

NDSU-KU 7th Annual Symposium

October 6-7, 2022

Memorial Union

NDSU Campus

Organizers: Mukund Sibi

Bonnie Hurner

Mohi Quadir

Acknowledgements

Generous Financial Support was provided by

Department of Chemistry and Biochemistry

Department of Coatings and Polymeric Materials

Department of Mechanical Engineering

College of Science and Mathematics

College of Engineering

Office of Research Administration

Symposium Schedule

Thursday October 6, 2022

Ballroom B, Memorial Union

7.45 to 8.45 AM **Registration/Breakfast** **Prairie Rose, MU**

8.45 to 9.30 AM Introduction (VPR Colleen Fitzgerald, Greg Cook, Yoshiro Kaneko, Dean Webster, and Mukund Sibi)

Session Chair: Dean Webster

9.30 to 10.15 AM **PL-1** Robert Allen (National Renewable Energy Laboratory)
Polymer Science and Sustainability at NREL

10.15 to 10.45 AM **Break**

10.45 to 11.15 AM **IL-1** Sanku Mallik (North Dakota State University)
Polymer nanoparticles for drug delivery to hypoxic solid tumors

11.15 to 11.45 AM **IL-2** Philip Boudjouk (North Dakota State University)
Cyclohexasilane (CHS), a source for silicon based nanorods, nanowires, quantum dots, a variety of silicides and 1-dimensional polymers

11.45 to 12.15 PM **IL-3** Yongki Choi (North Dakota State University)
Multiplexed nanosensing of cancer biomarkers

12.15 to 1.15 PM **Lunch** **Prairie Rose, MU**

Session Chair: Mohi Quadir

Ballroom B, MU

1.15 to 2.00 PM **PL-2** Yoshiro Kaneko (Kagoshima University)
New development of ladder-like inorganic and hybrid polymers

2.00 to 2.30 PM **IL-4** Seth Rasmussen (North Dakota State University)
Deviate from the norm: A new design paradigm for low bandgap polymers via donor-acceptor frameworks

| | | |
|------------------------|-------------|---|
| 2.30 to 3.00 PM | IL-5 | Hiroyuki Shinchi (Kagoshima University) Functional analysis and drug delivery using sugar chain-immobilized nanoparticles |
| 3.00 to 3.30 PM | | Break/Poster Set up/Refreshments Ballroom A, MU |
| 3.30 to 4.45 PM | | 90 Second Introduction to Posters (All Presenters) |
| 4.45 to 6.00 PM | | Posters |
| 6.30 to 8.30 PM | | Dinner Prairie Rose, MU |

Friday October 7, 2022

Ballroom B, Memorial Union

8.00 to 8.30 AM

Registration/Breakfast **Prairie Rose, MU**

Zoom Presentations **Ballroom B, MU**

Session Chair: Yoshiro Kaneko

8.30 to 9.00 AM **IL-6**

Kimihiro Matsukawa (Kyoto Institute of Technology)
**Organic-inorganic Hybrid Coating prepared by
Norbornene modified Zirconia Nanoparticles**

9.00 to 9.30 AM **IL-7**

Takeshi Ishikawa (Kagoshima University)
**Development and Application of a Computational
Method for Analyzing Protein-Protein Interaction**

9.30 to 10.00 AM **IL-8**

Kenji Matsumoto (Kagoshima University)
**Catalytic oxidative biaryl coupling of aryl amines
via aerobic oxidation with heterogeneous catalyst**

10.00 to 10.30 AM

Break **Legacy Lounge, MU**

In Person Presentations

Session Chair: Hiroyuki Shинchi

Ballroom B, MU

10.30 to 11.15 AM **PL-3**

Erin Pavlacky (H. B. Fuller)
**Adhesives for the Personal Care Industry:
Translating Megatrends to Innovations**

11.15 to 11.45 AM **IL-9**

Chad Ulven (North Dakota State University)
**Advancement in Continuous Carbon Fiber
Composite 3D Printing**

11.45 to 12.15 PM **IL-10**

Jessica Vold (North Dakota State University)
**Advanced Materials Creation from Local
Resources in Extreme Environments**

12.15 to 1.15 PM

Lunch **Prairie Rose, MU**

Session Chair: Chad Ulven

Ballroom B - MU

1.15 to 2.00 PM **PL-4**

Kevin Lewandowski (3M)
Efficient, Well Controlled, Geminal Photoiniferters

- 2.00 to 2.30 PM **IL-11** Andriy Voronov (North Dakota State University)
**Monomers, Polymers and Polymeric Materials
from Plant Oils**
- 2.30 to 3.00 PM **IL-12** Guodong Du (University of North Dakota)
**Zinc Catalyzed Ring Opening Polymerization and
Copolymerization for Sustainable Polymers**
- 3.00 to 3.30 PM **IL-13** Alena Kubatova (University of North Dakota)
**High-throughput approaches to characterization of
renewable materials using thermal carbon analysis
and electrospray mass spectrometry**

3.30 to 4.00 PM **Break** **Legacy Lounge - MU**

Session Chair: Andriy Voronov

- 4.00 to 4.30 PM **IL-14** Kalpana Katti (North Dakota State University)
**Cancer Testbeds: A new frontier for treating bone
metastasis**
- 4.30 to 5.00 PM **IL-15** Wenjie Xia (North Dakota State University)
**Multiscale Modeling of Microstructure and
Interface in Polymeric Structural Materials**
- 5.00 to 5.30 PM **IL-16** Alex Parent
**Modeling the Autoxidation of Linseed Oil by Metal
Driers**

6.00 to 7.00 PM **Reception** **McGovern Alumni Center**

7.00 to 9.00 PM **Banquet** **McGovern Alumni Center**

Legend

Scientific Sessions

PL Plenary Lecture

IL Invited Lecture

Breaks, lunch, etc.

Session Chairs

MU = Memorial Union

Polymer Science and Sustainability at NREL

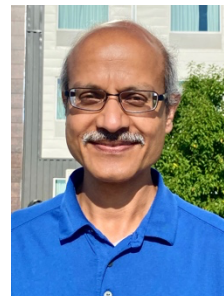
Dr. Robert D. Allen
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Synthetic polymer chemistry has provided the world with materials that make transformational contributions. As we are about to exceed one trillion pounds of polymers manufactured annually around the world, there is a growing focus on capturing the 'waste carbon mountain of produced polymers and ultimately creating a plastics (polymer) circular economy. NREL, an applied research laboratory in the U.S. Department of Energy ecosystem, has recently initiated a focused research program on Circular Economy. My lecture will introduce NREL, the BOTTLE consortium, and will include some recent research results.

Polymer nanoparticles for drug delivery to hypoxic solid tumors

Sanku Mallik, Department of Pharmaceutical Sciences,
North Dakota State University, Fargo, North Dakota, USA.



