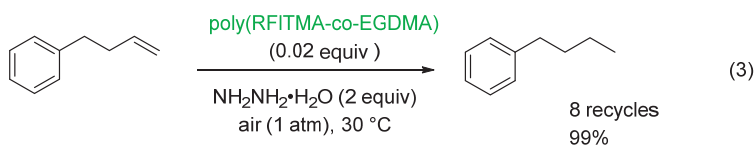
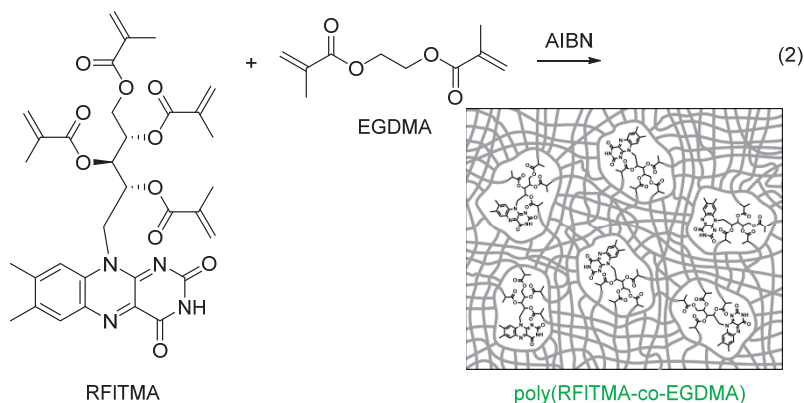


*Org. Lett.* **2010**, *12*, 32; *Chem. Eur. J.* **2011**, *17*, 5908;  
JP 5076103 (B2) (20120907)



### Content:

Organocatalysts have recently received considerable attention as a third group of catalyst in organic synthesis in addition to the conventional biocatalysts and metal catalysts. To meet the social demand to effectively and safely produce pharmaceuticals and functional materials on a large scale, it is highly desirable to design and develop organocatalysts with superior characteristics, including enhanced catalytic activities, handling ease, and stereochemical controllability.

We have been developed environmentally friendly aerobic molecular transformations using simple flavin molecules as organocatalysts. For example, olefins can be readily hydrogenated upon treatment with hydrazine hydrate and air in the presence of a catalytic amount of flavin molecules (Eq. 1). The reaction provides a highly environmentally benign and practical method for hydrogenation of olefins without using hydrogen gas and transition-metal catalysts.

To enhance the practicability of the flavin catalyst, we design and develop novel flavin-bound network polymer catalysts. Typically, poly(RFITMA-co-EGDMA), prepared by the radical copolymerization of riboflavin tetramethacrylate with ethylene dimethacrylate (Eq. 2), can be used as a robust and recyclable catalyst (Eq. 3).

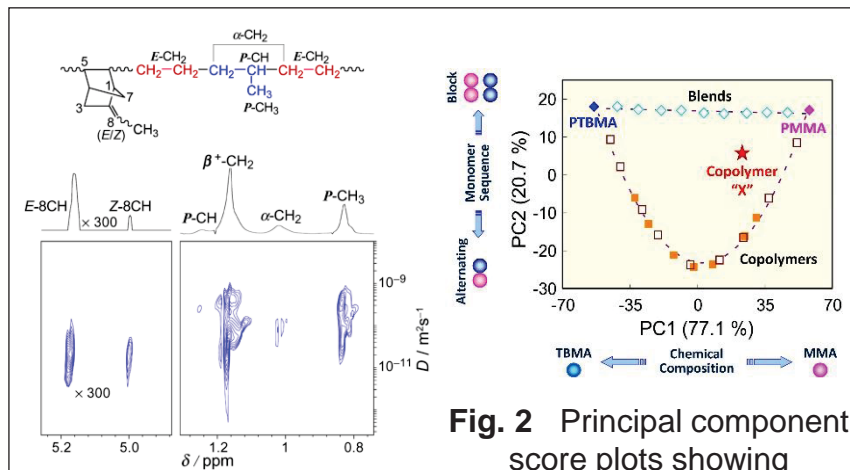
Keywords: organocatalyst, aerobic oxidation, polymer-supported catalyst

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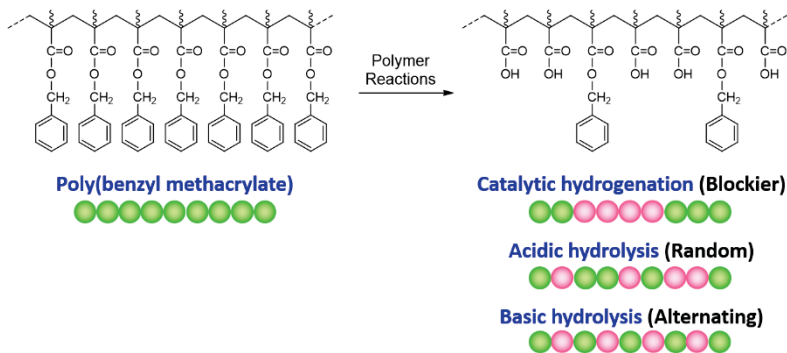
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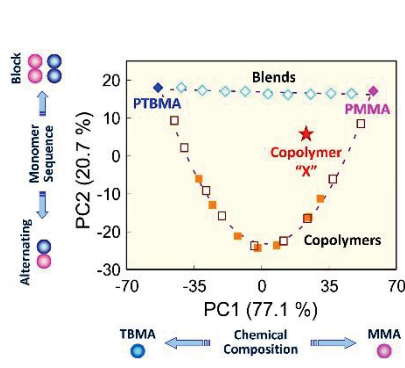


**Fig. 1** Molecular weight dependence of chemical composition in an ethylene-propylene copolymer.



**Fig. 3** Monomer sequence distributions in methacrylate copolymers prepared by polymer reactions.

**Fig. 2** Principal component score plots showing chemical composition and monomer sequence distribution in methacrylate copolymers.



## Content:

Recent research and development of industrial or functional polymers increasingly require precise analysis and control of their molecular parameters (molecular weight, comonomer sequence, stereoregularity, etc.).

The aims of my study are to develop useful methods of polymer characterization by modern NMR (nuclear magnetic resonance) and chromatographic techniques, and to **synthesize new polymer materials on the basis of the characterization.**

For example, DOSY (diffusion-ordered NMR spectroscopy) is a powerful technique to measure the molecular-weight dependence of chemical composition in copolymers (**Fig. 1**).

Multivariate analysis of the NMR spectra of copolymers is another example of my approaches to precise and quantitative characterization of synthetic polymers (**Fig. 2**). The use of this multivariate approach revealed the mechanism of polymer reactions (catalytic hydrogenation, acidic/basic hydrolysis, etc.) of methacrylate copolymers (**Fig. 2**).

