

## **Redox Polymers for Soft Energy Devices**

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We have focused on aliphatic polymers bearing redox-active groups per repeating unit. The redox polymers are characterized by an ultimate population of the electron-releasing and -gaining site that allows efficient redox-driven electron- or charge-transport and -storage throughout the polymer layers via self-exchange reactions. Challenges toward paper-like and bendable rechargeable batteries by molecular designing of the redox polymers will be demonstrated. We are also fabricating dye-sensitized photovoltaic cells with the redox polymer layers for charge-separation and -transport in the cell. The cells are being tested as a cord-less power source assisted with interior lighting.

Another example is anode-active redox polymers, such as a quinone polymer, which reversibly formed their hydrogen additives such as a hydroquinone polymer. The redox polymer resins are being examined as a new-type hydrogen carrier, of which advantages are non-explosive, non-leakage, safety transportation, storage, and facile evolution of hydrogen. Redox polymers are emerging as a new class of organic materials for energy-saving devices.

## Materials Science of DNA: Optical Properties of Natural and Modified DNAs

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This presentation discusses optical, electro-optic, and optoelectronic properties of natural and chemically modified DNAs<sup>1-3</sup>. Natural DNAs are water soluble. However, if the sodium ions of natural DNA molecules are replaced with long alkyl onium ions, the resulting modified DNAs (QDNAs) become soluble in common organic solvents and produce high optical quality films.

The natural and QDNAs, when they are in the form of double helix, commonly absorb at about 260 nm, which is the result of electronic transitions of nucleic bases. Moreover, QDNAs reveal practically the same CD spectra as the natural DNA, which is taken as a strong indication that replacement of Na<sup>+</sup> ions with onium(Q<sup>+</sup>) ions does not destroy the original double helical structure. Fluorescence behavior of DNAs themselves and DNA mixtures with conventional fluorescence dyes is very interesting. Especially, DNAs modified to bear various fluorophores in the Q<sup>+</sup>-part<sup>4-7</sup> can be utilized in tuning luminescence colors. DNA-based lasing provides us with a new approach to develop organic compositions, which will also be discussed in this presentation. In addition, light-emitting diodes based on DNA, photovoltaics of DNA containing solar cells, and nonlinear optical compositions of modified DNAs will be reviewed in this talk. DNAs may not be the ideal materials for various applications, but the science we learn from DNAs appears to be very important in expanding the horizon of materials science.

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## **Functional Aliphatic Polyesters With Tunable Degradation Properties**

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Biodegradable aliphatic polyesters have been used in biomedical fields as drug delivery carriers, tissue engineering scaffolds, and sutures etc. To meet different applications, it is very important to functionalize aliphatic polyesters and control over their degradation. This talk will focus on the development of new polymerization methods to synthesize functional polyesters and to modulate the degradation of these polyesters under different conditions. (1) An efficient method to synthesize thermoresponsive polyesters was developed by combination of atom transfer radical polyaddition and click chemistry. The thermoresponsive properties and degradation behaviors of these polyesters were investigated. These properties can be modulated by tailoring the OEG length and the main chain structure. (2) A new type of thermally labile polyesters with tunable degradation was designed and synthesized by atom transfer radical polyaddition. The effects of polymer structures on the thermal degradation rates were studied and elucidated, tunable rate of degradation was achieved by changing the main chain structure. (3) Passerini multicomponent polymerization was developed as a new method to synthesize functional poly(4-hydroxybutyrate)s. These polyesters exhibited unique degradation behavior in solution. The degradation was driven by the consecutive intramolecular cyclization to form stable a neutral  $\gamma$ -butyrolactone compound.

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## Living Anionic Ring-opening Polymerization of Ethylene oxide and Its Chain-end Functionalizations

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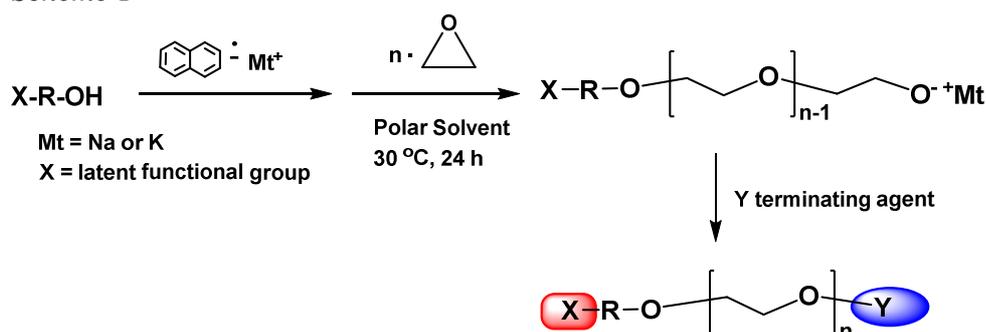
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Poly(ethylene glycol) (PEG) has received a great attention in the biomedical field because of its low level of cell and protein adsorption. In this respect, PEG must be an important material for modification of proteins, synthesis of drug-conjugates, and preparation of nanocarriers in the drug delivery system.<sup>1,2</sup> However, it is not simple to get well-defined PEG with controlling molecular weight and carrying functional groups at the chain-end. Up to date, the best method to synthesize PEG with well-defined structure has been known to be living anionic ring-opening polymerization of ethylene oxide leading to generation of poly(ethylene oxide) (PEO) showing the same chemical structure as that of PEG.<sup>3-6</sup> We have tried to develop living polymerization of ethylene oxide.<sup>7</sup> Especially, it is expected that the synthesis of heterobifunctional polymers can be readily achieved by ring-opening polymerization of EO using functional initiator and chain-end functionalization of the resulting polymeric alkoxides as shown in *Scheme 1*.

