No. A-11-8E

PJ: Development of Multi-lock Biopolymers Degradable in Ocean from Non-food Biomasses

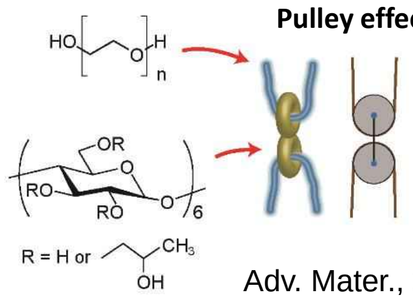
Theme: Research and Development of Degradable Supramolecular Polymers with Combined Multi-locking Mechanism and Toughness

Organization: The University of Tokyo （E1+E3）

Contact: Kohzo Ito（kohzo@edu.k.u-tokyo.ac.jp）, Shota Ando（s-ando@g.ecc.u-tokyo.ac.jp）

Background

Polythylene glycol

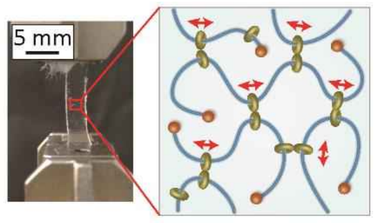


(2-Hydroxylpropyl)-α-cyclodextrin

Slide-Ring gel with freely moving cross-linking points

Pulley effect

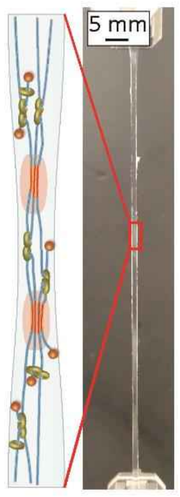
Adv. Mater., 2001



Slide-Ring (SR) gel

Stretch

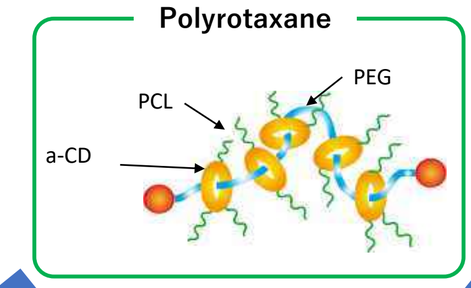
Release



Science, 2021

- Stress dispersion, elongation and toughness due to pulley effect.
- Effective when added in small amounts to other polymers.
- In low coverage rate Slide-RIng gels, the elongation-induced crystallization provides both additional toughness and immediate recovery.
- Composed of cyclodextrins and PEG, showing high biosafety and compatibility.

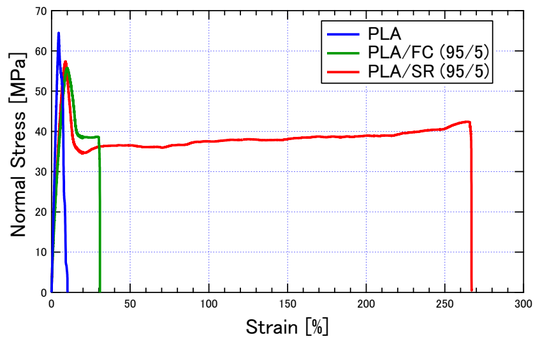
Combination of biodegradability and toughness



Toughness

Marine biodegradation

Biodegradable polymer

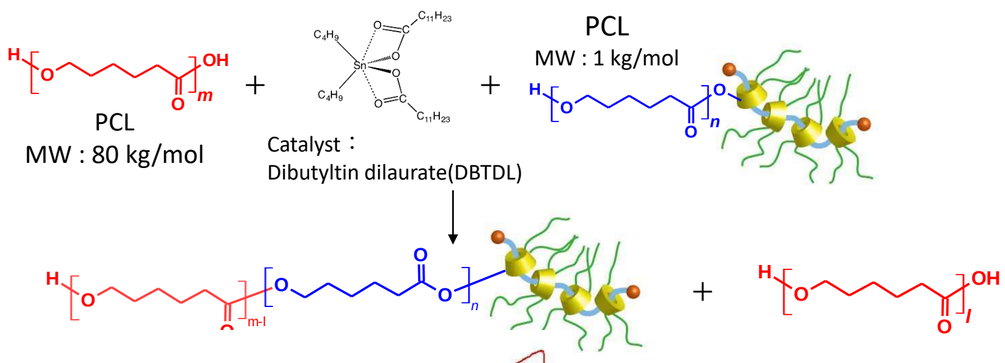


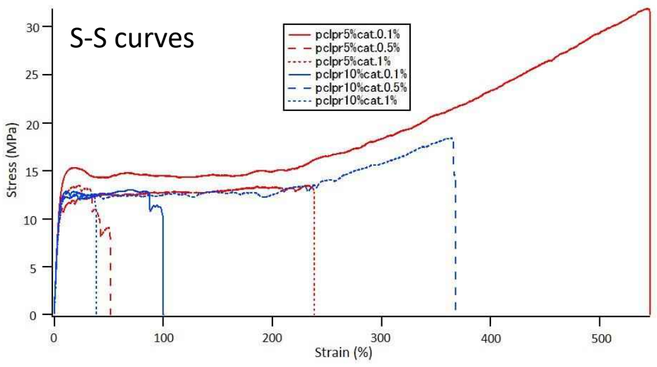
Durability/toughness of PLA due to pulley effect

?

There were no reports on biodegradability for polyrotaxane (PR).

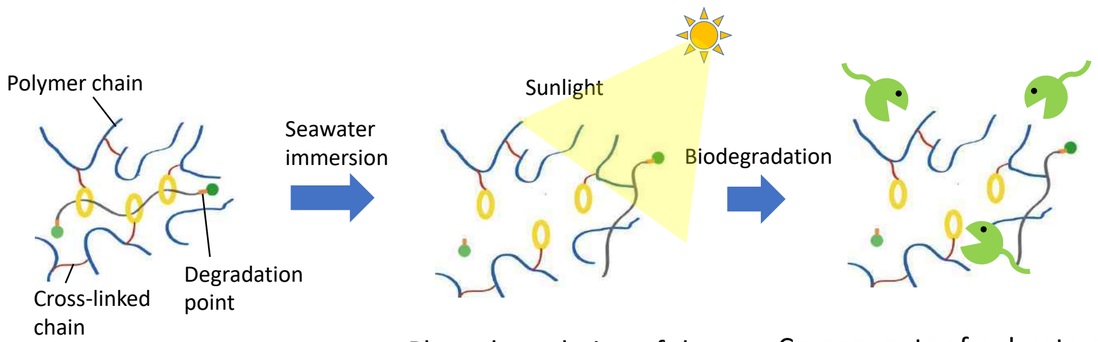
Toughened polyester resin design





The transesterification between PR and PCL increased the elongation at break by more than 5 times.

Multi-lock degradation by UV irradiation

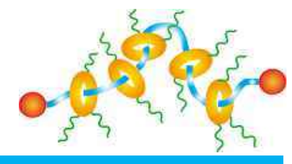


Polyrotaxane cross-linking for toughening under use

Photodegradation of the ends degrades the polyrotaxane structure (Point-control)

Components of polyrotaxane attract degradation bacteria as food and accelerate matrix biodegradation (Speed-control)

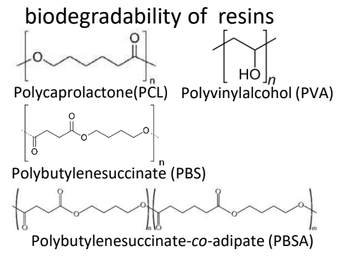
Assignment and Research Results



Research Objectives:
To achieve both toughness and biodegradability through the use of polyrotaxane (PR)

Effect of adding PR

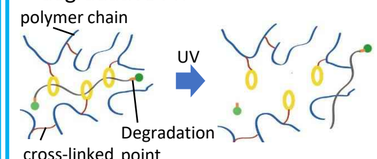
- Combination of toughness and biodegradability of resins



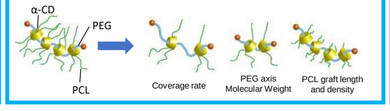
- Combines toughness and biodegradability through ester exchange reaction
- Achieved toughening and biodegradability of ester-exchange vitrimers

Multi-lock function

- Synthesis of end-stimulated degradative PR

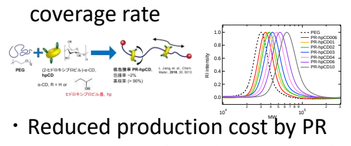


- Controlled structural parameters such as coverage ratio, axial molecular weight, and graft density

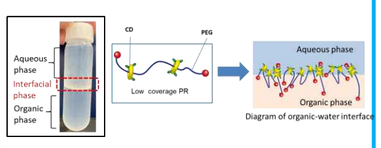


Social integration

- One-pot synthesis of PR to reduce production cost and control coverage rate



- Reduced production cost by PR extraction and purification method



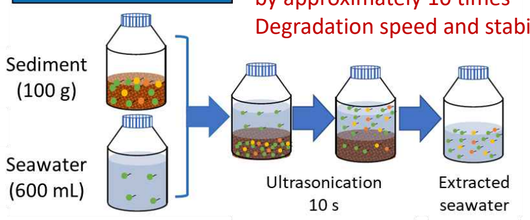
- Raw materials such as components, solvents, etc., for cost reduction.