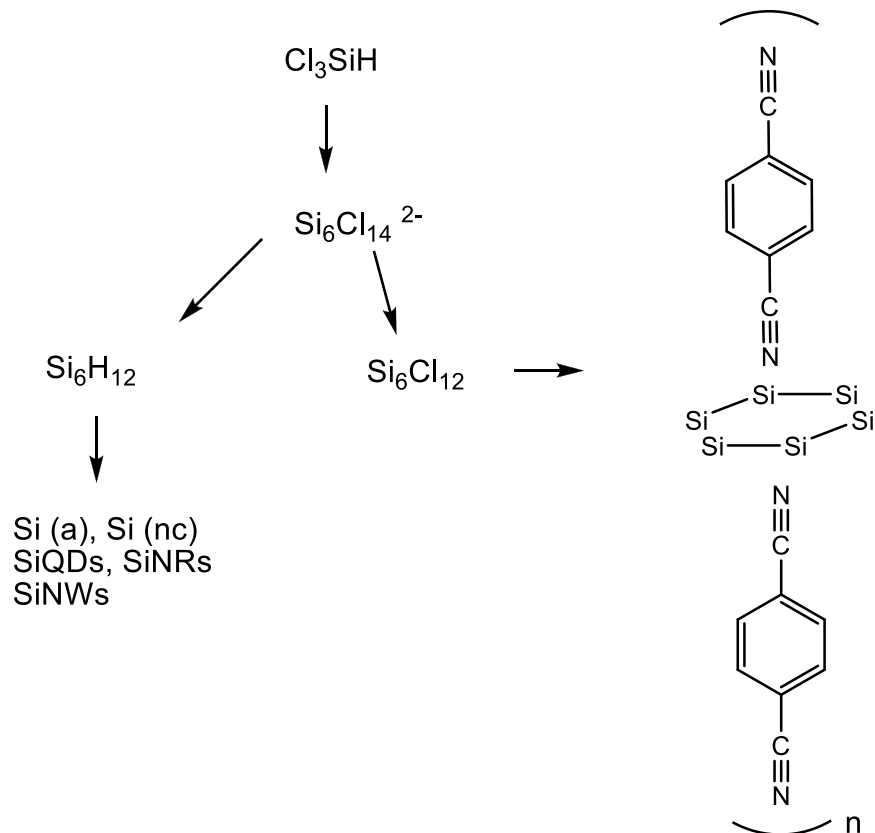
Polymersomes are bilayer vesicles prepared from amphiphilic block copolymers. Although they have many advantages compared to other nanoparticles, their applications as carriers for cytotoxic drugs and imaging agents remain under-developed. Hypoxia develops in many pathological conditions, including solid tumors, pulmonary hypertension, ischemia, altitude sickness, brain injury, stroke, etc. Hypoxia in solid tumors triggers remodeling of the extracellular matrix, epithelial-to-mesenchymal transition, cell survival, metastasis, cancer stem cell formation, and significant resistance to chemo and radiotherapy. We prepared targeted, deep-tissue-penetrating polymersomes responsive to hypoxia (0.2% oxygen) for drug delivery to the solid tumors of the pancreas and breast. The presentation will focus on (1) synthesis of hypoxia-responsive polymers and preparation of tissue-penetrating polymersomes and (2) demonstration of the functional efficacy of the hypoxia-responsive polymersomes using cellular and mouse models of hypoxic niches.

Cyclohexasilane (CHS), a source for silicon based nanorods, nanowires, quantum dots, a variety of silicides and 1-dimensional polymers

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The development of high yield syntheses of cyclohexasilane, CHS, (**1**) from trichlorosilane has provided a platform for easy access to novel compounds and materials. The details of the synthesis of CHS and its role as a very useful intermediate for silicon nanorods (SiNRs), silicon nanowires (SiNWs), silicon quantum dots (SiQDs) and 1-dimensional polymers containing Si₆ rings will be presented. Some molecular chemistry of CHS key to preparing a variety of silicides will also be discussed. Structural and theoretical investigations of the various aspects of Si₆ chemistry will be presented as well. Functioning as a Lewis Acid, Si₆Cl₁₂, can break C-halogen bonds



Multiplexed nanosensing of cancer biomarkers

Yongki Choi, Associate Professor

Department of Physics and Materials and Nanotechnology Program

North Dakota State University



Despite the promises of molecular biomarkers in disease diagnosis and cancer research, most biomarker sensing techniques such as enzyme-linked immunosorbent assay, immunofluorescence, western blotting, polymerase chain reaction, flow cytometry, surface plasmon resonance, are complex, take a long time to complete, consume large volumes of pre-treated samples and reagent, and require bulky and expensive laboratory instruments operated by highly trained technicians. In principle, nanotechnology, working at the molecular scale, provides opportunities to reverse this situation. The proposed research program seeks to discover and develop a highly parallelized, scalable, graphene-based electronic biosensing platform that combines high sensitivity, specificity, stability, minimal sample preparation, and rapid sample readout in a portable device. Thus, the electronic approach has the potential to overcome important limitations associated with conventional sensors. Specifically, the individual binding events of target cancer markers including tetraspanins, integrins, and epithelial cell adhesion molecules are directly transduced by electrical signals, rather than indirect pulses of light from the light-responsive molecules labeled to the secondary antibody or enzyme-substrates that require an extra validation due to the limited availability. Moreover, the sensitizing materials allow adopting any capture molecule such as tumor-specific peptides and antibodies, providing complementary detection as well as one-to-one comparison and evaluation of multiple biomarkers. Finally, integration of the electronic sensors with the microfluidic system permits high-throughput, multiplexed, and comprehensive detection of the biomarkers from the complex biological samples, greatly simplifying the detection processes using minimal sample volume and offering portable, point-of-care diagnostic devices for simple, timely, early disease diagnosis, and monitoring at resource-limited settings.

New development of ladder-like inorganic and hybrid polymers

Yoshiro Kaneko

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1. Introduction

Ladder-like polymers, in which two main chains are intramolecularly cross-linked in parallel, have restricted conformational changes and have rigid properties; therefore, they exhibit various properties different from ordinary single-chain polymers. In the field of inorganic polymers (polysiloxane), research on the preparation of ladder-like polysilsesquioxanes (PSQ) composed of two Si–O–Si bond main chains by hydrolytic polycondensation (sol–gel reaction) using organotrialkoxysilanes (silane coupling agents) as starting materials is known. We have reported on the preparation of ladder-like PSQs with various ionic side-chain groups capable of forming regularly stacked structures in the solid-state and their application as functional materials.¹ However, the types of ladder-like PSQs formed by this sol–gel method are limited. In this symposium, I would like to introduce the preparation of ladder-like polysiloxane composed of two Si–O–Si main chains and ladder-like organic-inorganic hybrid polymers indicating amphiphilic properties using “template polymerization method”. Furthermore, the properties of these ladder-like polymers are also introduced.

2. Preparation of ladder-like polysiloxane by template polymerization and its properties

A double-chain ladder-like polysiloxane (DC-PS) can be obtained by introducing dialkoxysilyl groups as polymerizable groups into the side chain of an ammonium-group-containing polysiloxane (PS-NH₃Cl),² followed by an intramolecular polycondensation (template polymerization) (Fig. 1).³ DC-PS had excellent thermal stability (T_{d10} : 407 °C), relatively high water repellency (water contact angle: 98°), and high adhesion to glass.