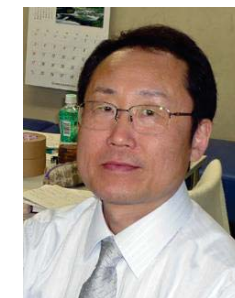
Keywords: polymer synthesis, NMR, chromatography, copolymers

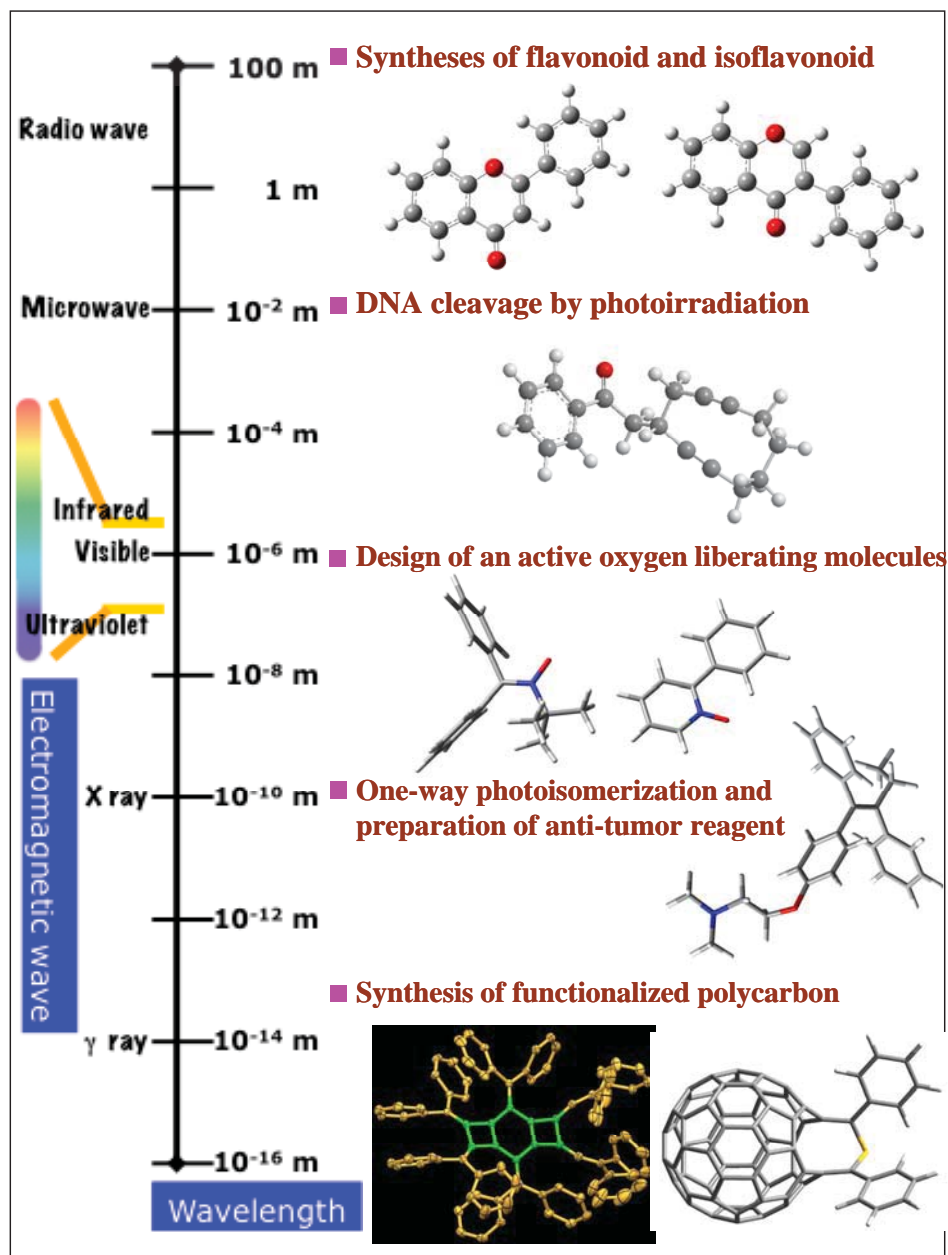
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## Content:

This research aims to develop new uses for electromagnetic waves like ultraviolet, visible light, and microwave. Light can be used in various forms, including ultraviolet light sources, white light sources similar to sunlight, or (ultraviolet) laser light sources and (ultraviolet) pulse laser light sources. By using the light energy, which possesses unique characteristics and called as “designer light” in organic synthesis and functional materials synthesis, environmentally-friendly production processes for intelligent materials with diverse functions and properties are developed.

LEDs are key technology of Tokushima Prefecture and currently, leading uses for LED light include illumination, decoration, display, and communication. Further application development is underway. LED light is a green and highly-efficient energy source, and this research also aims towards controlled use of LED light as an energy source that will produce useful compounds and functional materials. This research would enable the traditionally difficult chemical transformations and synthesis of functionalized materials to make easier just by exposing molecules to electromagnetic. Light (photons) is recognized to be “a reagent with no volume”. Also in line with the product study, by examining reaction intermediates produced during the chemical reactions upon irradiation of light and microwave, useful and competent chemical transformation processes will be created rationally.

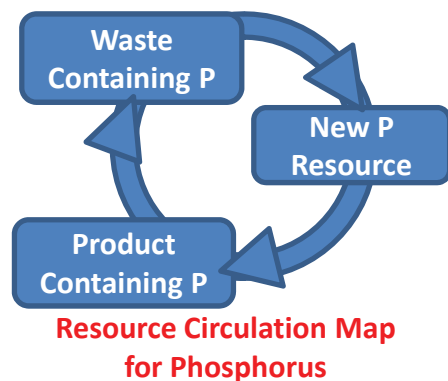
Keywords : photochemical reactions, reaction intermediate, functionalized molecule

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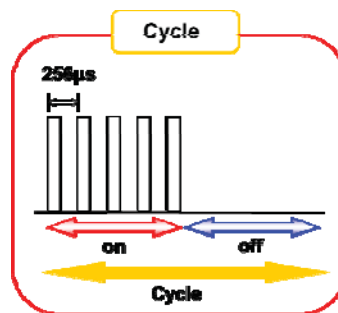
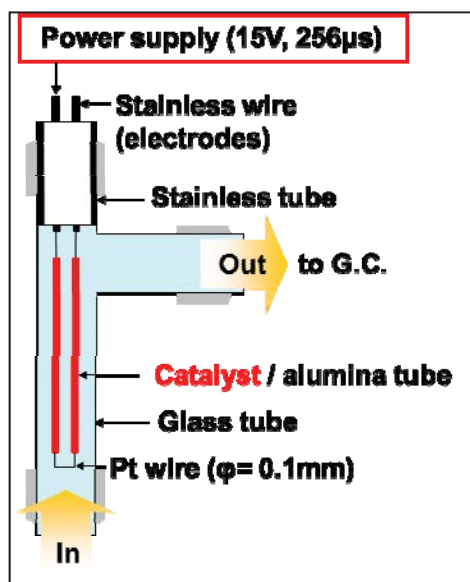
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(a) Circulation of phosphorus resource



(b) Microreactor for catalytic gas-phase reaction and concept of heater output.

Off: Adsorption.