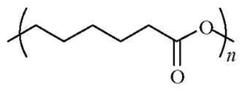
Polyrotaxane Seawater Biodegradability

Seawater sampling location:
Miyagawa beach, Miura city, Kanagawa

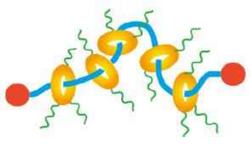
Preparation of extracted seawater

CERI Dr. T. Kikuchi's protocol
Degradation bacteria concentration was enhanced by approximately 10 times
Degradation speed and stability also improved



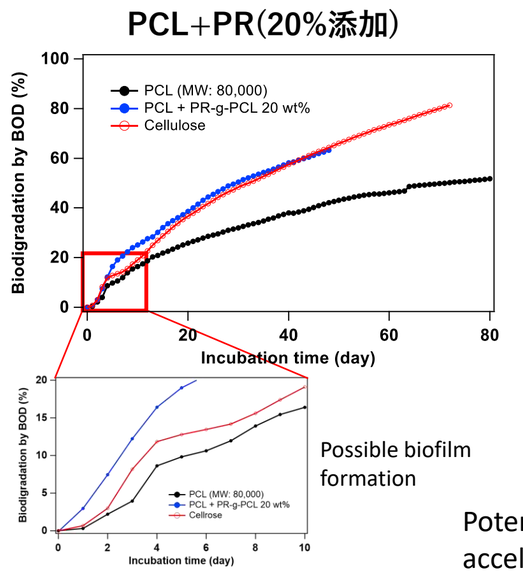


Polycaprolactone (PCL)

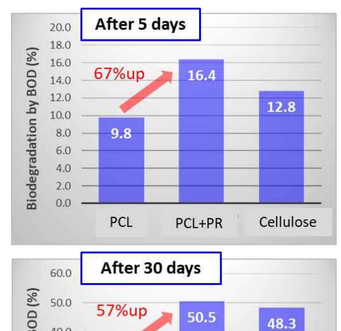


PCL-grafted Polyrotaxane（PR-g-PCL）

PCL+PR(20%添加)

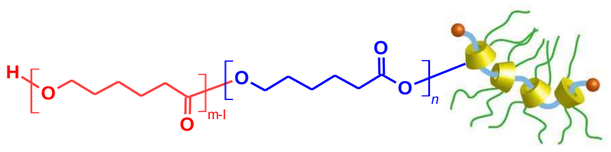


Possible biofilm formation



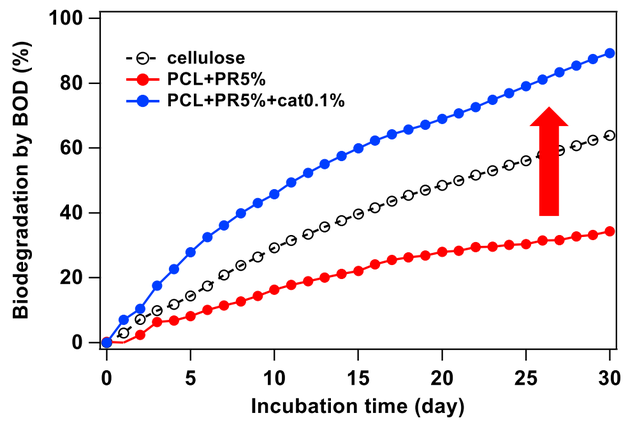
Potential as a marine degradability accelerator additive

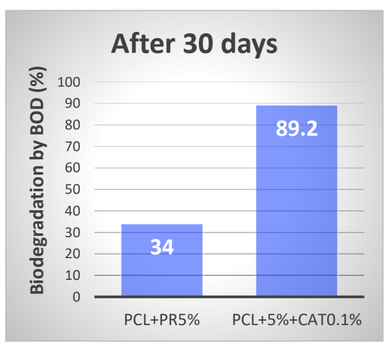
Highly biodegradable formulation of polyester



Seawater sampling location:
Miyagawa beach, Miura city, Kanagawa

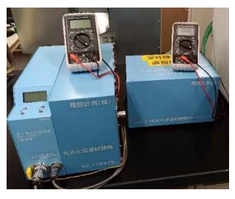
BOD test



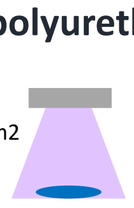


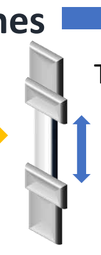
The transesterification between PR and polyester has greatly improved seawater biodegradability.

Toughening and point control of polyurethanes



Irradiation conditions :
- UV wavelength: 325 nm
- Irradiation intensity： 650 mW/cm2
- Irradiation time: 30 min

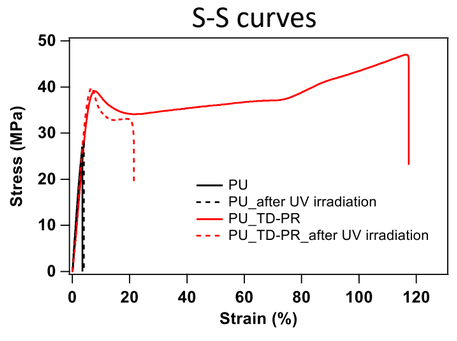




Tensile test

Measuring conditions :
- 10 mm/min
- Room temperature
- 1 kN load cell

S-S curves



Samples	Young's modulus (GPa)	Strain at Break (%)
PU	0.87	4.0
PU_after UV irradiation	0.85	4.1
PU_TD-PR	0.64	117.4
PU_TD-PRPU _after UV irradiation	0.65	21.6

- TD-PR increases elongation at break by about 30 times.
- UV irradiation of PU with TD-PR reduced elongation at break by about 1/5

→ Suggests degradation of PR by UV irradiation

No. A-11-9E

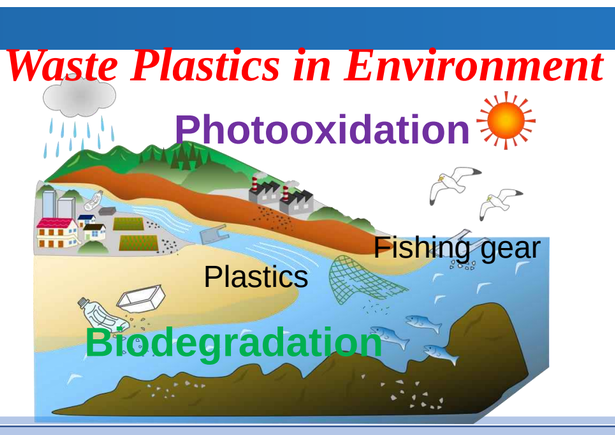
PJ: Development of Multi-lock Biopolymers Degradable in Ocean from Non-food Biomasses

Theme: Structure and Properties of Multi-lock Biopolymer during the Environmental Degradation

Organization: Kyushu University Takahara Group （E2）

Contact: takahara.atsushi.150@m.kyushu-u.ac.jp

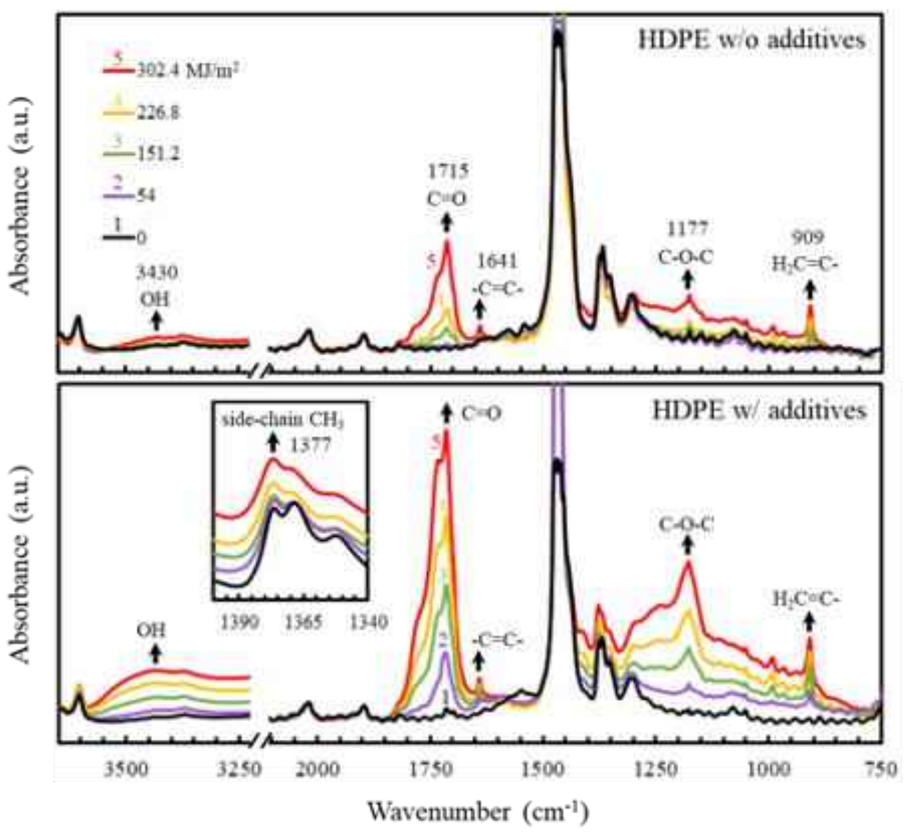
Introduction: Microplastics (MPs) has became global environment problems due to the environmental degradation of waste plastic products. In order to face this challenge, it is important and necessary to study the degradation behaviors of plastics in environment. Also, development of biopolymer which can be degraded by microorganisms will be a promising way to solve the MPs problems in environment. In this study, the environmental degradation behaviors of plastics were studied by simulating photooxidation and biodegradation behaviors of polymers in laboratory using weathering test chamber and extracted seawater.



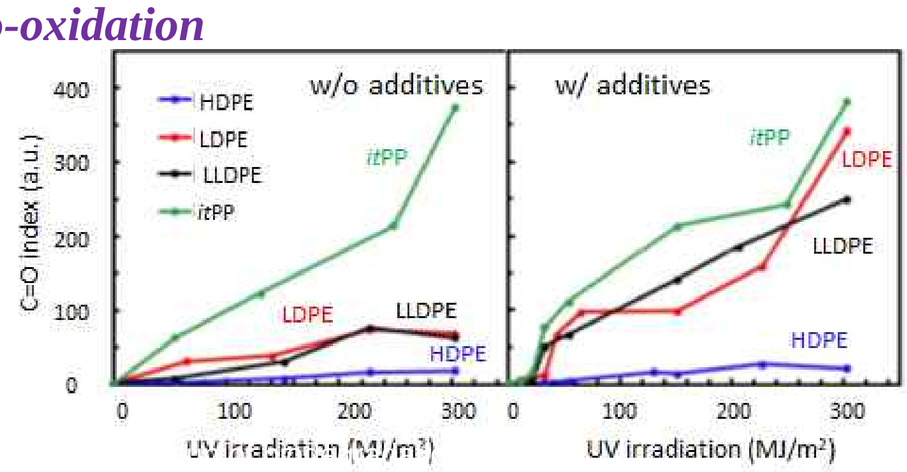
1.Photo-oxidation and biodegradation behaviors of polyolefins containing oxo-biodegradable additives

The effects of the commercially available pro-oxidants of the oxo-biodegradable type (P-Life Japan Inc.) on the photo-oxidation and biodegradation of polyolefin (HDPE, LDPE, LLDPE, and *it*PP) films were investigated.