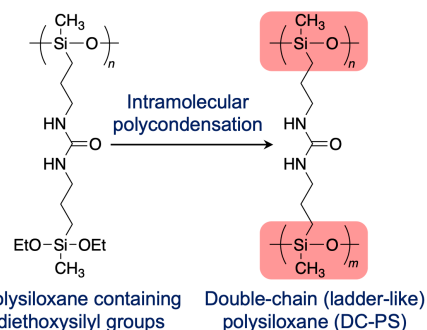


Fig. 1. Preparation of double-chain (ladder-like) polysiloxane (DC-PS).

3. Preparation of amphiphilic ladder-like hybrid polymers by template polymerization and its properties

Considering that the unique shape of double chain affects the stability of nanoaggregates such as micelles and vesicles in water, the preparation of a ladder-like polymer (PAAm-PAMS), in which a hydrophilic polyacrylamide (PAAm) chain and a hydrophobic polyalkylmethylsiloxane (PAMS) chain are linked in “parallel”, as nonionic amphiphilic copolymer was investigated.⁴ Although nonionic amphiphilic polymers that can stably form nanoaggregates in water at high temperature are limited (relatively low cloud point: T_c), PAAm-PAMS nanoaggregates were stable even at high temperature (ca. 90 °C). Detailed properties of this polymer will be explained on the day of the symposium.

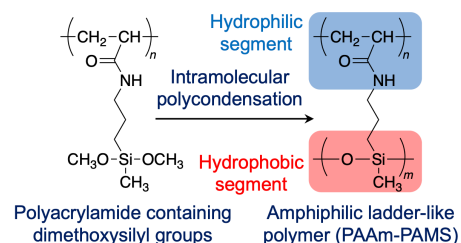


Fig. 2. Preparation of amphiphilic ladder-like hybrid polymer (PAAm-PAMS).

References

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2. S. Kinoshita, S. Watase, K. Matsukawa, and Y. Kaneko, *J. Am. Chem. Soc.*, **2015**, *137*, 5061.
3. M. Nobayashi, K. Shikinaka, and Y. Kaneko, *Polym. J.*, **2022**, *54*, 11.
4. K. Soda, S. Matsuo, and Y. Kaneko, *Macromolecules*, under revision.

Deviate from the norm: A new design paradigm for low bandgap polymers via donor-acceptor frameworks

Evan W. Culver,¹ Wyatt D. Wilcox,¹ Elsa Buyck,¹ Seth C. Rasmussen¹

¹Department of Chemistry and Biochemistry, North Dakota State University, NDSU Dept. 2735, P.O. Box 6050, Fargo, ND 58108-6050, USA



For conjugated polymers, bandgap reduction is perhaps the most common target of molecular tuning,¹⁻⁴ with the utilization of donor-acceptor (D-A) frameworks most often applied for the production of low bandgap ($E_g < 1.5$ eV)^{2,4} and reduced bandgap ($E_g = 1.5-2.0$ eV)^{2,4} polymers. Such D-A frameworks employ alternating electron-rich and electron-deficient moieties (Figure 1) in order to produce a hybrid material with HOMO levels characteristic of the donor and LUMO levels characteristic of the acceptor, with the goal of reducing the HOMO-LUMO energy and achieving a lower bandgap. The widespread application of such frameworks has resulted in various assumptions and misconceptions in the literature, including the view that monomers act exclusively as donors, acceptors, or neutral spacers.⁵⁻⁷ At odds with this, however, is the discovery that thieno[3,4-*b*]pyrazines (TPs),⁴ a commonly applied class of acceptors, also exhibit properties of very strong donors, leading to their current description as *ambipolar units*.⁵⁻⁷ As TPs exhibit a high-lying HOMO, this should allow for a new design model in which TP units are paired with an acceptor, rather than the traditional pairing with a donor. Several such ambipolar-acceptor frameworks have now been successfully produced via direct arylation polymerization to give materials with bandgaps of 0.97-1.12 eV.^{6,7} The synthesis and characterization of such ambipolar-acceptor frameworks will be presented, along with discussion of the potential broader applications of this new design for the production of polymeric non-fullerene acceptors for organic photovoltaic devices.

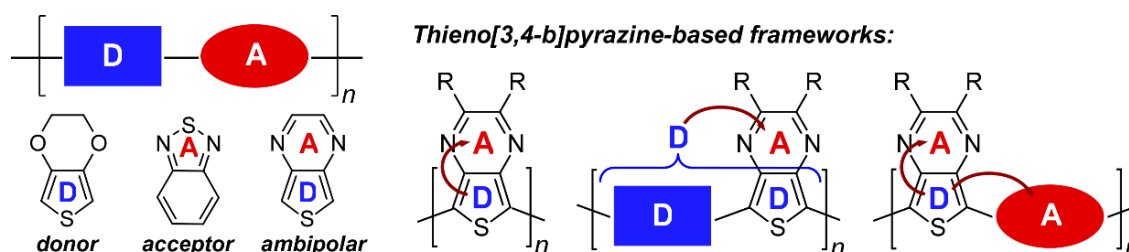


Figure 1. Donor-acceptor frameworks incorporating thieno[3,4-*b*]pyrazine

References

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Functional analysis and drug delivery using sugar chain-immobilized nanoparticles

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Sugar chains are biomolecules expressed as glycoprotein, proteoglycan, or glycolipid. Binding interactions of sugar chains are significantly important in various biological processes such as cell-cell recognition, differentiation, signal transduction, and pathogen infection. However, there are several technical challenges associated with the interaction analysis due to the limitation of analytical tools. Fluorescent nanoparticles such as quantum dots (QDs) have gained much attention as imaging tools because of their superior optical property and functionality. To develop novel analytical tools for interaction with sugar-binding proteins (lectins), we developed sugar chain-immobilized fluorescent nanoparticles (SFNPs) containing CdTe/CdS QDs. We demonstrated that SFNPs can be used for the simple visual detection of lectins and anti-sugar chain antibodies. Furthermore, we found that SFNPs can be applied to the bioimaging of surface sugar chain receptors of various cells.

Sugar immobilized nanoparticles can also be used as carriers of drug delivery systems (DDS). Agonistic ligands of toll-like receptors (TLRs), which activate innate immunity, have gained substantial attention as adjuvants (immunostimulants) for vaccines and immunotherapies. Among them, synthetic small molecule TLR7 ligands are promising candidates as adjuvants. However, there is a risk of inducing fatal adverse side events by systemic administration. As TLR7 is localized in the intracellular endosomal compartment in the immune cells, intracellular delivery via endocytosis through the specific receptors is essential for improving the pharmacokinetics of the TLR7 ligand. Thus, we examined sugar immobilized gold nanoparticles (SGNPs) as carriers of a synthetic small molecule TLR7 ligand (1V209). We then revealed that GNPs co-immobilized with 1V209 and α -mannose (1V209- α Man-GNP/Glyco-nanoadjuvants) enhance immunostimulatory activities more than 10,000-fold *in vivo*. The studies for developing vaccines against infectious diseases and cancers using Glyco-nanoadjuvants are ongoing.