On: Reaction and desorption.

## Content:

Phosphorus is an essential element for plant growth and has no substitute in food production. In the chemical industry, it is used in various advanced materials. Phosphate rock as a raw material of phosphorus is a finite, non-renewable. Therefore, the development of new raw materials containing phosphorus is an urgent issue in Japan. In our group, search of new resource containing phosphorus together with the development of the easy and economical recovery method of phosphorus from the resource is in progress.

As another topics in our group, the possibility of the combination of solid catalyst, reactor and reaction field is examined. For example, the combination of microreactor for gas-phase reaction and calcium hydroxyapatite catalyst resulted in the greatest selectivity, never reported, to the desired product in the oxidative dehydrogenation of propane to propylene. Not only catalyst improvements but also the development of the reactor and reaction field are our main target for the development of catalyst process.

Keywords: phosphorus resource,  
solid catalysts, reaction field

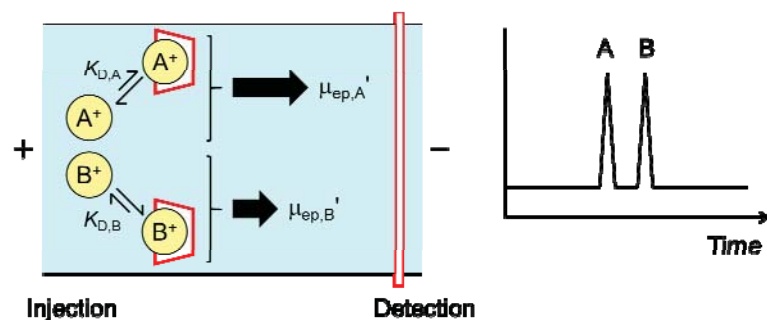
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(a) Molecular recognition with affinity (b) Chromatogram  
Fig. 1 Separation improvement by affinity interaction

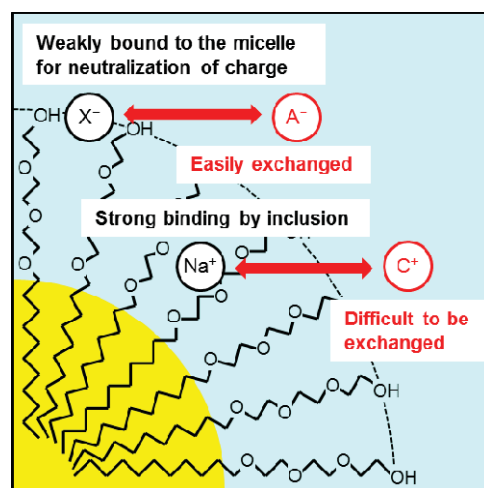


Fig. 2 Partition selectivity of ionic species toward nonionic surfactant micelle

## Content:

Nano-sized molecular assemblies of surfactant micelles, vesicles, microemulsions, and polymer gels possess hydrophobic environment. Specific surface area of the molecular assemblies is greatly larger than that of bulk water-organic solvent interface. Extraction-separation with the characteristic hydrophobic environment of the molecular assemblies works in pseudo-homogeneous aqueous solution. Liquid-liquid extraction is done in the pseudo-homogeneous aqueous solution without mechanical shaking of the two phases, with fast extraction kinetics, as well as with the selectivity towards ionic substances. Functional Molecular Assembly including micelles, microemulsions, and hydrophobic matrices are to be developed.

Based on equilibria and kinetics in aqueous solution, development of affinity reagents, analysis of affinity interactions, and investigation of selectivity expression factors are studied.

Keywords: Surfactant micelle, microemulsion, hydrophobic partition, aquatic solvent, analytical separation

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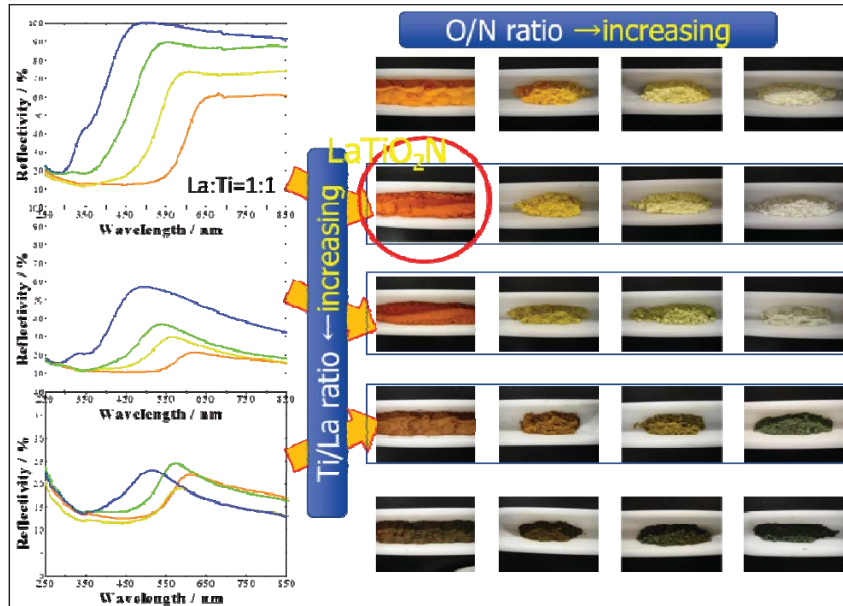


Fig. 1 Color tuning in LaTiO<sub>2</sub>N via control of anion and cation stoichiometries.

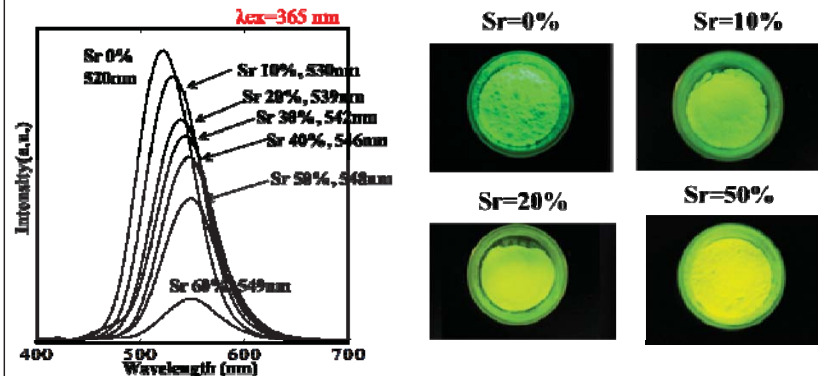


Fig. 2 Redshift of emission for Ba<sub>3</sub>Si<sub>6</sub>O<sub>12</sub>N<sub>2</sub>:Eu-type phosphors by substitution of Ba by Sr.

## Content:

We have demonstrated that a color of the perovskite-type LaTiO<sub>2</sub>N oxynitride could be tuned from orange through yellow and green to pale gray or white by proper adjustment of the O/N ratio. (Moriga et al., *phys. stat. sol. (a)*, **203**, 2818 (2006)), whereas increasing Ti/La ratio deteriorates the reflectivity after the absorption edge (Moriga et al., *J. Ceram. Soc. Jpn.*, **115**, 637 (2007)). We are now trying to make a redder or bluer oxynitride powders by partial substitution of the constituent cations, and by controlling of the cation and/or anion stoichiometries as well.

