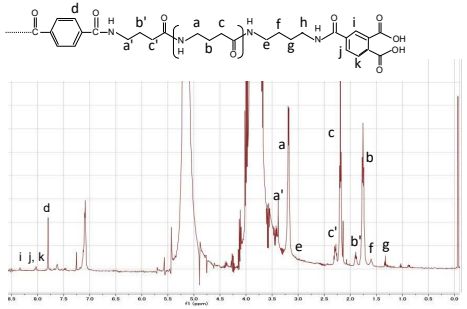


Polyamides with the terminal ligands

Succeeded in introduction of ligands into the chain-ends of aliphatic polyesters

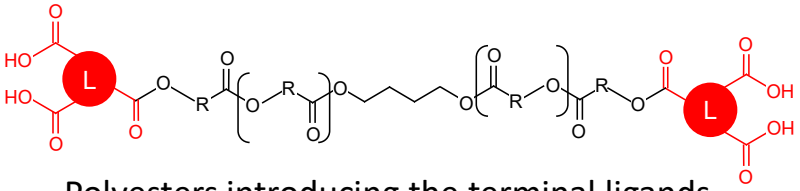


Succeeded in introduction of ligands into the chain-ends of aliphatic polyamides



Established the techniques to introduce the ligands into the chain-ends of biodegradable polyesters and polyamides

2. Biodegradation switch
2-1. Switching responded to salt concentration



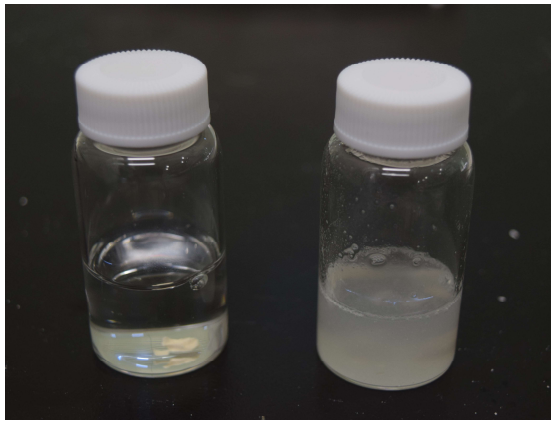
Polyesters introducing the terminal ligands