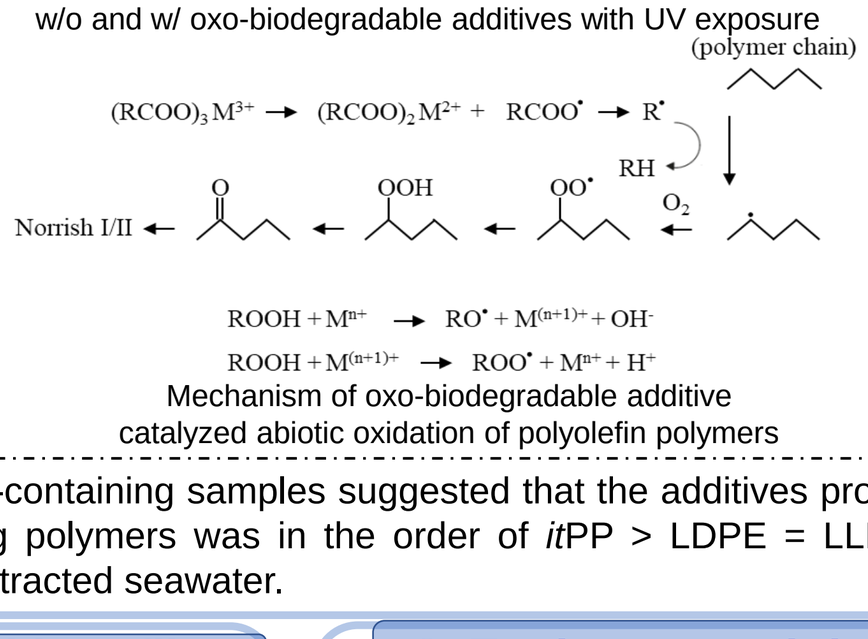
Photo-oxidation



FT-IR spectra of *it*PP w/o and w/ the oxo-biodegradable additives

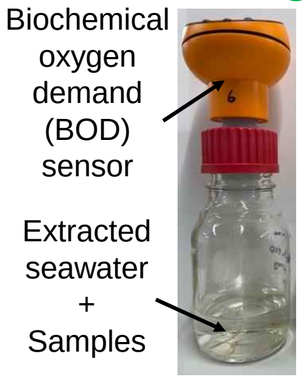


Variations of the C=O Index of HDPE, LDPE, LLDPE, and *it*PP w/o and w/ oxo-biodegradable additives with UV exposure



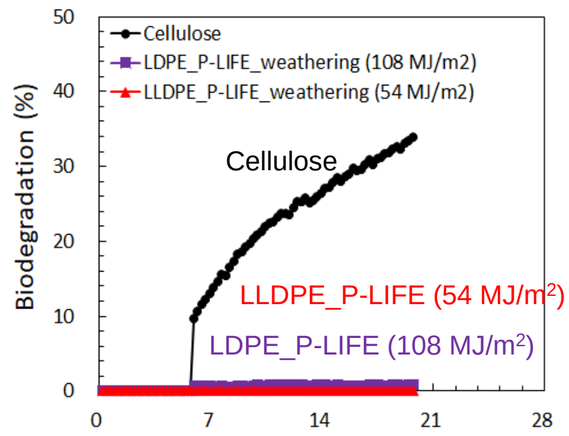
Mechanism of oxo-biodegradable additive catalyzed abiotic oxidation of polyolefin polymers

Biodegradation



BOD_{sample} (mg/L) = O_2, sample – O_2, blank

Biodegradation degree = (BOD/ThOD) × 100%



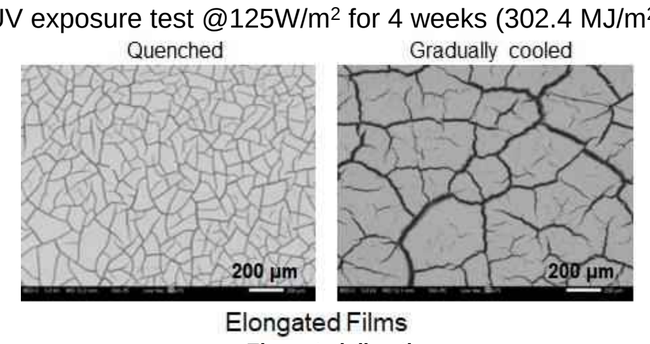
Biodegradation of LDPE & LLDPE with oxo-biodegradable additive

The carbonyl index calculated for the neat and additive-containing samples suggested that the additives promoted the photo-oxidative degradation. The overall degradation rate of the additive-containing polymers was in the order of *it*PP > LDPE = LLDPE >> HDPE. The biodegradation of additive-containing polyolefins was not proceeded in extracted seawater.

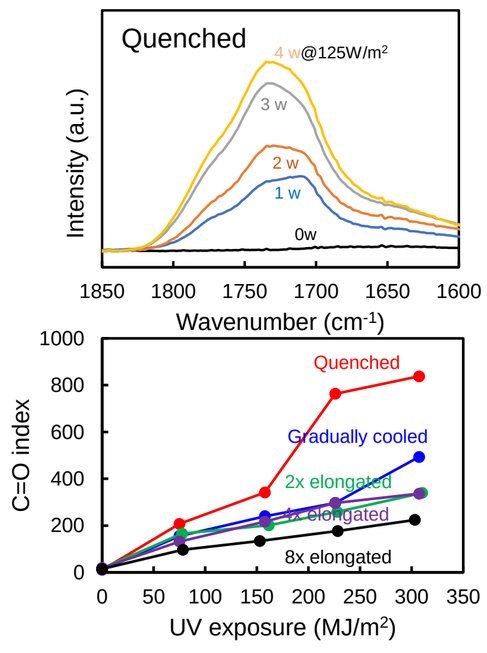
2. Photo-oxidation behaviors of elongated itPP films

Most of practical *it*PP products are oriented *it*PP. In this study, the photooxidative degradation of elongated *it*PP was examined.

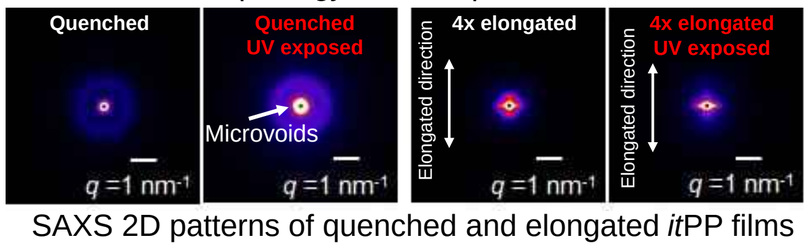
UV exposure test @125W/m² for 4 weeks (302.4 MJ/m²)



Surface morphology of UV exposed *it*PP films



IR carbonyl region and C=O index in *it*PP films



SAXS 2D patterns of quenched and elongated *it*PP films

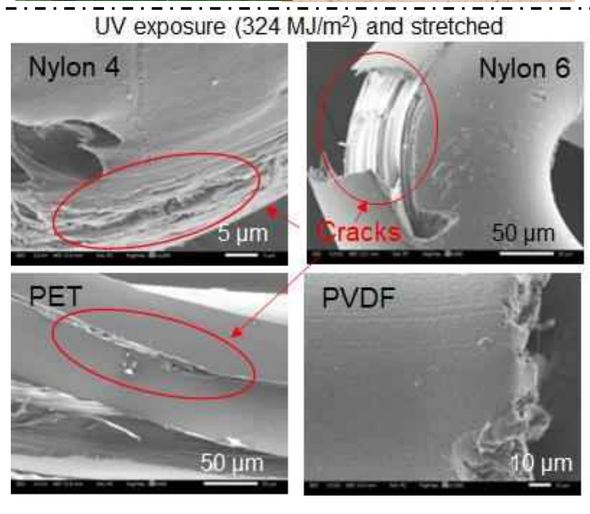
Microvoids formed in quenched *it*PP films after UV exposure

The oxidation susceptibility of *it*PP was in the order of quenched > gradually cooled > 2x elongated > 4x elongated > 8x elongated. Crystalline phase has strong resistance against photooxidation

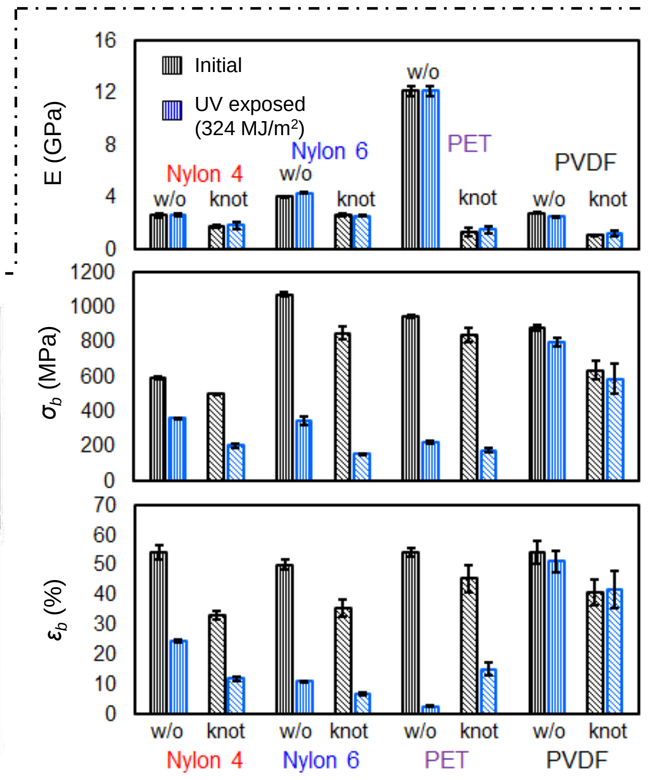
3. Environmental degradation of fishing lines

Ghost fishing caused by lost fishing gear has strongly affected the marine organisms. In this study, the environmental degradation behaviors of nylon 4, nylon6, PET and PVDF fishing lines were investigated.

Ghost fishing in Ocean



Surface morphology of fishing lines after UV exposure



Comparison of mechanical properties of fishing lines before and after UV exposure

PET, nylon 6 fishing lines were degraded after photooxidation while PVDF was stable against UV exposure. Also, biodegradability of nylon 4 fishing lines were confirmed in extracted seawater.

Acknowledgments: Processing of polyolefin films were carried out by Profs. Hiroshi Ito and Yutaka Kobayashi in Yamagata University. SAXS and WAXS measurement was carried out in collaboration with Prof. Sono Sasaki in KIT and Dr. Hiroyasu Masunaga in JASRI/SPring-８.

