

**Lamellae Morphology for the Biodegradable Hydrogen-bonding Complex of
Poly(ϵ -caprolactone) and Natural Polyphenol Catechin**

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Poly(ϵ -caprolactone)(PCL) can form strong hydrogen-bonding complex with (+)-catechin. The existence of strong inter-association between PCL and catechin greatly affects the thermal and mechanical properties of the complexes. Two kinds of ideal forms for associated catechin molecules were given. It was suggested that difference in mobility of catechin molecules leads to the different behavior of segregation from PCL lamellae.

**Bacterial Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate)s:
Comonomer Compositional Distribution and Thermal Properties**

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The bacterial poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) [P(3HB-co-3HH)] can be comonomer compositionally fractionated into several fractions by chloroform/n-heptane solvent/non-solvent system. Results of DSC measurements show that the melting behavior of P(3HB-co-3HH) fractions with different 3HH unit content are remarkably different from that of as-produced original P(3HB-co-3HH).

**Polymerization and Characterization of Poly(ϵ -caprolactone)
Using Yttrium Triflate**

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The ring-opening polymerization of ϵ -caprolactone (CL) has been initiated by yttrium triflate (trifluoromethanesulfonate) in air using simple glass vials at 60 °C without desiccation steps and stirring. The M_n and M_w/M_n of the obtained poly(ϵ -caprolactone) (PCL) was 5,000-12,000 and about 1.2, respectively. Direct molding method during polymerization of PCL at 40 °C by yttrium triflate was developed. It was

found that this direct molding PCL ($M_n = 2,000$, $M_w/M_n = 3.07$) was biodegraded very slowly in a buffer (pH 7.0) with a lipase produced by *Rhizopus arrhizus*.

B-04

Composites Consisting of Poly(ϵ -caprolactone) And Cellulose Fibers Directly Molded by Yttrium Triflate

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Composite samples consisting of poly(ϵ -caprolactone) (PCL) and cellulose fibers (CF) were prepared by the directly molding method. Monomer solution was mixed with yttrium triflate and 2-propanol. CF was added to the mixture and put into the syringe. The syringe was heated at 60°C for 48 hrs. After cooling, the sample was removed from the syringe and cut into a column shape specimen. The mechanical properties were measured by the compression test using the above specimen. The modulus and strength of composite samples are greater than those of PCL samples without CF.

B-05

Thermal and Infrared Spectroscopic Studies on Hydrogen-Bonding Interaction between Poly(3-hydroxybutyrate) and Catechin

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The effects of catechin on the properties of isotactic poly[(R)-3-hydroxybutyrate] (i-PHB) and highly-syndiotactic poly[(R,S)-3-hydroxybutyrate] (s-PHB) were investigated by differential scanning calorimetry and Fourier transform infrared. The miscibility and intermolecular hydrogen-bonding between PHB and catechin were observed. The effect of different stereochemical structures of i and s-PHB on the PHB-catechin interaction was discussed.

B-06

Sustainable Chemical Recycling of Biodegradable Polyester Using Enzymatic Reaction

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Unnatural type poly[(*R,S*)-3-hydroxybutanoate]s [P(3HB)s] were transformed into a reactive cyclic 3HB oligomer in an organic solvent passing through a column packed with immobilized *Candida antarctica* lipase. The obtained cyclic oligomer was readily polymerized by lipase and conventional chemical catalyst.

B-07

CHEMOENZYMATIC SYNTHESIS OF GLYCO-CONJUGATE POLYMER

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We investigated the enzymatic conversion of biomass into biofunctional materials. Enzyme-catalyzed transesterifications of sugars were achieved with high regioselectivity and yield, and the resulting sugar vinyl esters were polymerized by a radical initiator. Based on the glyco-cluster effect, the glyco-conjugate-conjugate polymers showed specific high affinity with lectins.

B-08

Chemical Recycling of Biodegradable Polyesters: PHB and PCL

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Thermal degradation behavior of well-known biodegradable polymers, poly(3-hydroxybutyrate) (PHB) and poly(ϵ -caprolactone) (PCL), was analyzed by the simulation methods. As a result, an interesting acceleration effect of Ca compound was indicated.

B-09

Chemical Recycling of PLLA: Influence of 1st-order structure

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Poly(L-lactic acid) {Poly(L-lactide), PLLA} can be produced from renewable sources, such as corn, potato, and other agriculture products. Among the biodegradable polymers, PLLA has many good properties, including mechanical strength, transparency, and hydrolyzability. Thus, the potential of PLLA and related copolymers now attracts many attentions. PLLA is generally prepared through the ring opening polymerization of L-lactide, while the pyrolysis of PLLA mainly results in the regeneration of L-lactide.

B-10

CHEMICAL RECYCLING OF PLLA : CONTROL OF RACEMIZATION

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Poly(L-lactide) [poly(L-lactic acid), PLLA] is a well known biodegradable polymer. It is traditionally employed in bio-medical, pharmaceutical, and environmental applications. Recently, because of its good properties, such as mechanical strength, transparency, and compostability, the PLLA and related copolymers attract many attentions as a promising alternative of the conventional petroleum based commodity resins.