+ Cl–M–Cl

Metal chlorides

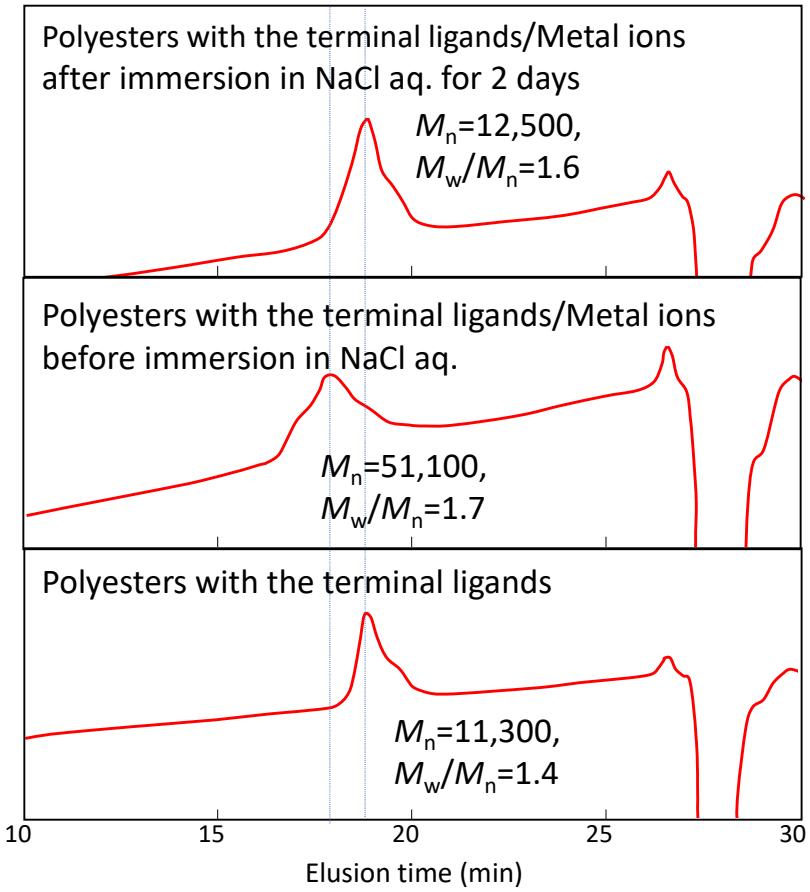
40℃, 12 h, Pyridine
in DCM

Polymers forming coordinate bonding between terminal ligands and metal ions



Water 3wt% NaCl aq. Sol.

Changes in molecular weights determined by GPC

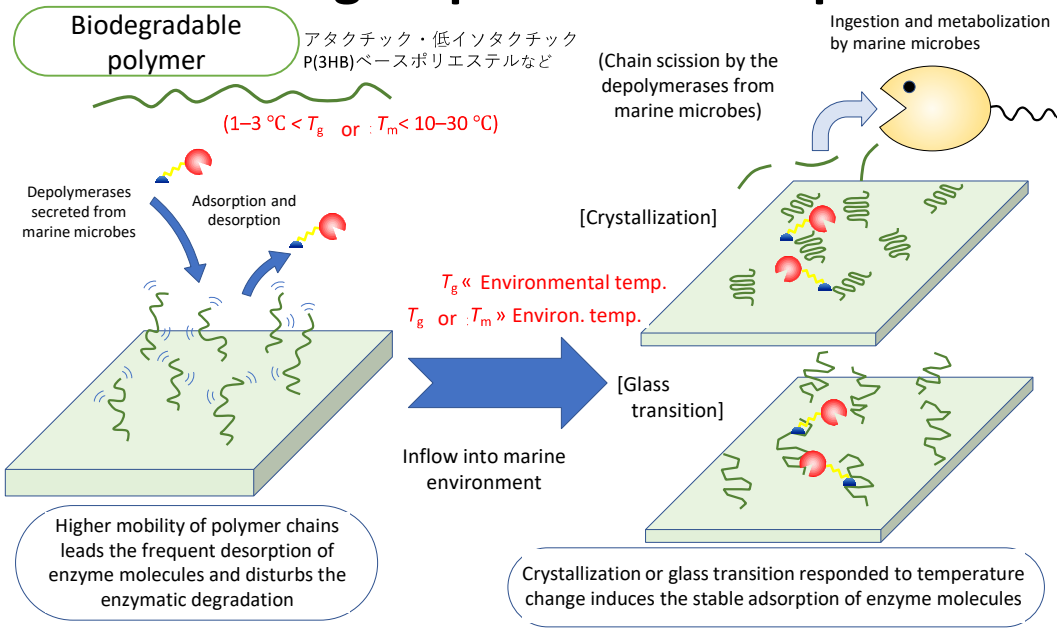


Confirmed the formation of coordinate bonding between metal ions with tetrahedral coordination and the terminal ligands of dicarboxylic acid group of polyesters

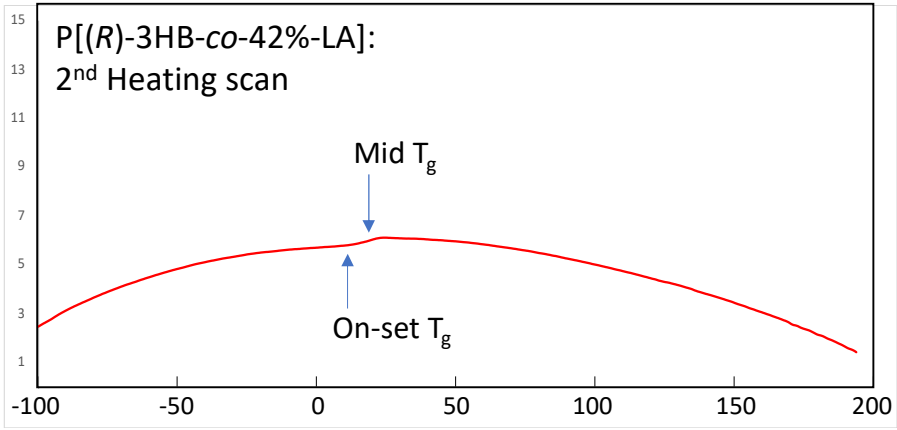
Confirmed the cleavage of coordinate bonding of polymers by the immersion into NaCl aq. solution with a concentration of 2wt% or more