Oxynitride phosphors are recently spotlighted as yellow or red phosphors for white LEDs because oxynitrides have no toxicity, blue light are available for excitation source and oxynitrides possess low thermal quenching behavior, compared with oxide phosphors. We have found that Ba<sub>3</sub>Si<sub>6</sub>O<sub>12</sub>N<sub>2</sub>:Eu-type phosphors showed considerable redshift in emission wavelengths from 520nm for the Sr-free oxynitride up to 550nm for 50%-substituted oxynitride by Sr, with increasing Sr content.

Keywords: Perovskite oxynitrides, oxynitride phosphors,

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Fig. 1 Volumetric apparatus for measurement of adsorption & desorption velocity of water on adsorbents..

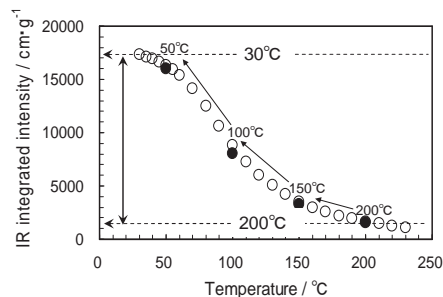


Fig. 2 Temperature dependence of IR integrated intensity of adsorbed H<sub>2</sub>O at 10 Torr on NaY zeolite, O: 1st, ●: 2nd.



Fig. 3 special IR cell.

### Content:

The utilization of waste heat for the regeneration of desiccant material in a desiccant dehumidifier system is one of the best alternatives because regeneration cost is eliminated. However, it is only suitable for equipment which can exhaust waste heat at temperature 60 °C and 140 °C. Usually, these types of equipment are only available in factories or supermarkets.

We develop estimation method of water adsorbents (desiccant materials) and propose two kinds of estimation methods for water adsorption.

- (1) Estimation of adsorption and desorption velocity of water on adsorbents by volumetric apparatus (Fig. 1).
- (2) Estimation of temperature behavior of adsorbed water on adsorbents by IR spectroscopy.

In particular, temperature dependence (Fig. 2) of adsorbed water on desiccant can be gotten easily by using special IR cell (Fig. 3). The profile was corresponding to the equilibrium adsorption data.

Keywords: water adsorbent, adsorption velocity,  
IR spectroscopy

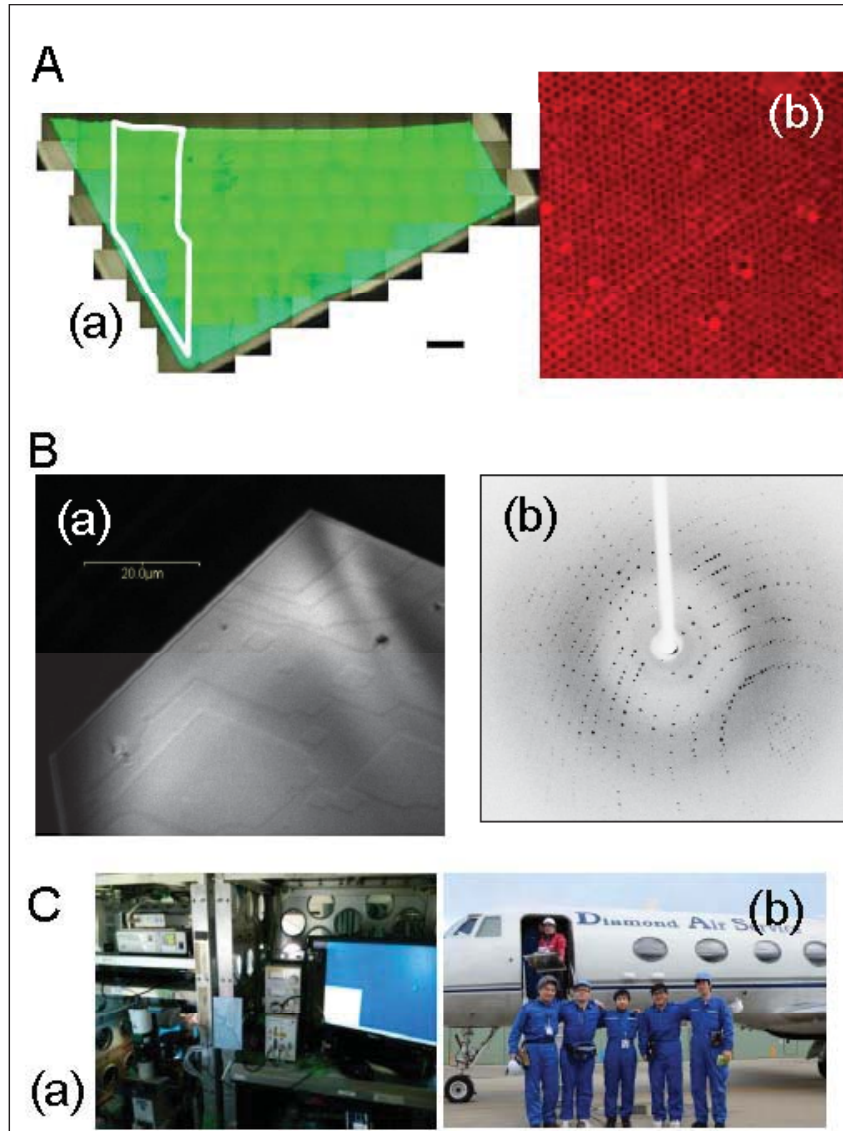
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Content:

- A. Colloidal crystallization under external fields:** Colloidal crystals are promising materials for optical circuits and optical computer in the future. We have successfully fabricated bulky grains ( $\sim 6.1 \text{ mm}^3$ ) of a close-packed polystyrene colloidal crystal ((a)) by centrifugation. We have also succeeded in controlling nucleation of the crystals using an optical trapping method (b).
- B. In situ observation of molecular steps on protein crystal surfaces and novel crystallization techniques without any precipitants:** Fundamental studies and developments of novel techniques of protein crystallization are important for obtaining high quality crystals, which are prerequisites of genomic drug discovery. We are now studying kinetic behaviors of molecular steps on the surface of a glucose isomerase crystal ((a)). We have also succeeded in fabricating high quality lysozyme crystals without using any precipitants ((b)) for the first time.
- C. Precise growth mechanisms of protein crystals under microgravity:** Microgravity is known to be a good environment for obtaining high quality protein crystals. Now we are preparing for near future space experiments using parabolic flight opportunities ((a) and (b)).