B-11

Synthesis of a Novel Class of Polyhydroxyalanoates Utilizing Short-Chain-Length Intermediates of β -Oxidation in Plant Cells

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Poly[(R)-3-hydroxyalkanoates] (PHAs) are very promising bacterial polyesters that provide a range of biodegradable, thermoplastics and elasticity with useful properties. One of natural PHA producing bacteria, *Aeromonas caviae* FA440 is capable of synthesizing copolymer consisting of 3-hydroxyalkanoate units with C4 to C7¹⁾.

Oxidative Degradation of *cis*- and *trans*-1,4-Polyisoprenes and Vulcanized Natural Rubber with Enzyme-mediator systems

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Synthetic *cis*- and *trans*-1,4-polyisoprenes were treated with enzyme/mediator system in which a low molecular substrate is activated by catalysis of enzyme to attack polymer. In this system, the low molecular compound mediate catalytic reaction of enzymes and degradation of polymer and thus we call it 'mediator'. Two enzyme/mediator systems, (1) Horseradish peroxidase/1-hydroxy-benzotriazole (HRP/1-HBT) and (2) lipoxygenase/linoleic acid were used for degradation of *cis*-1,4-polyisoprene and *trans*-1,4-polyisoprene. The resulted polymers were analyzed by GPC showing significant depolymerization in all case.

Molecular Cloning of Poly(aspartic acid) Hydrolases from *Sphingomonas* sp. KT-1, and Characterization of Their Gene Products

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Poly(aspartic acid) (PAA), which belongs to water-soluble and biodegradable polymers, has been extensively studied. PAA is composed of β -amide (70%) and α -amide units (30%). The distribution of α - and β -amide units is random in the PAA sequence.

Crystalline/Noncrystalline Nano-Structure of Biodegradable Poly(butylene adipate-co-butylene terephthalate)s as Revealed by High-Resolution Solid-State ^{13}C NMR

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Crystalline/noncrystalline nano-structures of biodegradable poly(butylene adipate-co-butylene terephthalate)s with different comonomer composition have been characterized by solid-state ^{13}C NMR. The obtained results give a clue to design good materials with appropriate biodegradability and mechanical property.

Microbial Degradation of Poly(ethylene terephthalate) and Its Degradation Mechanism

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Poly(ethylene terephthalate) (PET) is one of the most widely spread engineering plastics, which causes serious environmental problems, such as dry up of natural resources, waste matters, and global warming. Recently, we have found and succeeded to isolate several microorganisms that degrade and assimilate PET. In this paper, the degradation mechanism was investigated by scanning electron micrograph and various spectroscopic measurements and the endo-type hydrolysis of ester linkage by certain enzymes were proposed.

Polyhydroxyalkanoate (PHA) biosynthesis from Waste Oil

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Biosynthesis of polyhydroxybutylate (PHB) by *Pseudomonas oleovorans*, *Pseudomonas putida*, and *Ralstonia eutropha* from waste plant oil was investigated. Under nitrogen-limited condition, each bacterium accumulated PHB, and *R. eutropha* showed the highest activity in biosynthesis. Various waste plant oils were assimilated and converted to PHB, and the yield was approximately 65 % of the bacterial cell dry weight. The molar masses of the obtained polyesters were relatively constant and ranged from 2.3 to 5.5 $\times 10^5$ g/mol.

Synthesis of Polyglactin by Melt/Solid Polycondensation of Glycolic/L-Lactic acids

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Polyglactin was successfully synthesized by the melt/solid polycondensation of a mixture of glycolic acid (GA) and L-lactic acid (LA) using methanesulfonic acid as the catalyst. At first, a solid oligocondensate was prepared by melt-polycondensation at 190 °C with a GA to LA monomer ratio of 90/10. It was mechanically crushed into particles with various sizes (150~180, 180~212, 212~250, 250~300 and 300~355 μ m) and subjected to solid-state post-polycondensation at 170 °C for 10 - 20 h. The polyglactin finally obtained from the particles of 212 ~ 250 μ m was colorless solid whose number-average molecular weight reached 57,000 Da. This process can afford a facile route to large-scale synthesis of polyglactin with high molecular weight.

Enzymatic Synthesis of Chitin- and Chitosan-graft-Aliphatic Polyester and Their Reactivity

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New graft polymers were synthesized by the lipase-catalyzed graft polymerization of ϵ -caprolactone (ϵ -CL) or γ -butyrolactone (γ -BL) onto chitin and chitosan. The reactivities of the natural polymers and lactones were found to be: chitosan > chitin; ϵ -CL > γ -BL >> γ -BL (no reaction).

B-19

Effect of Acetate and Lactate on the Methane Monooxygenase Activity of *Methylosinus trichosporium* OB3b

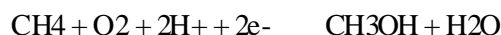
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Methanotroph *Methylosinus trichosporium* OB3b contains methane monooxygenase (MMO) which catalyses methane hydroxylation as follows.



Methanol production with *M. trichosporium* OB3b has been established by inhibiting further metabolism of methanol. In the reaction system, reducing power is required because the redox cycle is also inhibited in the bacterium. In this study, the effect of acetate and lactate, which are easily synthesized by fermentation, on MMO activity in *M. trichosporium* OB3b was examined.