No. A-11-10E

PJ: Development of Multi-lock Biopolymers Degradable in Ocean from Non-food Biomasses

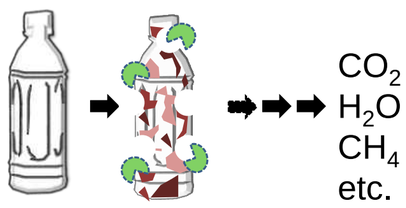
Theme: Analysis and Regulation of Degradation Behaviors of Biopolymers in Underwater Environments

Organization: Kyushu University （E2）

Contact: Hisao Matsuno, h-matsuno@cstf.kyushu-u.ac.jp

Background

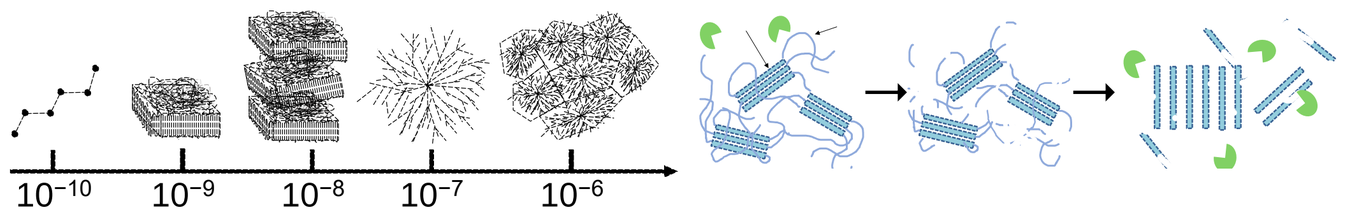
Biodegradable polymers



- **Agricultural mulch films**
- **Fishing nets**
- **PET bottles**

http://www.jbpaweb.net/gp/

Hierarchical structures and degradation process



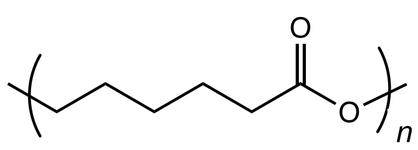
A detailed understanding of the relationship between hierarchical aggregation structures and degradation behaviors of polymers is required.

Objective

To reveal the relation between the crystalline lamellar structures of polymers and their biodegradability.

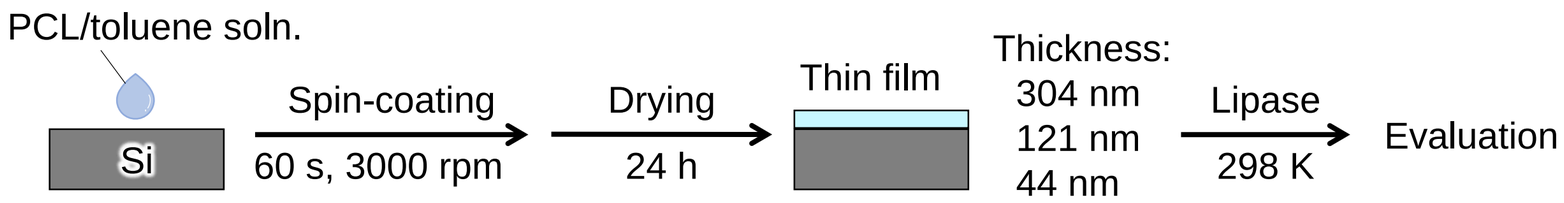
Method

Poly(ε-caprolactone) (PCL)



M_n : 113k
M_w/M_n : 1.46
T_g : 211 K
T_m : 330 K

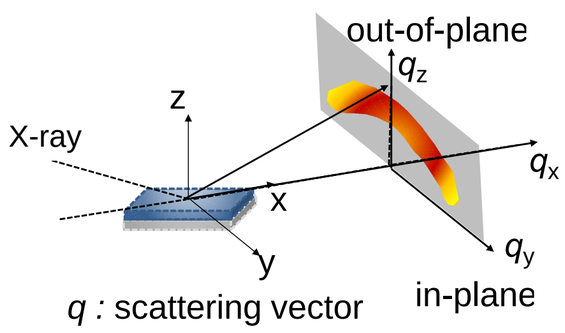
Thin film preparation & enzymatic degradation



Aggregation structures

GIWAXD measurements

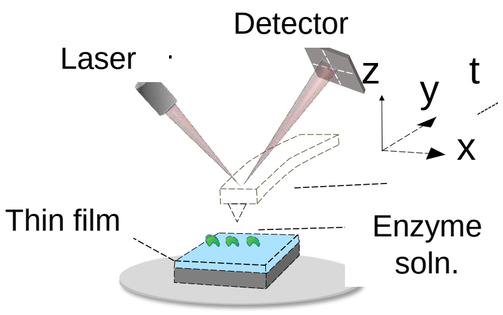
SPring8 BL03XU (2022A7218)
Sample to camera distance : 294 mm
Wavelength : 0.1 nm
Incident angle : 0.13 °