Keywords: Crystal Growth, Protein, Colloid, Microgravity

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# Development of Surface-Functionalized Nanosheets Catalysts

## Associate Professor Keizo Nakagawa

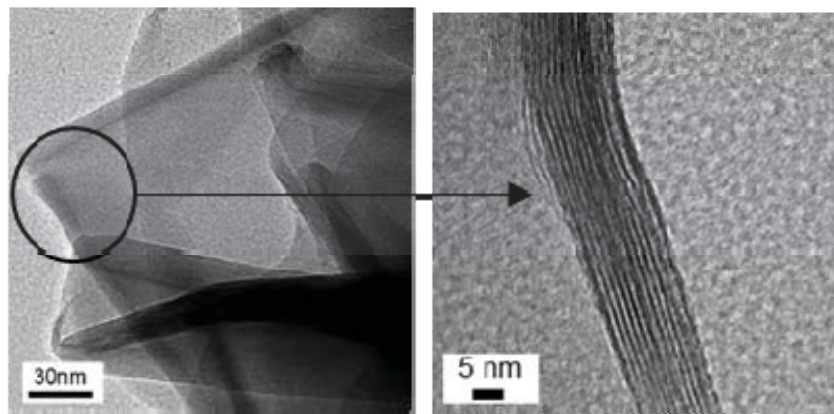


Fig.1 TEM images of layered nanosheets

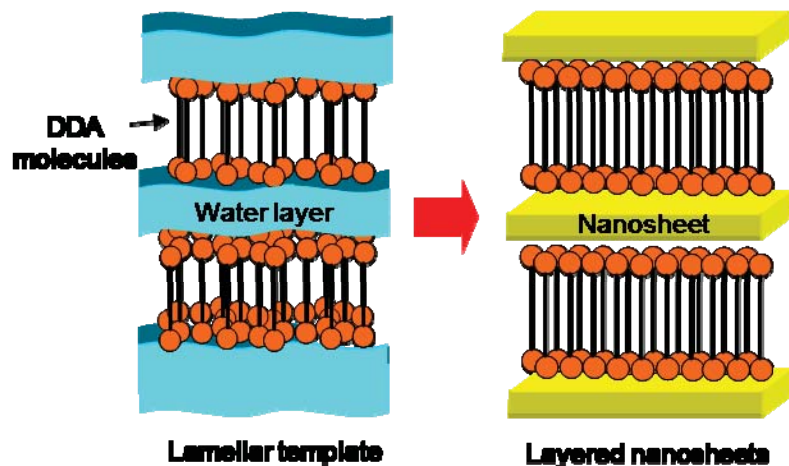


Fig.2 Schematic illustrations of the formation process of Nanosheets using lamellar self-assembly as a template

### Content:

Two dimensional metal oxide nanosheets have attracted much attention as a new class of nanoscale materials because of their unique physical and chemical properties. Therefore, applications that use nanosheets as various kind of catalysts such as photocatalysts and solid acid catalysts have been reported.

However, a conventional method requires prolonged continuous processes such as calcination for the synthesis of layered compounds at high temperature and successive acid treatment.

In our method, layered nanosheets forms by using the lamellar self-assembly of surfactant as a template. This method is effective for the mass production of metal oxide nanosheets. This approach leads to titanate nanosheets with new properties such as visible light absorption and a high adsorption of cationic organic compounds, which results in the effective photodegradation of organic dye under visible-light irradiation. This approach has important implications for the use of metal oxide nanosheets in environmental and industrial applications.

Keywords: nanostructure, surfactant, layered compound, photocatalysts

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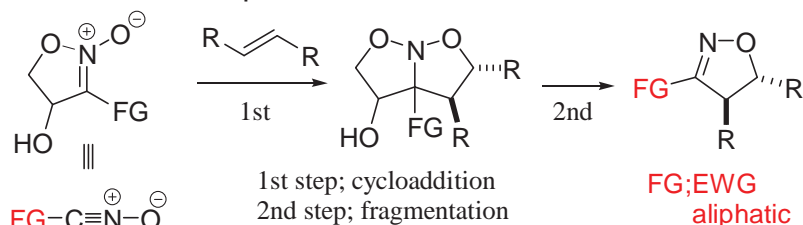
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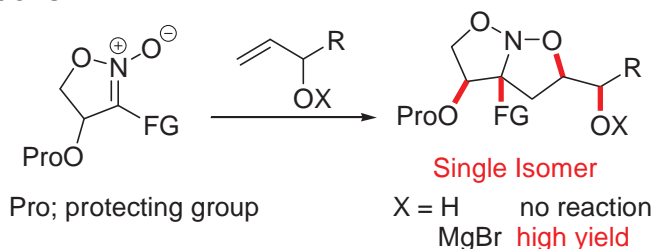
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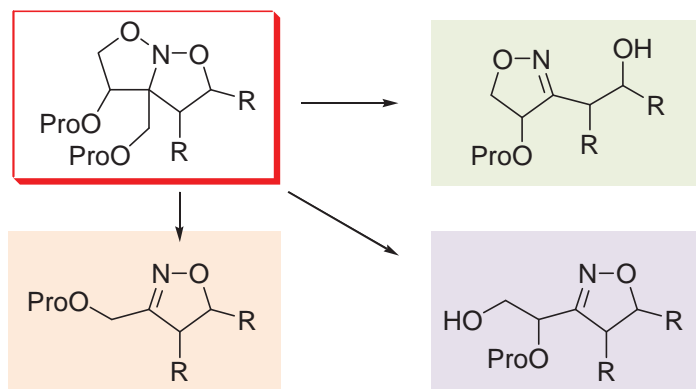
### $\alpha$ -Hydroxy Cyclic Nitronates as a Synthetic Equivalent of Functionalized Aliphatic Nitrile Oxides



### Stereoselective Cycloadditions and Activation of the Reactions



### Regioselective Fragmentation to give 3-Functionalized 2-Isioxazolines from Bicyclic Isoxazolidines



### Content:

Heterocycles are important compound group included in core structure of many biologically active substances, organic functional materials and as intermediates masked synthetically important functionalities.

Cycloaddition reactions of nitrile oxides with alkenes produce 2-isoxazolines as cycloadducts in which a variety of synthetically important functionalities are masked such as  $\beta$ -hydroxy ketones, 1,3-diols,  $\gamma$ -amino alcohols, and others. Although 2-isoxazolines have been often utilized in synthetic works of complex molecules, synthesis of 3-substituted 2-isoxazolines still remains difficult due to the limited availability of functionalized or aliphatic nitrile oxides as starting materials.

We have found that  $\alpha$ -hydroxy cyclic nitronates act as synthetic equivalents of nitrile oxides. The reactions of **3-substituted** 4-hydroxy-2-isoxazoline-*N*-oxides with a variety of alkenes; the resulting perhydroisoxazolo[2,3-*b*]isoxazoles as cycloadducts are then regioselectively transformed under the acidic conditions to give 2-isoxazolines through elimination of hydroxylacetaldehyde.