*Scheme 1*



In this presentation the preliminary results for the synthesis of heterobifunctional PEOs using several functional initiators will be discussed.

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## **Precise Design of Antifouling, Lubrication and Intelligent Adhesion Surfaces through Polyelectrolyte Brush Immobilization**

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Surfaces and interfaces of soft materials play an important role in various functional applications. Polyelectrolyte brushes provide soft interfaces with unique functionality. However, systematic studies on the structure and functionality of polyelectrolyte brushes at liquid interfaces have not been done yet. Various polyelectrolyte brushes with anionic, cationic, and zwitter ionic side chains were prepared on initiator immobilized Si-wafer and macroinitiator-modified polypropylene by surface-initiated atom transfer radical polymerization (SI-ATRP). Surface wettability and chain conformation of polymer brushes at water/solid interfaces were characterized by contact angle measurement and neutron reflectivity, respectively. Super hydrophilic surfaces, antifouling surfaces, environmentally friendly water lubrication systems, and repeatable environmentally friendly adhesion systems without organic solvents were realized through polyelectrolyte brushes immobilization.

## **Enzymatic Polymerization of Monomer Derived from Oil Palm Empty Fruit Bunch**

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Oil palm empty fruit bunch fiber (OPEFB) is a lignocellulosic waste from palm oil mills. It is a potential source of glucose and xylose which can be used as raw materials for high value products such as succinic acid. The interest on use of lignocellulosic waste for bioconversion to fuels and chemicals is increasing as these materials are relatively low cost and renewable. The objective of the present study is to produce biodegradable polyesters from OPEFB-derived monomer via enzymatic polymerization. Cellulose and glucose were used as intermediates to produce succinic acid. Organosolv pretreatment was used to extract cellulose from OPEFB. The solvents used were mixtures of ethanol and water. Batch enzymatic hydrolysis of OPEFB cellulose was performed at 40°C using celluclast and Novozyme 188. The highest glucose concentration produced is 167.4 g/L (sugar recovery is 0.73 g/g from OPEFB). Fermentation using *Actinobacillus Succinogenes* was carried out on glucose to produce succinic acid with highest conversion of 26 %. Enzymatic polymerization was carried out on the succinic acid that was produced from OPEFB with the presence of 1,4-butanediol, glycerol, or ethylene glycol to form biodegradable polyesters using Lipase (*Candida Antartica* CALB) as a catalyst. Molecular weight for the obtained poly(butylene succinate), poly(glyceryn succinate), and poly(ethylene succinate) were  $5.90 \times 10^4$ ,  $6.20 \times 10^4$  and  $4.53 \times 10^4$  g/mol, respectively. For the characterization of cellulose, succinic acid and polyesters, Thermogravimetric Analysis (TGA), Fourier Transform Infrared (FTIR) Spectroscopy, Nuclear Magnetic Resonance (NMR) Spectroscopy, Differential Scanning Calorimetry (DSC) and Field Emission Scanning Electron Microscope (FESEM) were used. High Performance Liquid Chromatography (HPLC) and Gel Permeation Chromatography (GPC) were used to determine the quantity of glucose and succinic acid produced, and to measure the molecular weight of biodegradable polyesters. Polyesters with degree of polymerization of more than 100 were achieved. Degradation of about 80% can be achieved after polyesters being exposed to lipozyme for 3 days.

## Hybrid Poly(vinyl alcohol) Hydrogels for Artificial Cartilage on Bionic Design

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There have been attempts to develop artificial cartilage made of soft materials with super lubricity based on a bionic design by elucidating the lubrication mechanisms of natural synovial joints. Among the soft materials, poly(vinyl alcohol) (PVA) gel is one of the most-often-studied hydrogels for such applications. Some PVA gels show a low coefficient of friction under specific conditions and high water content comparable to natural articular cartilage. For example, it was reported that PVA gels prepared by a freeze–thawing method (FT gel) show a very low friction coefficient under walking conditions lubricated with hyaluronate solution containing protein [1]. A simple method to prepare a physically crosslinked PVA gel by a cast-drying method (CD gel), which was recently reported [2], is also promising.

For the application of hydrogels as artificial articular cartilage, there are several essential properties required, such as biocompatibility, low friction, high wear resistance, suitable water content, and high mechanical strength (i.e., stiffness, fracture toughness, and fatigue resistance). The CD and FT gels both have high water absorbance and excellent mechanical properties as compared with other hydrogels. However, the mechanical strength of each gel is not enough to be of practical use, and FT or CD gel alone cannot satisfy all required properties. Of the required properties, the mechanical strength and wear resistance of these gels are not enough as compared with natural synovial joints and further improvements are needed for practical uses.

As candidates for practical use as artificial cartilage, new methods of preparing PVA hydrogels have been studied, such as combining different types of PVA gels with different structures, elastic moduli, and characteristics of permeability. A lamination method and hybrid techniques using FT and CD gels were examined in order to improve the mechanical and tribological properties [3]. This lecture presents a method for preparing biomimetic artificial PVA cartilage for use as artificial cartilage with superior lubricity based on bionic design.

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