Surface morphologies

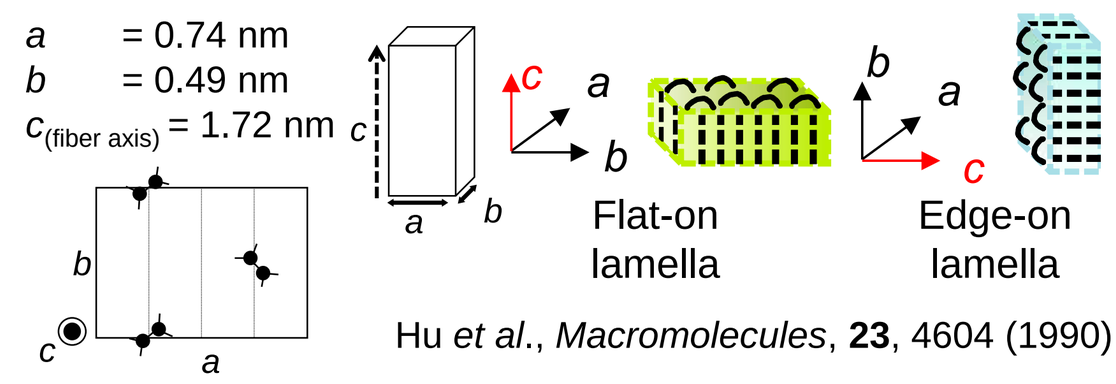
AFM observations

Cypher ES (OXFORD)
Mode : AC mode
Temperatures : 298 K

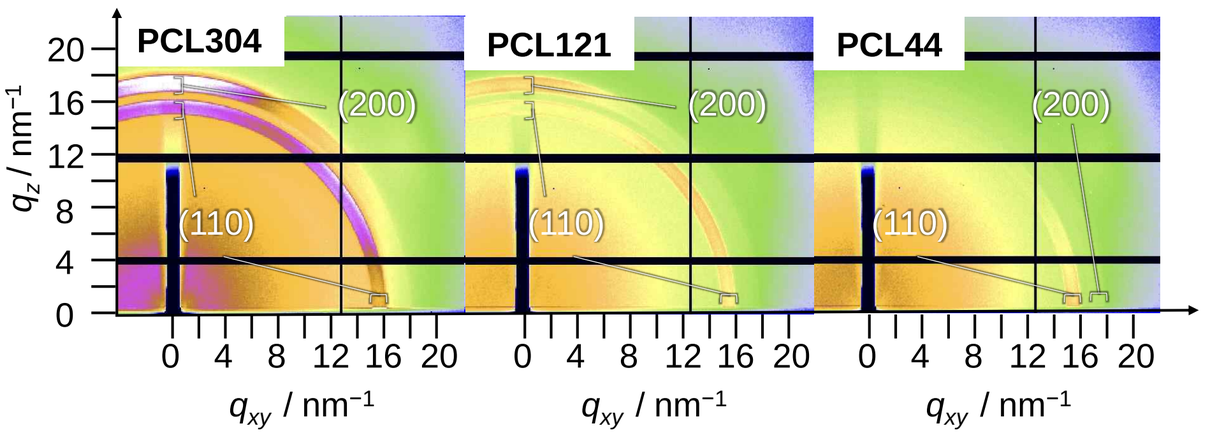


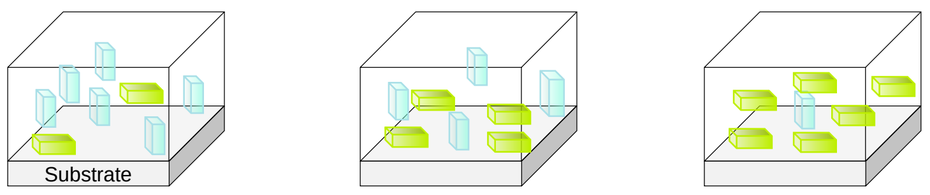
Results & Discussion

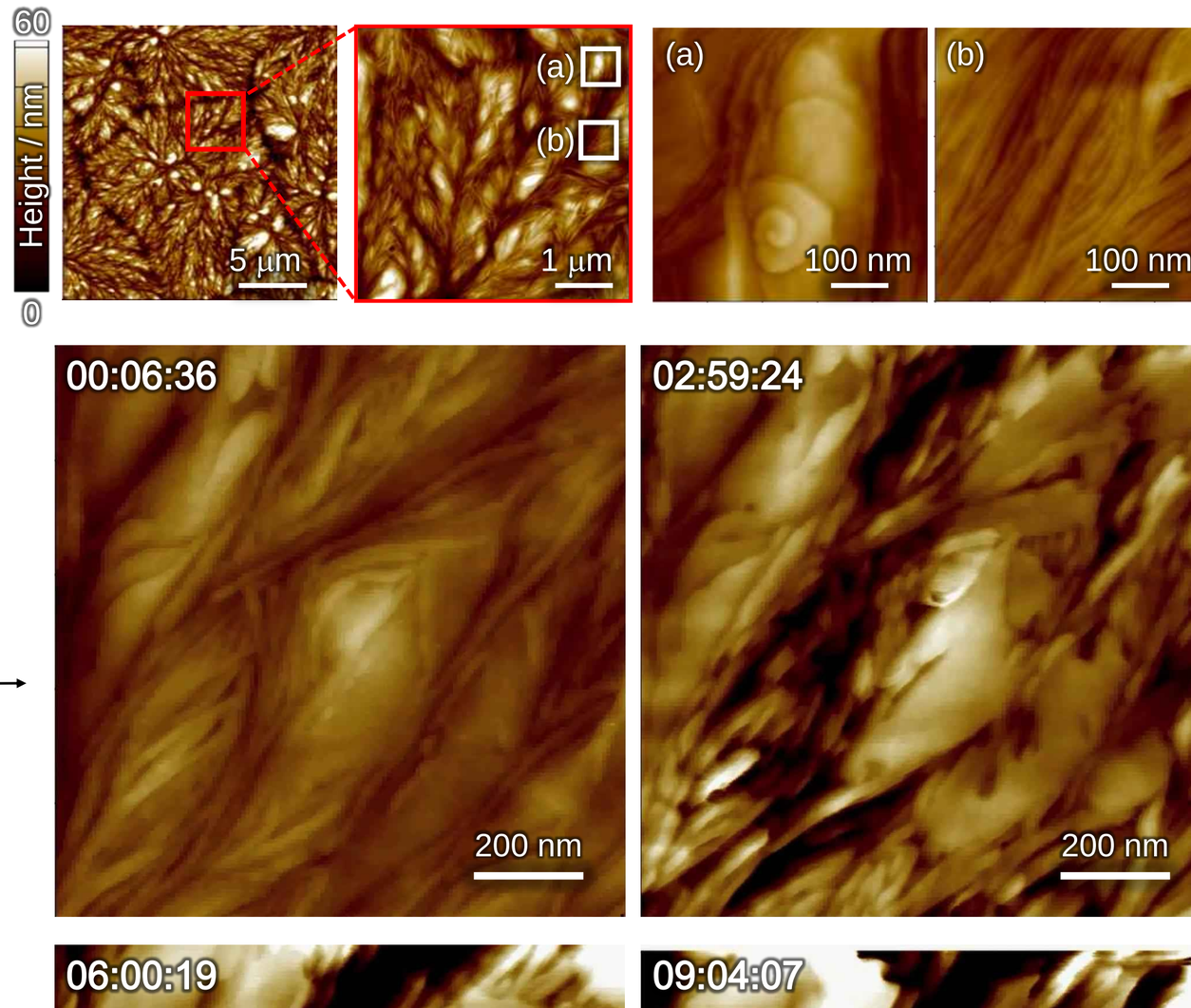
a = 0.74 nm
b = 0.49 nm
$c_{(fiber\ axis)}$ = 1.72 nm



Hu *et al.*, *Macromolecules*, **23**, 4604 (1990)

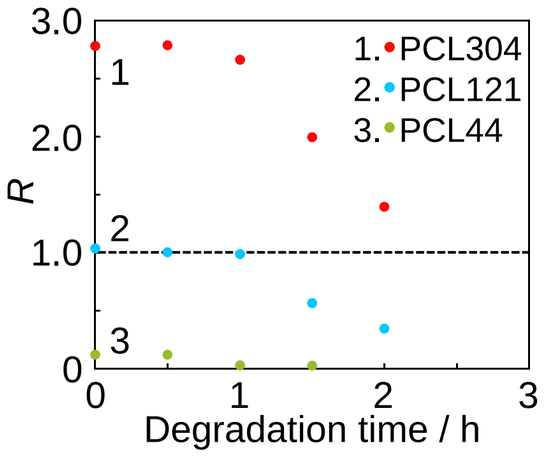






Degradation time dependence of edge-on lamella to flat-on lamella (*R*)

$$R = \frac{I_{\text{out of plane}\ (110)} + I_{\text{out of plane}\ (200)}}{I_{\text{in-plane}\ (110)} + I_{\text{in-plane}\ (200)}}$$



Conclusions

Biodegradability of polymeric materials can be controlled depending on the orientation of crystal lamellae.

（Acknowledgement: JPNP18016）

No. A-11-11E

PJ: Development of Multi-lock Biopolymers Degradable in Ocean from Non-food Biomasses

Theme: Research and development of multi-scale analysis methods for marine degradable polymers from a hierarchical point of view

Organization: National Institute of Advanced Industrial Science and Technology

Contact: Hiroshi Morita

1. Introduction

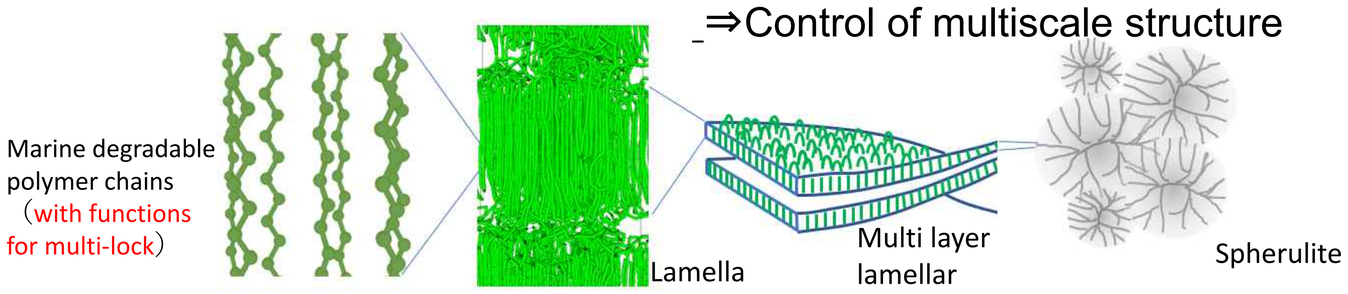
Our technology

・Multi-scale simulation technology for polymer materials from atomic to mesoscopic scales.

・Material analysis using informatics technology

Problems in development of polymer materials

⇒Control of multiscale structure



Objective until end of FY2022

・ Model study of degradation process of polymer crystals ：Major parts of marine plastic is the crystalline polymer, and we must consider the function degrading the crystal of polymer by unlocking. In this study, we perform the model simulation of the degradation of polymeric crystalline body by heat to analyze the degradation mechanism. We develop the precise analysis method to distinguish the crystalline and melt parts using machine learning, and using its tool we clarify the degradation process in detail.

・ Model study of degradation of multi-lock polymer ：Yoshie et al developed the dynamic bond elastomer having the functions of toughness in use and degradation in marine. In this study, we made the model of dynamic bond elastomer to clarify the functions of both toughness and degradation. In the near future, we will design its material having those functions in high level.

2. Model study of degradation process of polymer crystals

2.1 development of analysis method of local structure

Problems：

▪Too many candidates of order parameter

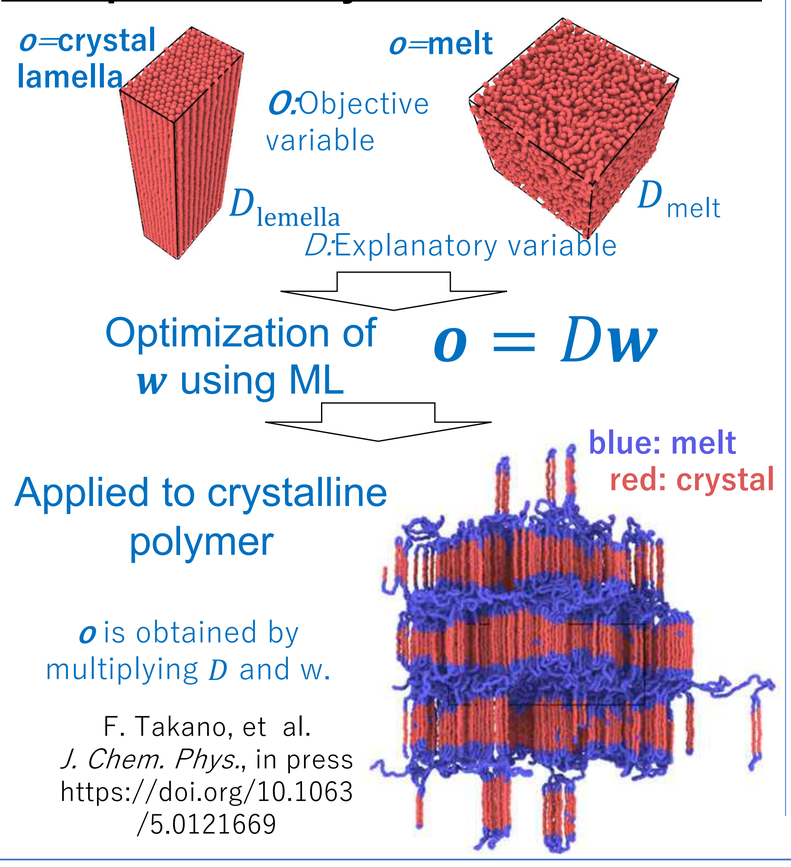
▪Arbitrariness to choose order parameter

⇒We develop the software to identify the local structure automatically using machine learning technique. Its name is Molecular Assembly structure Learning package for Identification of Order parameters (MALIO)

MALIO can identify local structures 40 times faster than the previous our software which is developed in another NEDO project.

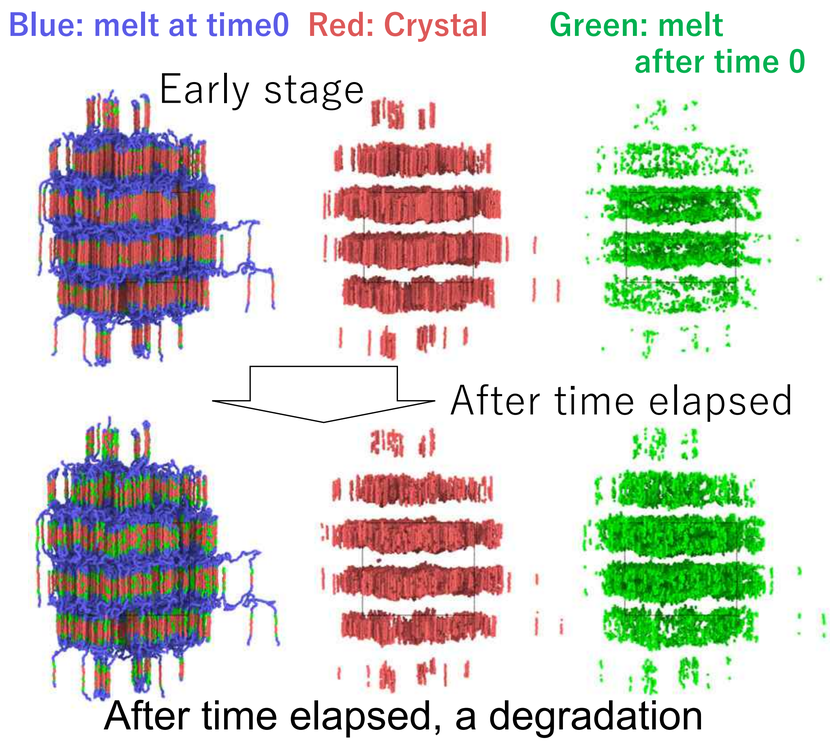
K. Z. Takahashi, Phys. Chem. Chem. Phys. (in press)
DOI: 10.1039/D2CP03696G

2.2 precise analysis of local structure



F. Takano, et al.
J. Chem. Phys., in press
https://doi.org/10.1063/5.0121669

2.3 Analysis of degradation process

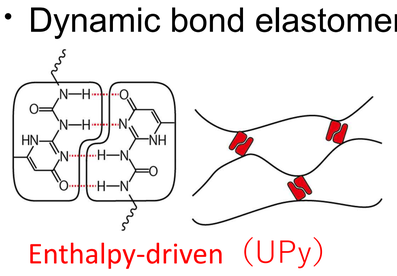


After time elapsed, a degradation proceeded not a simple but a complex mechanism in our interim reporting.