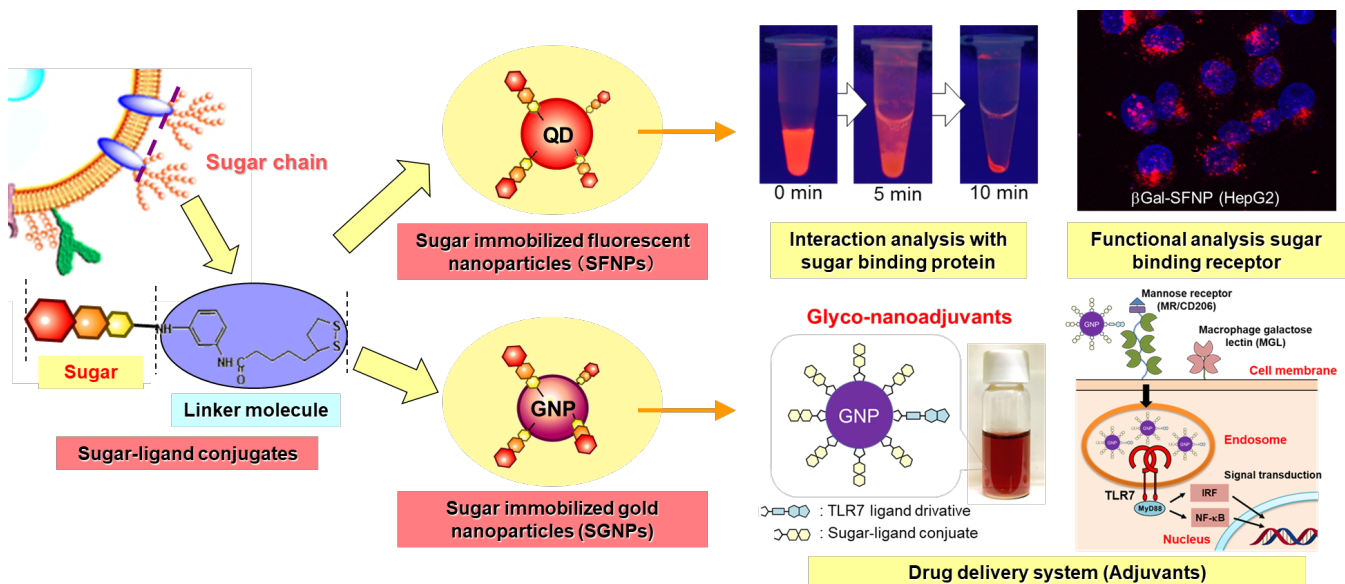


Figure. Application of sugar immobilized nanoparticles

Organic-inorganic Hybrid Coating prepared by Norbornene modified Zirconia Nanoparticles

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Organic-inorganic hybrids containing zirconia nanoparticles are practical materials focused on the high refractive index coating. We have studied the high refractive index materials using zirconia nanoparticles which can be dispersed in organic solvent, monomers, and polymers. As the fine dispersion of zirconia is necessary to prepare the transparent hybrid coating, its surface modification was carried out by using 5-norbornene-2,3-dicarboxylic acid anhydride (NDCAA) which could be formed the ester bonding as shown in Fig. 1. Ester formation between zirconia surface and NDCAA could be confirmed by appearance of peaks around $1400\sim 1600\text{cm}^{-1}$ in FT-IR spectra.

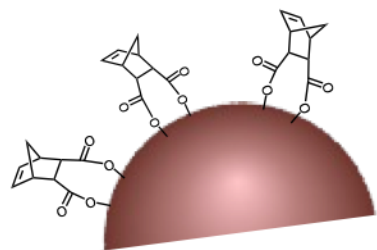


Fig. 1 Estimated surface structure of zirconia nanoparticles modified by NDCAA.

The internal olefin of norbornene skeleton is a useful component for Thiol-Ene reaction which can be used in a wide range of applications. The C=C units of NDCAA on zirconia nanoparticles and triallyl isocyanurate (TAIC) were reacted with the S-H groups of pentaerythritol tetrakis (3-mercaptopropionic acid (PEMP)) by Thiol-Ene reaction to form multiple cross-linked structures as shown in Fig. 2. Thus obtained photo-cured coatings exhibited the properties of high transparency and high refractive index. The coatings and free-standing films were found to have excellent flexibility in spite of the hybrids containing zirconia nanoparticles.

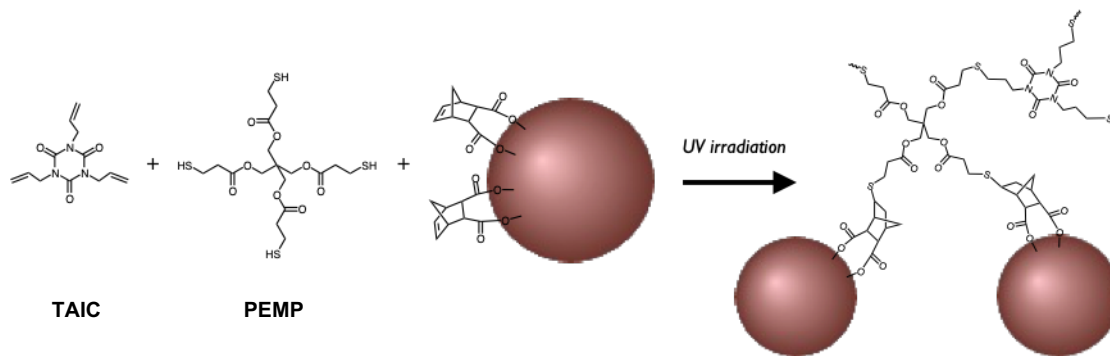


Fig. 2 Preparation of photo-cured hybrids from TAIC, PEMP, and NDCAA modified zirconia nanoparticles

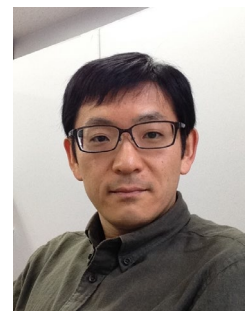
Also, it was found that the mono layer immobilization of zirconia nanoparticles was prepared onto the glass substrate treated with a mercapto-propyl silane coupling agent by Thiol-Ene reaction and the surface of mono layer particles has the unique properties of adhesion and surface functions.

Development and Application of a Computational Method for Analyzing Protein-Protein Interaction

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Protein-protein interaction (PPI) has significant roles in various biological processes and, consequently, attracts much attention as a prospective therapeutic target. Adequate understanding of PPI is also essential for the logical design of antibody drugs, whose demand has been rapidly increasing. Thus, computational methods providing a physicochemical insight into the PPI are strongly required. To properly evaluate the polarization and charge transfer caused to the complex formation, a quantum chemistry-based approach is desired.