Keywords : Organic Chemistry, Synthesis of Heterocycles, 1,3-Dipolar Cycloaddition, Asymmetric Synthesis

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Temperature response:  
Reversible physical gelation of a polymer solution

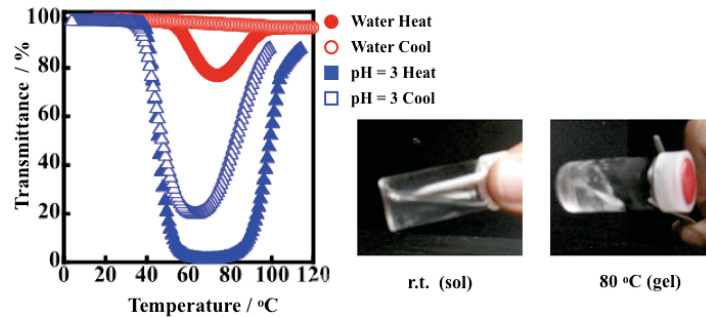
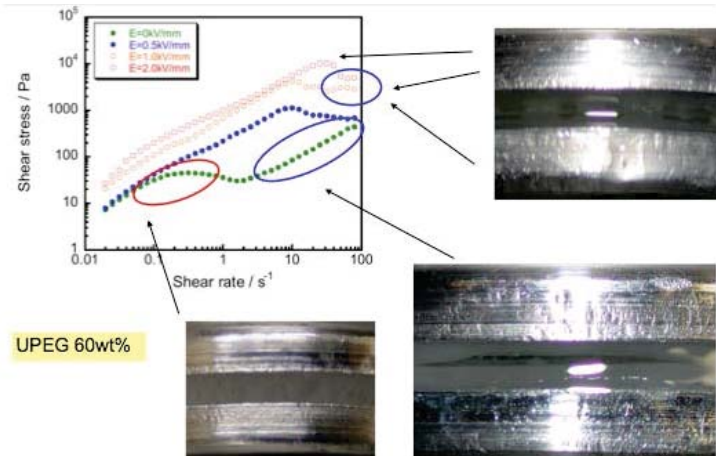


Fig. Temperature-transmittance curves of 0.5 wt% of P(NnPAM125-co-AA75) solution, without Na<sub>2</sub>SO<sub>4</sub> (1 °C/min)

Electric-field response:  
Viscoelasticity change of an immiscible ER fluid



Content:

### 1. Thermoresponsive polymers

Various substituted vinyl polymers showing a temperature-sensitive soluble-insoluble transition in water have been prepared. These polymers have unique characteristics such as extraordinary large hysteresis in the temperature-induced phase transition. Copolymers based on these polymers can further modify the interesting properties, e.g., double-responsibility to temperature and pH, physical gelation, and controllable hysteresis.

### 2. Electrorheological fluids (ER fluids)

Suspensions and immiscible liquid blends, which show a reversible change in rheological property under an electric field, have been prepared. These fluids are called electrorheological fluids (ER fluids). Various polymers and inorganic compounds can be used as the materials of ER fluids. The controllable rheological properties by an electric field are expected to be useful for design of smart devices.

Keywords : thermosensitive polymer, ER fluid, rheology

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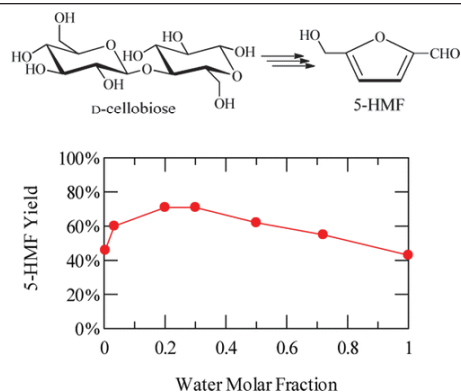


Fig. 1. 5-HMF yield in the cellobiose decomposition in DMSO/water mixture solvent.

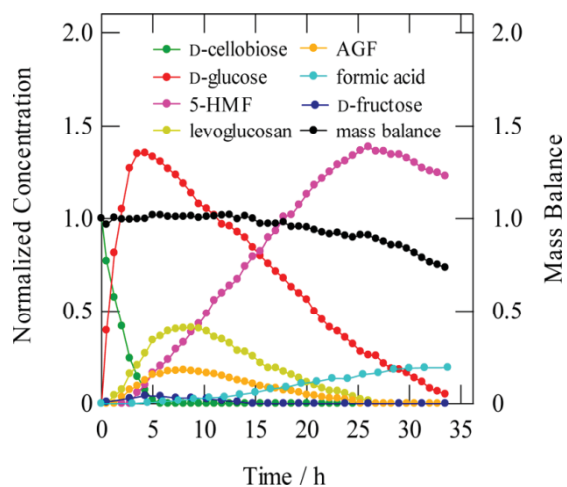


Fig. 2. Time course of the reactant and product of the decomposition of cellobiose determined by using  $^{13}\text{C}$  in situ NMR monitoring.

## Content:

Biomass-derived poly-saccharides have attracted attentions as the novel renewable sources. Recently we succeeded in the production of 5-hydroxymethyl-2-furaldehyde (5-HMF) from cellobiose, the model disaccharide for cellulose (H. Kimura et al., *J. Phys. Chem. A*, 117, 10987 (2013); Fig. 1). 5-HMF is a center of focus today as a biomass-derived valuable that can be converted into biofuels, fine chemicals, and polymers.

In the decomposition reaction steps of saccharides, a variety of isomers, tautomers, and precursors are generated as intermediate products. Solution NMR spectroscopy is a powerful method to monitor all of those species involved in the reactions. By using  $^{13}\text{C}$  NMR, each of the individual species can be distinguished from each other. The positions of the glucose units in the oligomers can be specified. The in situ NMR method allows us to determine the time course of the product and reactant species. As shown in Fig. 2, reliable data are obtained with a single setup of the in-situ experiment. The best conditions for the target species can be determined on the basis of the reaction kinetics.

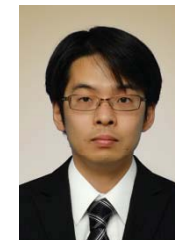
Keywords: saccharides, in situ NMR, 5-HMF

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# Aerobic Oxidations in Flow with Immobilized Flavin Organocatalysts

Assistant Professor Yukihiro Arakawa

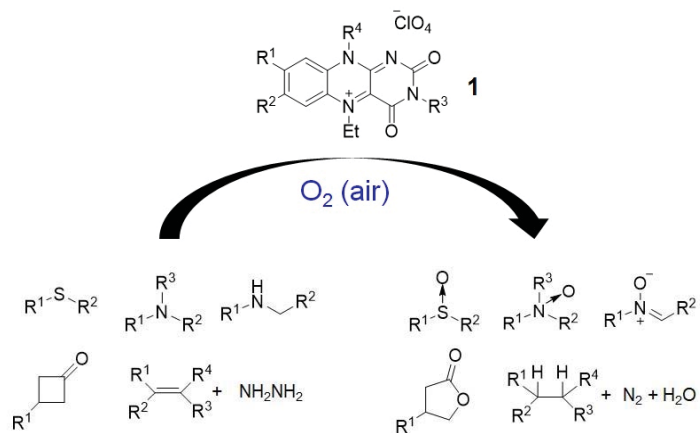
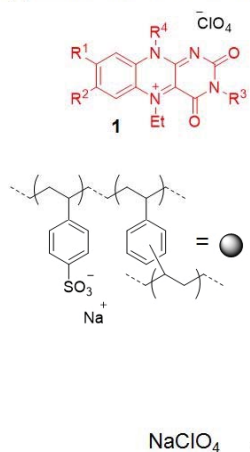