Coordinate bonding was also formed between ferrous ions and terminal ligands of terpyridine group of polyesters, however, the bonding was hardly cleaved in NaCl aq. solution

2. Biodegradation switch
2-3. Switching responded to temperature



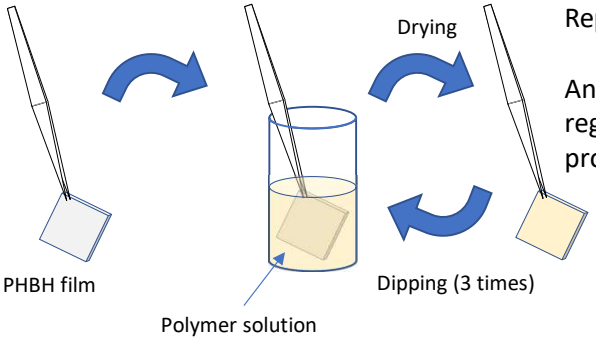
Ring-opening copolymerization of lactones：
M/I= 50 (mol/mol), DCM 20 mL, Temp.=60℃, Time= 3 days



Succeeded in syntheses of polymers having the phase transition as crystallization or glass transition at eligible temperature region

Coating of copolymer on the surface of PHBH(5mol%3HH) films

Dipping into the copolymer solution

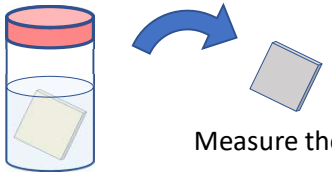


Solvent：Acetone/Chloroform（70/30(v/v)）
Conc.：10 mg/mL
Repetition： 3 times

Annealed at 50 °C to eliminate the crystalline regions formed at the solvent-evaporation process

Enzymatic degradation by PHB depolymerase from *Ralstonia pickettii* T1

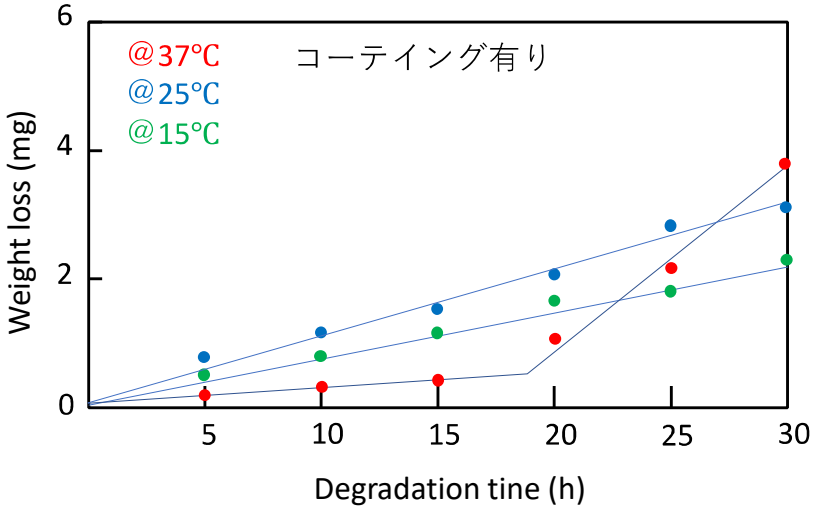
0.1M Phosphate buffer（pH 7.4）：1 mL
PHB depolymerase：2 μg
Temp.：37℃、25℃、15℃



Films were washed with distilled water and dried

Measure the film weight

Enzymatic degradability of PHBH (5mol%3HH) films coated with synthesized copolyester layer



Evaluated the enzymatic degradability of PHBH films coated with synthesized copolyester layer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