Recently, Ishikawa et al. proposed a method called “visualization of the interfacial electrostatic complementarity (VIINEC)”[1,2] based on the fragment molecular orbital (FMO) method, which is a quantum chemical approach for large molecules like proteins. In this method, the interface of the proteins forming a complex is determined using the partial electron density (pEDN), and the electrostatic complementarity between them is visually analyzed by drawing the partial electrostatic potential (pESP). The degree of complementarity is also quantified by the ratio of the attractive electrostatic interaction to the total electrostatic interaction at the interface. As the first application of VIINEC, the PPI of the receptor-binding domain of severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2) and human angiotensin-converting enzyme 2 (ACE2) or antibodies was evaluated.[3] In this study, it was shown that VIINEC may be used for examining the change of the PPI brought by mutations of viral proteins.

In my talk, methodological aspects of the VIINEC are explained. After that, the potential of VIINEC is demonstrated using several applications.

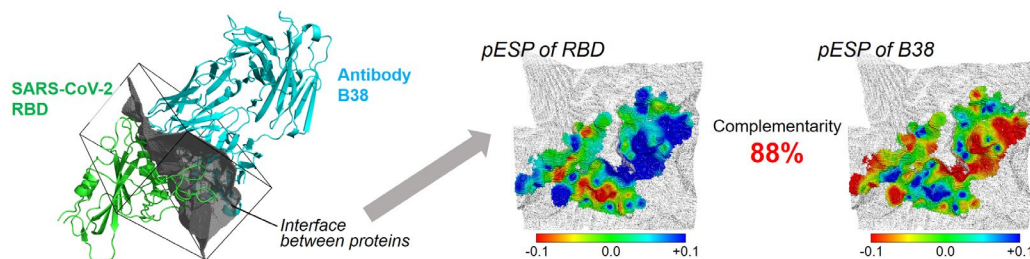


Figure: An example of VIINEC (application to SARS-CoV-2 RBD and antibody (B38))

References:

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Catalytic oxidative biaryl coupling of aryl amines via aerobic oxidation with heterogeneous catalyst

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Biaryl compounds are important functional molecules widely used in the material science such as organic EL devices and organic solar cells, drug discovery and organic synthetic chemistry. The oxidative biaryl coupling reaction is an excellent biaryl scaffold construction method that allows direct oxidative cleavage of the C–H bond to construct the carbon–carbon bond with high atom efficiency without pre-functionalization of the aromatic ring. The catalytic oxidative coupling of 2-naphthols using homogeneous and heterogeneous metal catalysts, leading to BINOL derivatives, has been extensively studied. However, when an aryl amine is used as a substrate, it is generally difficult to control the reaction due to the facile oxidation property of aryl amine. Particularly, catalytic processes for the oxidative biaryl coupling of aryl amines are limited. Against this background, we have developed a heterogeneously catalyzed oxidative coupling reaction of amino aromatic rings under mild aerobic conditions¹. First, we discovered that the heterogeneous rhodium on carbon (Rh/C) catalyst in trifluoroacetic acid as a solvent promoted the oxidative homocoupling reaction of 2-aminonaphthalenes and 2-aminoanthracenes in air. The catalyst can be recovered and reused, and the reaction proceeded smoothly without deactivation even with a catalyst content of 0.1 mol% or less. In addition to aminonaphthalene as a substrate, the reaction of more simple aromatic compounds such as anilines and anilides also proceeded catalytically. In addition, the intramolecular oxidative coupling reaction of tetramethoxybiarylamine proceeded smoothly to provide poly-substituted carbazoles in high yields².

We also developed a catalytic oxidative cross-coupling of 2-aminonaphthalenes. The cross-coupling reaction proceeded selectively with various aniline derivatives and phenol derivatives. Furthermore, we succeeded in developing a highly selective cross-coupling between different anilines and anilines with very similar reactivities, and achieved the synthesis of a wide variety of asymmetric biaryl compounds³.

In this presentation, our recent research on development of oxidative transformation reaction of aryl amines will be discussed.

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Adhesives for the Personal Care Industry: Translating Megatrends to Innovations

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Adhesives are a critical component in the final construction of consumer articles and products in the personal care industry. Strong alignment with the megatrends in absorbent hygiene articles, health devices, and beauty/cosmetic products drives the innovation in this industry. In this presentation, the shifting market dynamics and trends (such as sustainability, population changes, and post-pandemic recovery) will be discussed, and how H.B. Fuller is creating new adhesives to drive value and performance.

Advancements in Continuous Carbon Fiber Composite 3D Printing

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Due to design flexibility polymer 3D printing is become an emerging manufacturing technique, however its application as a structural material is still limited due to the poor mechanical strength and thermal stability of 3D printed parts. Because of the superior mechanical strength of carbon fiber, 3D printing of continuous carbon fiber reinforced thermoset composites could overcome this barrier of mechanical strength and thermal stability. Our UV curing based 3D printing of continuous carbon fiber approach shows a promising potential in manufacturing energy efficient, high strength, complex structures. This proposed 3D printing technologies successfully demonstrated the manufacturing of custom objects having comparable mechanical and thermal strength with similar composites manufactured by conventional manufacturing process. Proper tuning of the process parameter of this proposed 3D printing technique has great potential to replace conventional manufacturing process of composites by 3D printing.

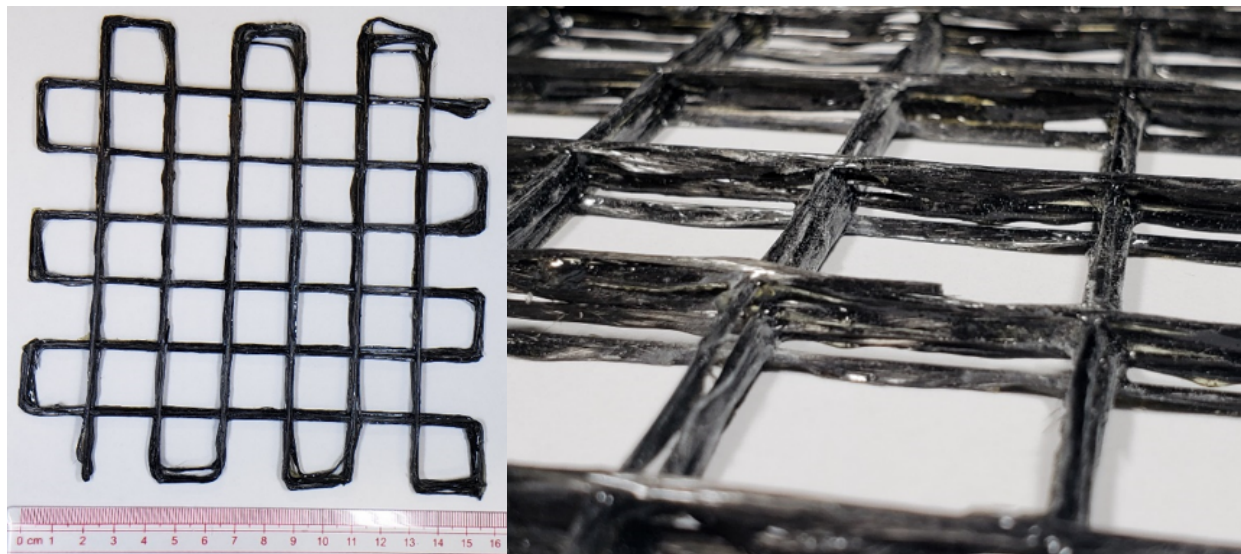


Figure. Continuous Carbon Fiber 3D Printed Complex Structure

- [1] Rahman, M.A.; Islam, M.Z.; Gibbon, L.; Ulven, C.A.; La Scala, J.J. *Polymer Composites* **2021**, *42*(11), 5859-5868.