Fig. 1

(a) Immobilization of cationic flavins



(b) Aerobic oxidations in flow

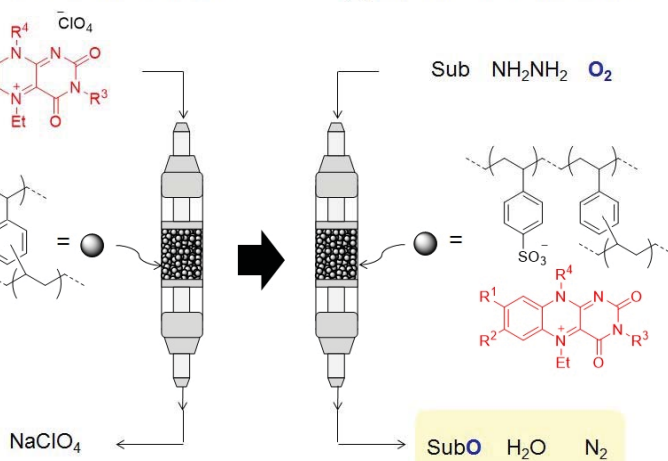


Fig. 2

## Content:

Organocatalysts have become valuable tools for synthetic chemistry over the last 15 years, but their industrial application has so far been limited nevertheless. One of the major issues is arguably the difficulty of catalyst separation, recovery and reuse. Immobilizing organocatalysts onto an insoluble support such as a crosslinked polymer is therefore highly emphasized since it allows in principle for facile catalyst recycling as well as the development of a continuous flow system.

This writer previously reported an immobilization method of quaternary ammonium salts onto sulfonated polymer supports for an asymmetric reaction (*Angew. Chem. Int. Ed.* **2008**, *47*, 8232). On one hand, the research group this writer currently belongs to has pioneered aerobic oxidation reactions with cationic flavin organocatalysts **1** (Fig.1). This knowledge prompted us to investigate whether the versatility of the cationic flavin catalysts can be further improved by immobilization on a sulfonated anionic polymer. The development of practical aerobic oxidation reactions in continuous flow with immobilized flavins is currently ongoing in our laboratory (Fig. 2).

Keywords: organocatalyst, aerobic oxidation, immobilized catalyst, flow system

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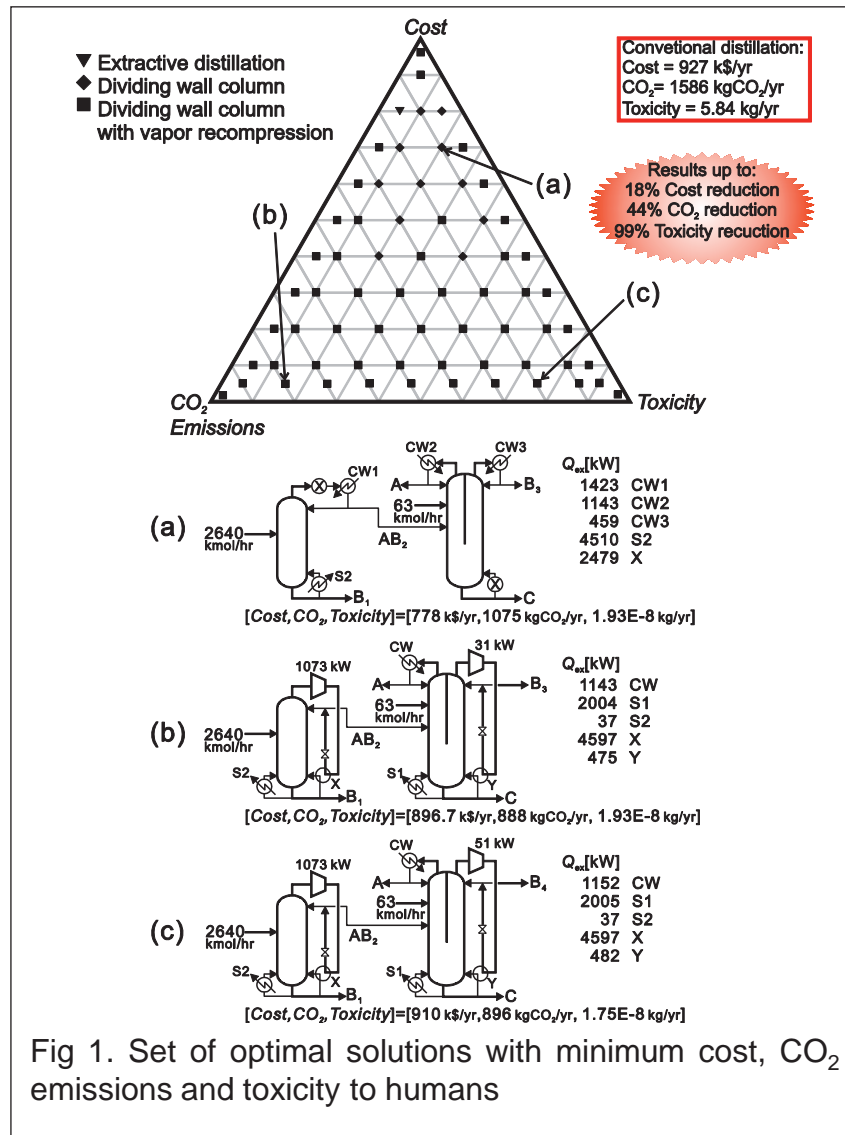


Fig 1. Set of optimal solutions with minimum cost, CO<sub>2</sub> emissions and toxicity to humans

## Content:

Distillation is widely used in the Chemical and Petrochemical Industry to separate liquid mixtures, however, it inherently entails high energy consumption.

Process intensification by means of heat integration and energy reuse are being researched by our group to find sustainable and reliable distillation systems with low energy consumption, CO<sub>2</sub> emissions, environmental impact, and cost. These criteria oppose each other in most cases, therefore, we propose multi-objective optimization procedures to find the set of optimal solutions to assess the trade-off between conflicting criteria.

Fig. 1 shows a set of Pareto-optimal solutions with low cost, CO<sub>2</sub> emissions, and toxicity to humans when glycerin, which is an environmental friendly solvent, is used to obtain fuel grade ethanol in a bioethanol plant. In the figure, CW means cooling water, S1 and S2 mean steam at different pressure, X and Y mean heat integration. The results show that heat integration and vapor recompression are appealing alternatives.