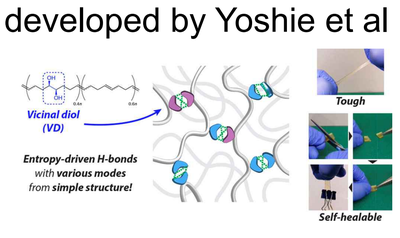
3. Model study of degradation of multi-lock polymer

3.1 Modeling of dynamic bond elastomer

・ Dynamic bond elastomer developed by Yoshie et al

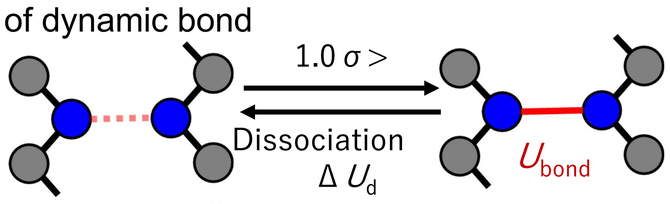


Enthalpy-driven（UPy）



Entropy-driven(vicinal diol)

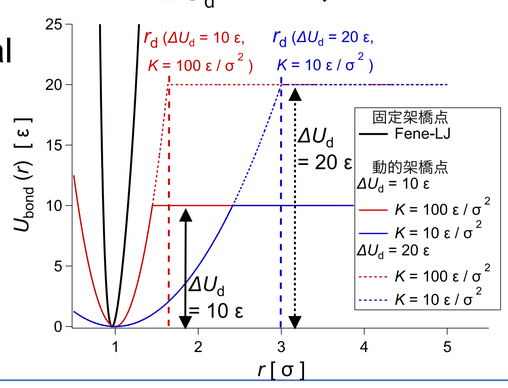
・ Model of dynamic bond



Controled potential

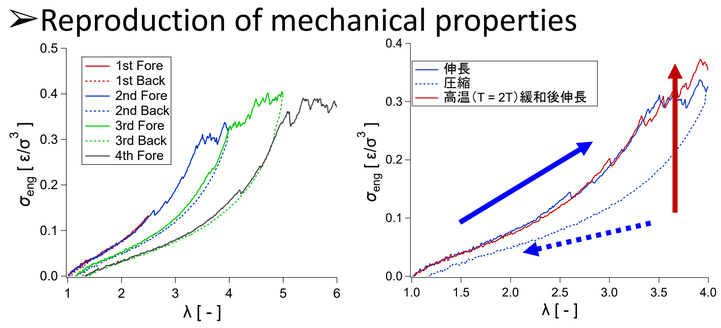
Enthalpy-driven

Entropy-driven



3.2 Reproducing experimental results

➢Reproduction of mechanical properties

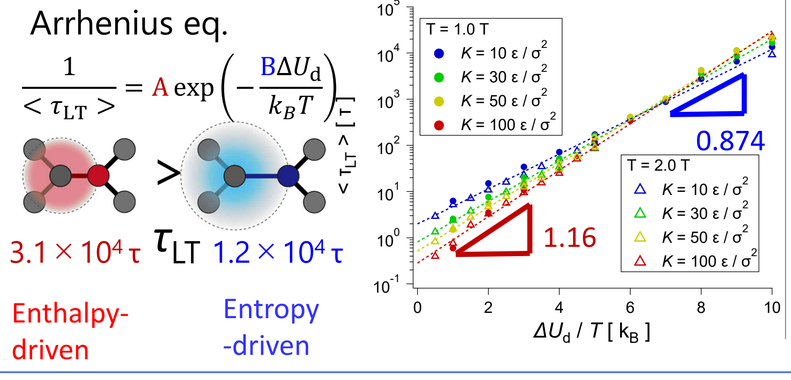


・We can realize the self-healing character using our model.

3.3 Analysis of lifetime of dynamic bond

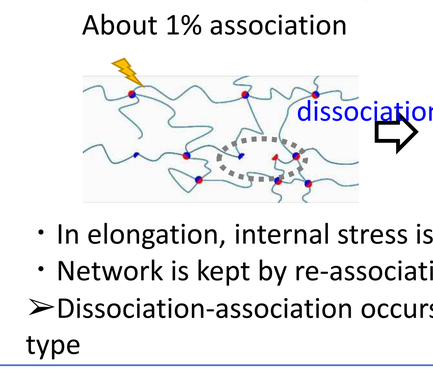
Arrhenius eq.

$$\frac{1}{<\tau_{LT}>} = A\exp\left(-\frac{B\Delta U_d}{k_B T}\right)$$



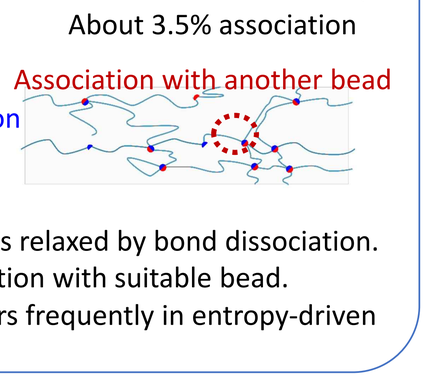
3.4 Dissocciation-association in each model

・Enthalpy-driven (Reactive beads 10％)

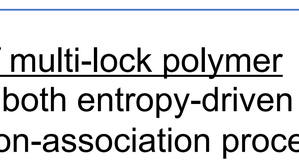


・about 2% dissociation、
About 1% association

・Entropy-driven (Reactive beads 20％)



・about 4% dissociation 、
About 3.5% association



・In elongation, internal stress is relaxed by bond dissociation.

・Network is kept by re-association with suitable bead.

➢Dissociation-association occurs frequently in entropy-driven type

4. Summary and Future work

Model study of degradation process of polymer crystals

・Development of MALIO which can be identify the local structure.

・Application study of MALIO to the problem of dynamic structure in degradation.

Future work

・MALIO is applied to the degradations of other polymers.

⇒We will consider proposal to accelerate degradations due to unlocking effect

Model study of degradation of multi-lock polymer

・Development of models for both entropy-driven and enthalpy-driven types.

・Detail analysis of dissociation-association process which cannot be observed in experiments.

Future work

・Development of updated model and design of suitable elastomer for marine degradation.

⇒Our simulation is applied to the collaborative study with company team.

No. A-11-12E

PJ: Development of Multi-lock Biopolymers Degradable in Ocean from Non-food Biomasses

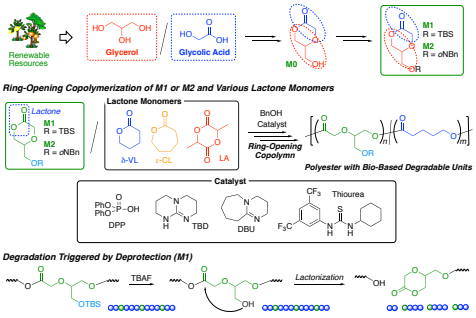
Theme: Development of Degradable Polymers Based on Plant-Derived Renewable Resources

Organization: Nagoya University, Graduate School of Engineering (E3-1)

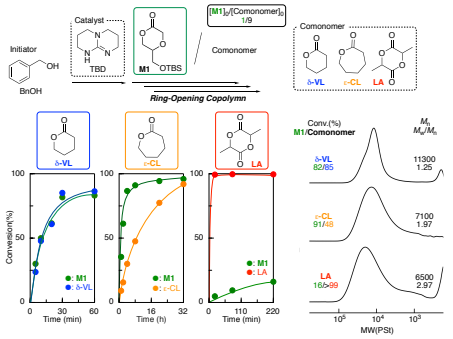
Contact: Masami KAMIGAITO kamigait@chembio.nagoya-u.ac.jp

Ring-Opening Polymerization of Novel Lactones with Protected Hydroxy Group Derived from Biomass and Deprotection-Induced Polymer Degradation

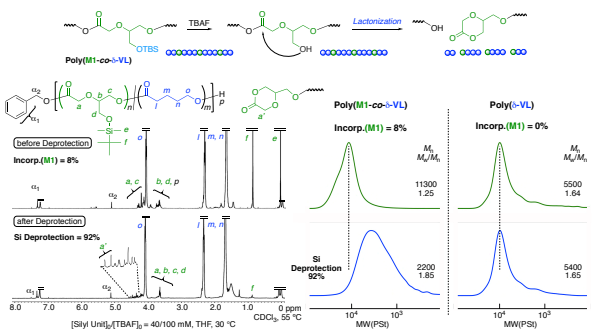
Introduction



Ring-Opening Copolymerization of Silyl-Protected Lactone

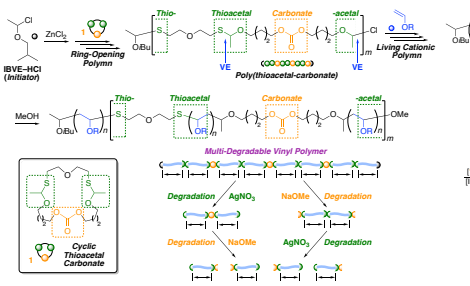


Deprotection-Induced Polymer Degradation

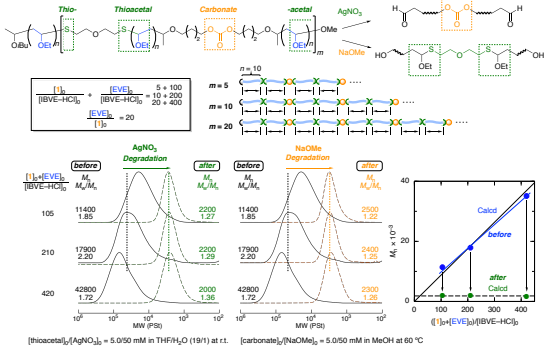


Synthesis of Multi-Degradable Vinyl Polymers by Living Cationic Polymerization of Cyclic Thioacetals with Cleavable Bonds