Advanced Materials Creation from Local Resources in Extreme Environments

Jessica Vold, Abigail Olson, Christopher Matetich

Department of Mechanical Engineering, North Dakota State University, USA
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As NASA looks to create a long-term human presence on the surface of the Moon and Mars, how can we ensure those living in extra-terrestrial environments can extract the necessities of life from available resources? The extreme environment of outer space poses unique challenges for sustaining human life. With the cost to launch a kilogram of material aboard the SpaceX Falcon 9 rocket over \$2,900, it is unrealistic to launch all the required Earth-generated materials to build a permanent habitat to sustain human life on the Lunar or Martian surface. There is an urgent need to develop methodologies for in-situ resource utilization that autonomous rovers can utilize to help build habitats on the Lunar surface to support a long-term human presence on the Moon and one day Mars. When we can develop methods of material generation using only locally available resources on the Moon and Mars, we can translate those technologies back to Earth and modify those rovers to be deployed in remote, hard-to-reach locations guaranteeing the protection of human life everywhere.

My long-term goal is to create methodologies for extracting polymeric materials from locally available resources to create advanced composite materials for 3D printed habitats. The overall objective of this project is to understand the compatibility of regolith, or the unconsolidated rock and dust found above bedrock, with commercial polymers that could be created in-situ. My central hypothesis is that pretreatment of regolith will provide advanced composite materials for 3D printing that have a non-porous surface finish and have comparable material properties to conventionally created specimens. This hypothesis comes from preliminary data that created a porous-rough surface when parts were 3D printed from untreated Martian regolith filled polypropylene composites. The rationale for this work stems from a preliminary analysis of the regolith constituents that indicates the pretreatment of regolith can prevent individual constituents from thermally decomposing and generating oxygen that leads to a poor surface finish in an open to atmosphere manufacturing process such as 3D printing.

My research group has been focusing on the impact the addition of various regolith simulants has on commercially available polymers. We first started working with Martian regolith simulant, as the Martian atmosphere has theoretical paths to in-situ polymerization for several polymers including polypropylene. To limit the amount of polymer needed to create viable building materials my group investigated the addition of 10, 20, 30, and 40 wt% regolith in polypropylene. To further understand how the location of building sites on the Martian surface would impact the mechanical properties of the in-situ created materials, my team utilized four different Martian simulants developed at Exolith Labs. The global Martian regolith simulant is called MGS-1 and simulates the Rocknest windblown soils on Mars. MGS-1 enriched with smectite is designated MGS-1C. MGS-1S is MGS-1 enriched with polyhydrated sulfate gypsum. Finally, JEZ-1 simulates regolith found in the Jezero Crater deltas.

Additive manufacturing trials were conducted on a re:3D Terabot X pellet fed large area additive manufacturing printer with a roughly one cubic meter print volume. The biggest hurdle my team came across in our initial study was the surface finish of the 3D printed parts. The injection molded specimens had a smooth surface finish. The 3D printed specimens on the other hand had a very rough surface finish and the team noticed significant foaming of the extrudate as it exited the extruder on the printer. We are currently exploring the impact of Lunar regolith in commercially available polymers along with ways to improve the surface finish of the 3D printed parts.

Efficient, Well Controlled, Geminal Photoiniferters

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The polymerization of acrylate monomers initiated by photoiniferters is convenient, rapid, and capable of good control of molecular weight. We have designed novel geminal xanthate initiators that enable rapid polymerization kinetics with early initiation under a variety of light intensities. In addition, geminal dithiocarbamate initiators polymerize acrylate monomers more slowly, but conversely provide a greater level of control over molecular weight at high conversions when polymerized with high intensity LEDs. These differing properties are likely of value in a variety of practical applications, including the simple preparation of acrylic block copolymers.

Monomers, Polymers and Polymeric Materials from Plant Oils

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For last few decades industry is looking for new oleochemical materials as an alternative to crude oil-based counterparts. Since the early 90s renewable raw materials, most commonly vegetable oils, became increasingly attractive for making oleobased materials, particularly biobased polymers. Some of the biobased polymer materials can surpass existing petroleum-based polymers in various applications on a cost-performance basis.

We developed one-step method that converts fatty acid esters of plant/vegetable oils into biobased acrylic monomers for free radical polymerization. Current library of fifteen monomers from oils broadly varying in fatty acid esters chemical composition can be applied in the synthesis of polymers (including latexes) that utilize acrylic monomers. Plant oil-based monomers (POBMs) offer unique functionality due to combination of fatty acid fragments of varying unsaturation with saturated ones, which allows “on-demand” cross-linking, as well as may facilitate formation of crystalline domains, thus providing an ability to tune thermomechanical properties and performance of resulted polymeric materials.

This presentation discusses synthesis of POBM-based latexes, their potential to be used in adhesives, coatings, personal care products etc., as well as how incorporation of plant oil-based ingredients into bioplastic materials broadens an opportunity to substitute petroleum-based counterparts, and not only improve product sustainability but also enhance its performance.

Zinc Catalyzed Ring Opening Polymerization and Copolymerization for Sustainable Polymers

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Research efforts towards sustainable materials have been growing because of the finite nature of the petroleum resources and the potential hazardous effect of environmentally persistent plastics. In this context, polymeric materials that are biodegradable and can be wholly or partly bio-derived could play a key role in a sustainable future. Herein we present a series of amido oxazolinato zinc catalysts and their activity for the synthesis of polycarbonates, polylactides, and polyesters via ring opening polymerization and copolymerization. In particular, synthesis of isospecific polylactides and cyclic polyhydroxyalkanoates via ring opening polymerization of *rac*-lactides and lactones, respectively, has been achieved with zinc catalysis.

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1. Star-Shaped Poly(hydroxybutyrate)s from Bio-based Polyol Cores via Zinc Catalyzed Ring-Opening Polymerization of β -Butyrolactone. Omar, R.; Shaik, M.; Griggs, C.; Jensen, J. D.; Boyd, R.; Oncel, N.; Webster, D. C.; Du, G. *Eur. Polym. J.* **2021**, *160*, 110756.
2. Cyclic and Linear Polyhydroxybutyrates from Ring-Opening Polymerization of β -Butyrolactone with Amido-Oxazolinato Zinc Catalysts. Shaik, M.; Peterson, J.; Du, G. *Macromolecules* **2019**, *52*, 157-166.