Keywords : Optimization, Process Intensification, Multi-objective Optimization, Multivariate Control

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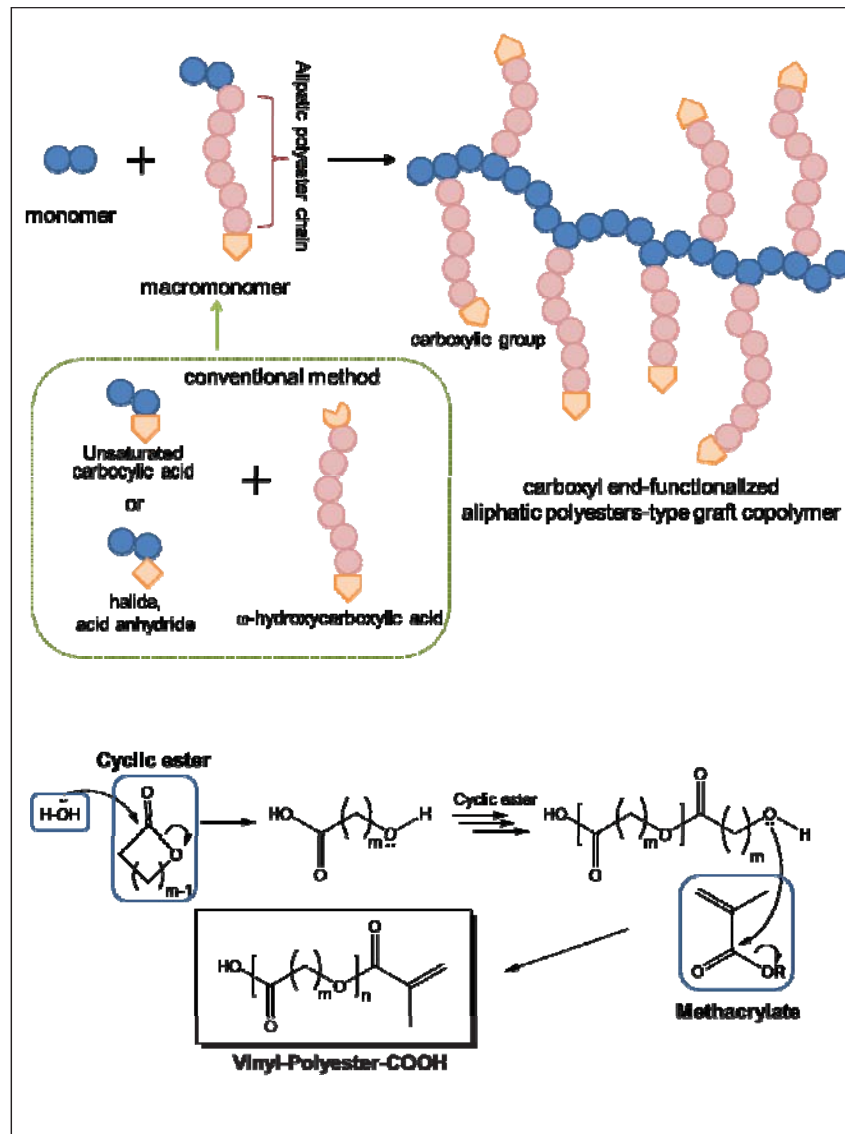
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# Synthesis of Carboxyl End-functionalized Aliphatic Polyesters

Assistant Professor Miyuki Oshimura



## Content:

Graft copolymers are prepared by monomer and polymerizable group end-functionalized polymer, namely macromonomer. Polymerization of carboxyl end-functionalized vinyl monomers used as macromonomers gave graft copolymers having carboxyl group at the side chain easily. The carboxyl functionalized graft copolymers are used for high-functional materials such as resist material, cross-linking agent, or thermosetting coating. Especially, carboxyl end-functionalized aliphatic polyesters-type vinyl monomers (Vinyl-Polyester-COOH) are important in the field. New synthesis method without using halide or acid anhydride are required from the perspective of green chemistry.

So, carboxyl end-functionalized aliphatic polyesters were prepared by ring-opening polymerization of cyclic esters and transesterification between methacrylates and the aliphatic polyesters obtained in the presence of *tert*-butylzincate.

Keywords : high-functional materials, biodegradable polymer

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HP : <http://poly.chem.tokushima-u.ac.jp/>

## I. Syntheses of Nanosheets of Layered Metal Hydroxides

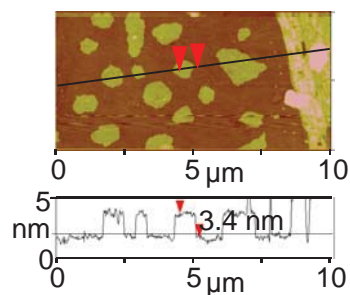
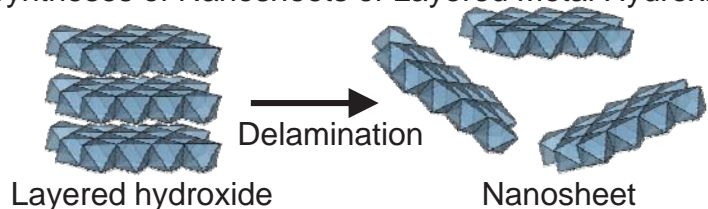


Fig. 1 AFM image of cobalt hydroxide nanosheets

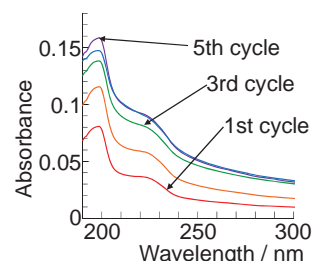
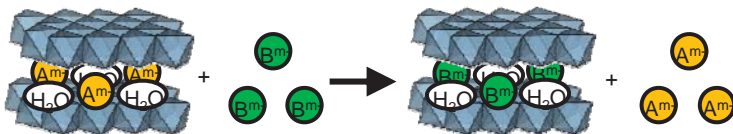


Fig. 2 UV absorption spectra of restacking of nickel hydroxide nanosheets

## II. Control of Interlayer ions in Layered Metal Hydroxides



- Adsorption of polyoxomolybdate and borate
- Control of elution of phosphate

Fig. 3 Growing tests of Japanese mustard spinach using a Mg/Fe-type layered double hydroxide



## Content:

The layered metal hydroxide is a layered compound consisted of repeating stacking of nano-meter-sized metal hydroxides. This compound is mainly synthesized by addition of base into the metal solution.

Inorganic nanosheets have been prepared by delamination of layered materials. Nanosheet has an ultimate two-dimensional anisotropy and manifests unique physical properties arising from size effects. We have synthesized nickel and cobalt hydroxides nanosheets (Fig. 1) and assembled these nanosheets by stacking on the glass slide to make new lamella structure (Fig. 2).

Layered double hydroxide is a layered compound that contains divalent and trivalent metal ions. It consists of hydroxide layer and interlayer anion, and the interlayer anion is captured and able to exchange. We use this property for adsorption and controlled-release of anions. Adsorption of polyoxomolybdate and borate control of elution of phosphate have been investigated and try to apply it to fertilizer (Fig. 3).

Keywords: layered compound, metal hydroxide, nanosheet, ion exchange

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