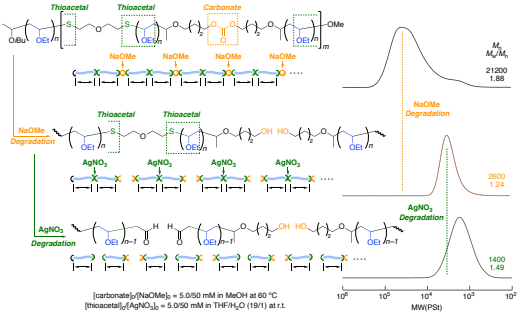
Introduction



Control of Molecular Weights before and after Degradation

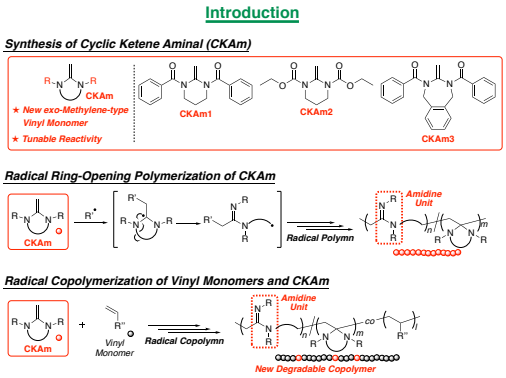


Multi-Degradation Based on Carbonate and Thioacetal Bonds

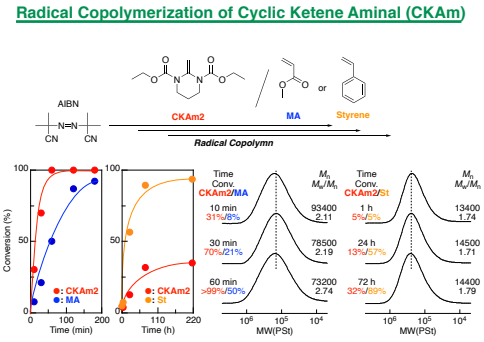


Synthesis and Radical Polymerization of Cyclic Ketene Aminals for Degradable Vinyl Polymers

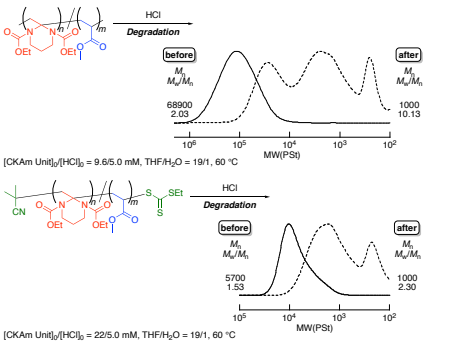
Introduction



Radical Copolymerization of Cyclic Ketene Aminal (CKAm)



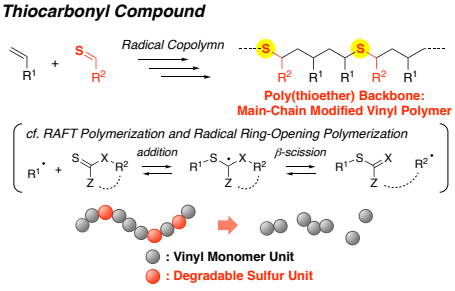
Degradation of Copolymers of Acrylate and CKAm



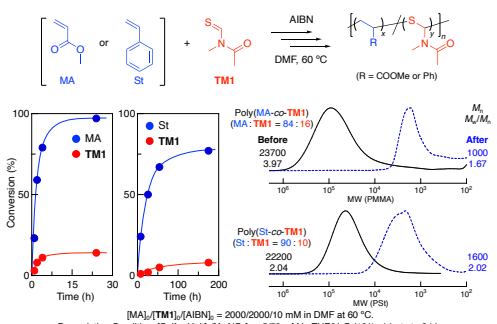
Direct Radical Polymerization of Thiocarbonyl Group for Degradable Vinyl Polymers

Introduction

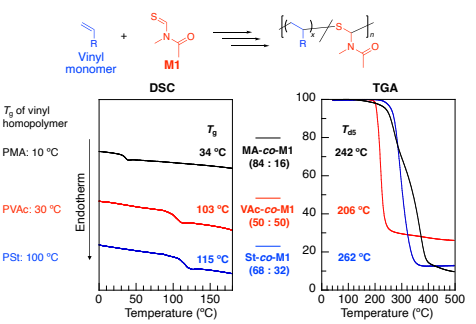
Direct Radical Copolymerization of Vinyl Monomer and Thiocarbonyl Compound



Radical Copolymerization of Thioamide and Vinyl Monomers



Thermal Properties of Vinyl Copolymers with Thioamide



No. A-11-13E

PJ: Development of Multi-lock Biopolymers Degradable in Ocean from Non-food Biomasses

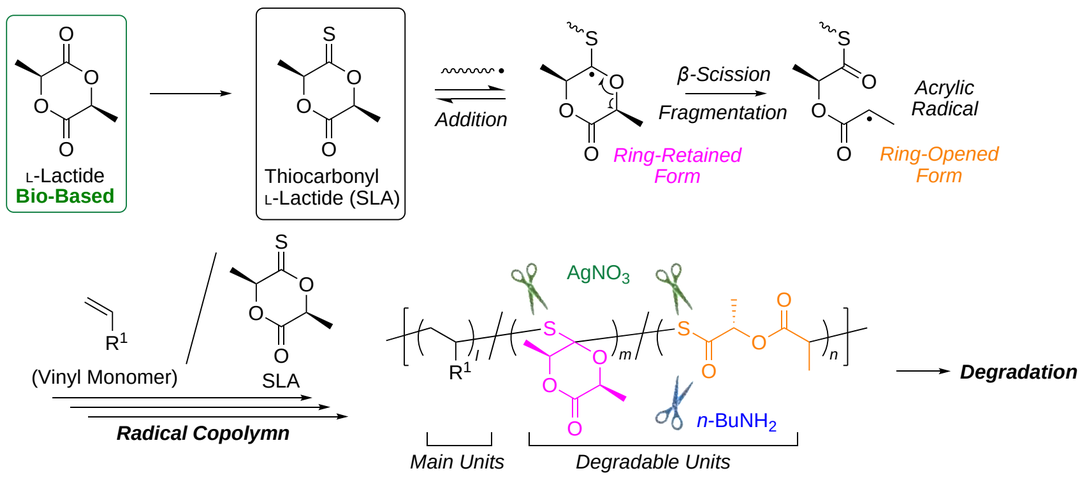
Theme: Precision Polymerization of Plant-Derived Monomers for Multi-Locked Degradable Biopolymers

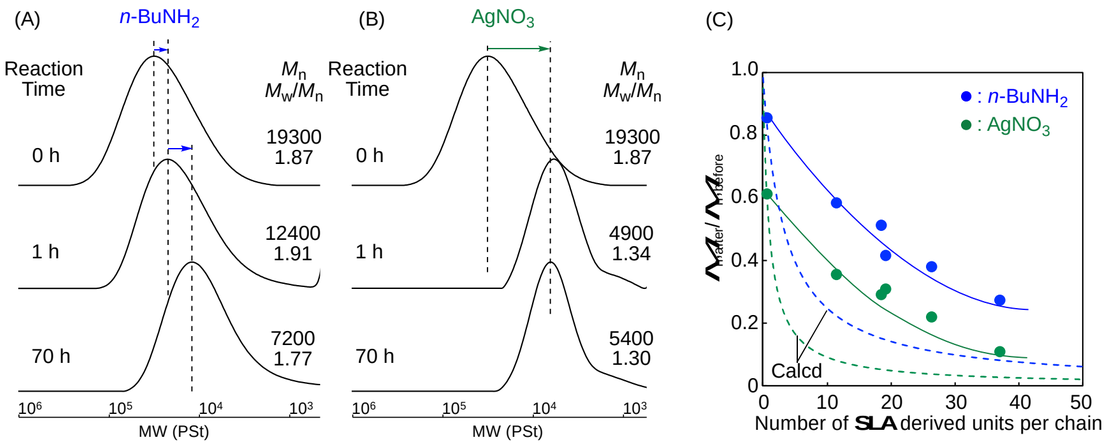
Organization: Tokyo Institute of Technology (E3-1)

Contact: Kotaro Satoh (satoh@cap.mac.titech.ac.jp)

For developing multi-locked degradable polymers from non-edible biomass, we will develop a multi-lock technology by utilizing the technology of precision polymerization, which we had cultivated in the petroleum chemicals, to biomass-based and multi-locked degradable polymers. By the polymerization of non-edible biomass as a raw material, we propose the concept of a manufacturing method for multi-lock biopolymers that can be degraded in the ocean collaborating with industry.