High-throughput approaches to characterization of renewable materials using thermal carbon analysis and electrospray mass spectrometry



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When investigating approaches to lignin processing, developing high-throughput methods providing comprehensive product analysis is essential.

We present thermal carbon analysis (TCA) as a novel method allowing for fast quantification and thermal fractionation of carbonaceous constituents. The TCA provides insights on low and high molecular weight species, including repolymerized components (including volatile, semivolatile and pyrolytic fractions). This method allows for the determination of whether the commonly used gas chromatography with mass spectrometry (GC-MS) has merit to be employed for further product characterization. For detailed chemical characterization, the TCA can be used in combination with thermal desorption-pyrolysis GC-MS while employing a similar temperature programming, providing further insights on analyte speciation. The TCA quantification provided results similar to thermogravimetric analysis while being more effective in the characterization of thermally evolved fractions not visible by thermal gravimetry and specific to carbon, i.e., distinguishing the organic matter of lignin from water and other inorganic impurities.

For the determination of molecular weight distribution, we employ direct infusion electrospray ionization high-resolution time of flight MS. Under the optimized conditions, this method accounted for the production of multiply-charged ions and provided comparable results to those obtained by size exclusion chromatography.

Cancer Testbeds: A new frontier for treating bone metastasis

Kalpana Katti, Haneesh Jasuja, Sharad Jaswandkar, Hanmant Gaikwad, Preetham Ravi, Farid Solaymani, Shrinwanti Ghosh, Dr. Anu Gaba, Dr. Jiha Kim, Dr. Dipayan Sarkar, Dr. Kalidas Shetty, Dr. Dinesh Katti

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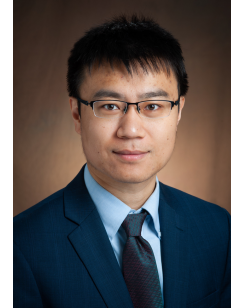


Bone biomaterials is a vast industry due to demands for bone replacement due to injuries, war and diseases. An important emerging for bone biomaterials is the need for robust invitro models of bone metastasis of cancer. According to WHO there are 3.4M incidences of breast and prostate cancer and 1M deaths per year due to bone metastasis. A novel tissue engineered bone construct is developed using nanoclays and the ability of the nanoclays to induce and promote osteogenesis. Experiments on seeding commercial and patient derived cancer cell lines on the tissue engineered bone are facilitated wit use of novel bioreactors that simulate physiologically relevant fluid-flow enabled shear stresses. The invitro model as presented represents a robust testbed for screening anti-cancer drugs. As the bone niche influences cancer cells, the vice versa is also observed. We report that the Wnt/β -catenin signaling governs osteogenesis within the cancer proximity. The initiation of metastasis is evaluated by experimental measurement of adhesion forces between cancer cells and bone using an aspiration-based AFM and molecular dynamics simulations. The novel testbed represents unique platform for investigation and treating bone metastasis.

Multiscale Modeling of Microstructure and Interface in Polymeric Structural Materials

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Department of Construction and Environmental Engineering
North Dakota State University



Natural and engineered load-bearing polymers and composites often achieve remarkable and intriguing structural and mechanical performance by confining their microphases in smaller dimensions. However, understanding and predicting their thermomechanical and deformational behaviors are inherently challenging due to their complex hierarchical microstructures and interfaces within the systems. In this talk, I will present a multi-scale modeling paradigm for understanding these complex phenomena occurring in nanocomposite materials. I will first introduce the scale-bridging computational techniques, namely the predictive coarse-grained modeling approach, for simulating complex materials at extended time and length scales. Following this, I will discuss several cases where the coupling between nanoconfinement and interface leads to intriguing phenomena in polymers and engineered materials. Using multiscale modeling, in conjunction with machine learning, I will illustrate how understanding microstructure and interfaces at molecular level can help us better design load-bearing composites and lightweight multifunctional materials.

Modeling the Autoxidation of Linseed Oil by Metal Driers

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Protective coatings derived from drying oils have been in use since at least the 15th century,¹ but have been substantially replaced with coatings made using petroleum products in the 20th century. New awareness of the health and environmental impacts associated with petroleum-based coatings has led to increased efforts to transition back to bio-derived coatings, however these efforts have been hindered by a relatively sparse understanding of the mechanisms by which drying oils convert into coatings.

The general mechanism by which drying oils form coatings is known as autoxidation. Autoxidation can be catalyzed by the addition of transition metal compounds known as driers. The precise role of the drier in the autoxidation process has been the subject of significant debate. My group recently developed a method for monitoring the autoxidation of drying oils using FT-IR and global analysis.² Using this method, we identified an intermediate species formed during the drying process that corresponds to a *cis-trans* conjugated species previously observed in studies of model compounds.³ The implications of this discovery will be discussed.

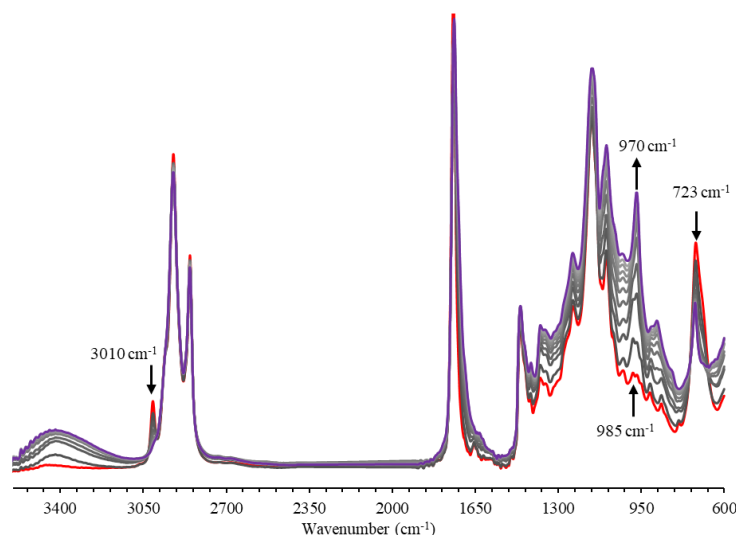


Figure. FT-IR time course for autoxidation of linseed oil by $\text{Co}(\text{hfac})_2$.²

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Poster Presentations

NDSU-KU Symposium Poster Presentations

10/6/2022

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| p-2 | Iryna | Bon | North Dakota State University |
| p-3 | Guodong | Du | University of North Dakota |
| p-4 | Azumi | Fukuyoshi | Kagoshima University |
| p-5 | Shokoofeh | Ghasemi | North Dakota State University |
| p-6 | Spencer | Gilman | North Dakota State University |
| p-7 | Alex | Hart | North Dakota State University |
| p-8 | Mitsuki | Hashiguchi | Kagoshima University |
| p-9 | Ryoma | Hayase | Kagoshima University |
| p-10 | Ivan | Hevus | North Dakota State University |
| p-11 | Wataru | Imamura | Kagoshima University |
| p-12 | Melody | Johnson | North Dakota State University |
| p-13 | Andrew | Kalbach | North Dakota State University |
| p-14 | Takaoka | Kyoka | Kagoshima University |
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| p-22 | Jufuku | Ryo | Kagoshima University |
| p-23 | Maryam | Safaripour | North Dakota State University |
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Fundamental adhesion studies of PDMS-based polymers for anti-icing applications using a JKR and shear test technique