Addition–Fragmentation Ring-Opening Polymerization of Bio-Based Thiocarbonyl L-Lactide for Dual Degradable Vinyl Copolymers

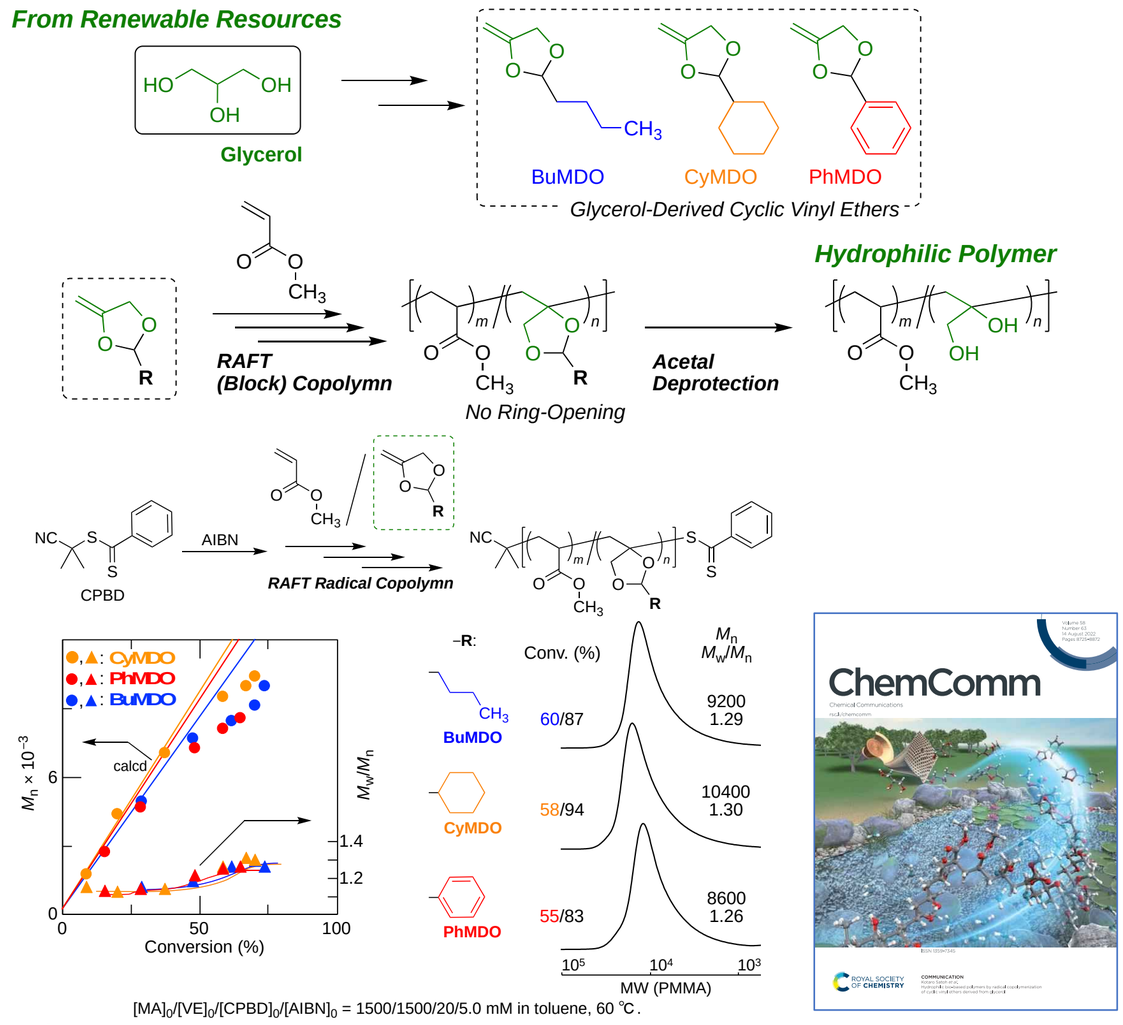




Japanese Patent Application 2021-131293

Macromol. Rapid. Commun. **2022**, *in press*.

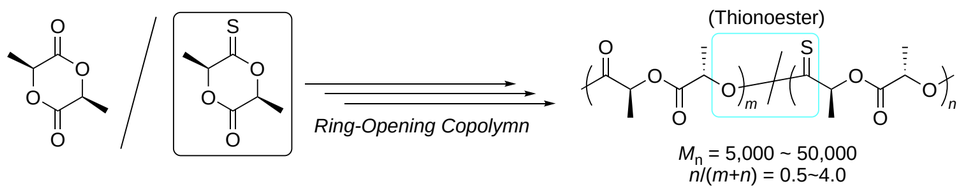
Hydrophilic Bio-Based Polymers by Radical Copolymerization of Cyclic Vinyl Ethers Derived from Glycerol

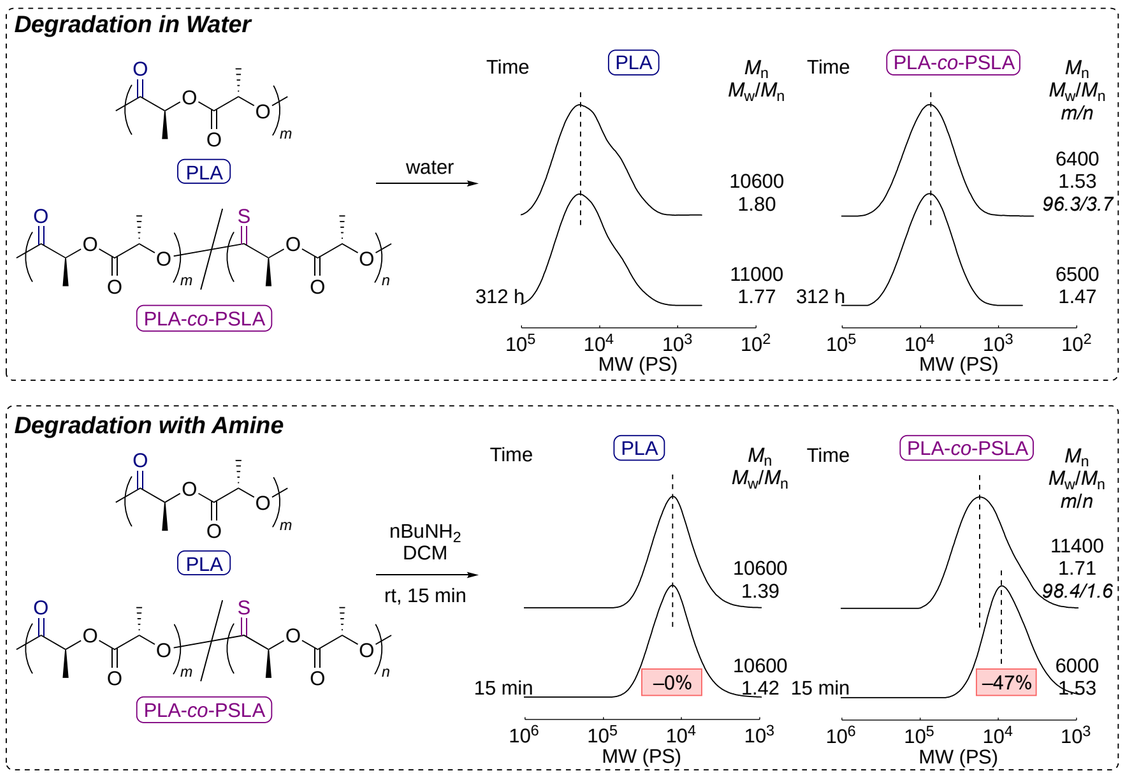


[MA]$_0$/[VE]$_0$/[CPBD]$_0$/[AIBN]$_0$ = 1500/1500/20/5.0 mM in toluene, 60 ℃.

Chem. Commun. **2022**, *58*, 8766.

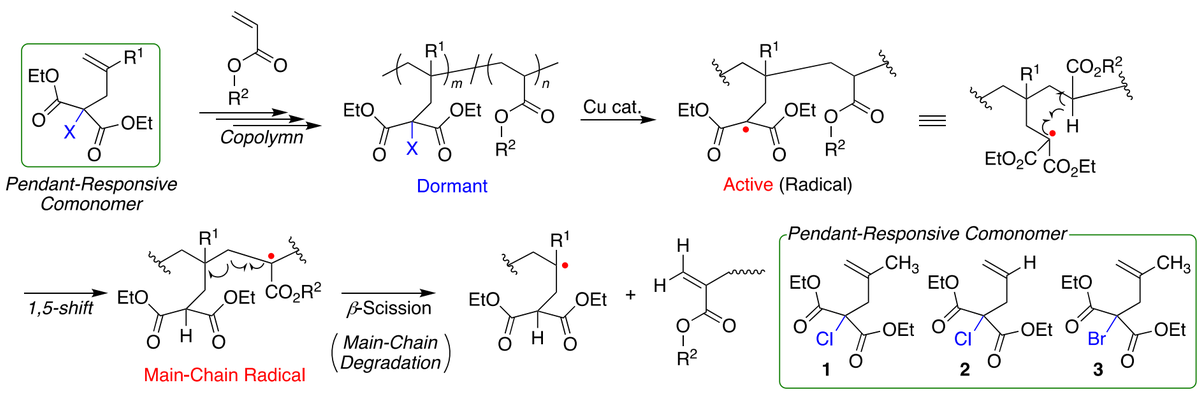
Improved Degradability of Poly(Lactic Acid) by Introducing Thionoester Linkages via Ring-Opening Copolymerization

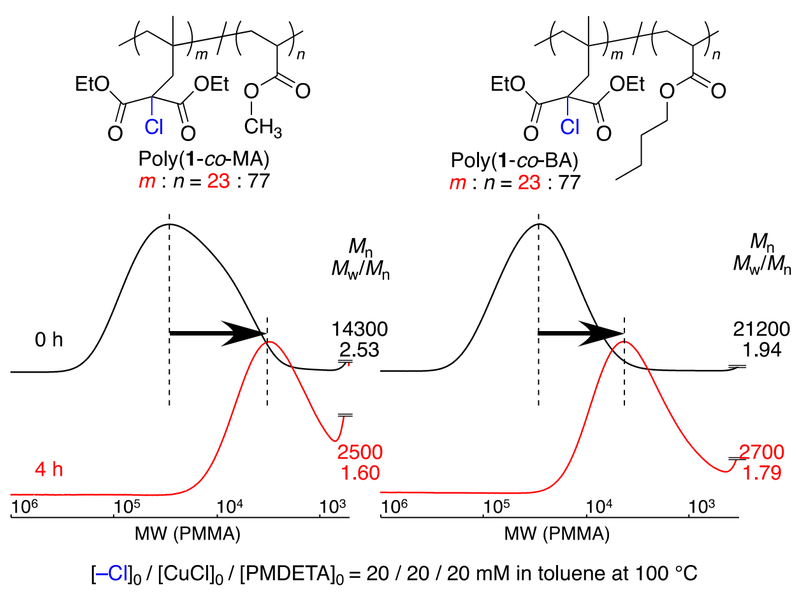




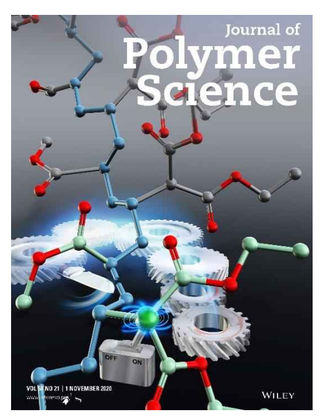
Japanese Patent Application 2021-131293

Interlocking Degradation of Vinyl Polymers via Main-Chain C–C bonds Scission by Introducing Pendant-Responsive Comonomers





[–Cl]$_0$ / [CuCl]$_0$ / [PMDETA]$_0$ = 20 / 20 / 20 mM in toluene at 100 °C



J. Polym. Sci. **2022**, *in press*.