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Ice accretion continues to be an ongoing threat for the performance of infrastructures or vehicles that work under cold conditions where ice is naturally formed. One possible approach to overcome ice accretion is the use of protective coatings that have low affinity to ice (anti-icing properties). Among the reported anti-icing coatings, PDMS coatings are still considered promising candidates for anti-icing applications. One of the challenges in the field is the lack of availability of trustworthy materials and interfacial properties. In this study, we aimed to provide robust data on the adhesion properties of several commonly used PDMS systems, including commercial PDMS and our own formulated PDMS made in house. Glass and ice adhesion tests were performed using two different techniques: a microscale technique by a JKR device and a macroscale shear testing technique using a universal testing machine. To the best of our knowledge, a JKR device to measure ice adhesion properties is introduced for the first time. The energy release rates (G) and Young's modulus (E) of the polymer coatings were measured at different temperatures and rates. Both techniques provided glass adhesion and ice adhesion values with certain similarities and differences. Results showed that adhesion depends not only on the surface chemistry of the samples but also on their mechanical properties.

Abstract

Sustainability improvement the biobased latex coatings

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A growing demand for developing sustainable materials has created an urgent need for identifying the best raw material resources such as renewable feedstocks and efficient pathways for their conversion to new products. Plant and vegetable oils have been shown as suitable sources for biobased monomer production with aim of widespread application in chemical industry, especially coatings and adhesives. In this work, several plant oil-based acrylic monomers (POBMs) for free radical polymerization were synthesized at lab-scale through transesterification reaction of camelina [*Camelina sativa* (L.) Crantz] oil and N-hydroxyethyl acrylamide (HEAA). Fragments of plant oil-based acrylic monomers (POBMs) have tendency to impact the thermomechanical properties of the resulting copolymers and enhance water resistance of the coatings made from latex. A comprehensive analysis is required to determine sustainability improvement of biobased materials, taking into consideration balance of the properties and cost efficiency. Laboratory-based data was used for prediction of the scaled-up production using process simulation in Aspen Plus while Life cycle assessment (LCA) method was used to evaluate the relative performance of the main designs with alternative solvents. To investigate the economic viability of the proposed design, techno-economic assessment (TEA) was further conducted to estimate the minimum selling price (MSP) of the monomer. Our analysis showed that using biobased solvents during monomer production can significantly improve its environmental performance. Results indicate positive contributions to monomer sustainability when recycling of solvents is implemented. Same is justified from economical point of view. Biobased alternative solvents not only reduce the toxicity of the monomer but also simplify the purification step. Finally, production cost efficiency is controlled by effectiveness of recycling lines and energy usage. Overall, analysis showed that the multi-criteria approach that combines TEA and LCA methodologies is a useful tool for the sustainable chemical development.

Zinc Catalyzed Ring Opening Polymerization and Copolymerization for Sustainable Polymers

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Research efforts towards sustainable materials have been growing because of the finite nature of the petroleum resources and the potential hazardous effect of environmentally persistent plastics. In this context, polymeric materials that are biodegradable and can be wholly or partly bio-derived could play a key role in a sustainable future. Herein we present a series of amido oxazolinato zinc catalysts and their activity for the synthesis of polycarbonates, polylactides, and polyesters via ring opening polymerization and copolymerization. In particular, synthesis of isospecific polylactides and cyclic polyhydroxyalkanoates via ring opening polymerization of *rac*-lactides and lactones, respectively, has been achieved with zinc catalysis.

References:

1. Star-Shaped Poly(hydroxybutyrate)s from Bio-based Polyol Cores via Zinc Catalyzed Ring-Opening Polymerization of β -Butyrolactone. Omar, R.; Shaik, M.; Griggs, C.; Jensen, J. D.; Boyd, R.; Oncel, N.; Webster, D. C.; Du, G. *Eur. Polym. J.* **2021**, *160*, 110756.
2. Cyclic and Linear Polyhydroxybutyrates from Ring-Opening Polymerization of β -Butyrolactone with Amido-Oxazolinato Zinc Catalysts. Shaik, M.; Peterson, J.; Du, G. *Macromolecules* **2019**, *52*, 157-166.

Development of low-viscosity adhesives by mixing catechol-functionalized siloxane copolymers with different compositional ratios

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In recent years, multi-material technology is mainly expected in the automobile industry, and it is important to develop an adhesive that can strongly adhere between dissimilar materials. Meanwhile, it has been reported that polymers with catechol structures, which are components of adhesion protein, exhibit strong adhesiveness.

So far, our group reported that siloxane copolymers (**PDMS/PS-Ph(OH)₂**) (compositional ratios A:B = 5:5, 6:4, 7:3, and 8:2) (Figure 1) with polydimethylsiloxane (PDMS) and catechol-functionalized polysiloxane (PS-Ph(OH)₂) components.¹ Especially, **PDMS/PS-Ph(OH)₂ (7:3 or 8:2)**, whose compositional ratios were 7:3 or 8:2, exhibited fairly strong adhesion to metallic materials (tensile shear stress when peeled off: >20 MPa). However, these adhesives were hard pastes at room temperature and need to be heated to ca. 50 °C when applied. For practical application of these adhesives, it is necessary to make them into a soft paste at room temperature.

In this study, we prepared **PDMS/PS-Ph(OH)₂** with different compositional ratios (7:3 and 19:1) (Figure 1) of PDMS and PS-Ph(OH)₂ components and mixed them to prepare a soft paste strong adhesive. Then, their viscosity and adhesion to metal materials were investigated.²

When two aluminum plates were adhered with **PDMS/PS-Ph(OH)₂ (19:1)**, the adhesion was not very strong (tensile shear stress when peeled off: 1.98 MPa). Therefore, **PDMS/PS-Ph(OH)₂ (19:1)** (viscosity: low, adhesion: weak) and **PDMS/PS-Ph(OH)₂ (7:3)** (viscosity: high, adhesion: strong) were mixed in a 1:3 weight ratio, resulting in a soft paste adhesive. When two aluminum plates were adhered with this mixture, the tensile shear stress when peeled off was ca. 10 MPa and these plates did not peel off by impact load, indicating relatively strong adhesion.

Furthermore, an aluminum plate and a stainless-steel plate having different thermal expansion coefficients were adhered using this mixture. When these plates were heated (to 150 °C) and cooled (to room temperature) with a 5 kg weight hung, the plates did not peel off.

We consider that the above strong adhesion is due to the well-balanced contribution of the strong interaction (mainly hydrogen bonding) of the catechol component with the metal substrate, the formation of chemical crosslinks between the catechol components, and the flexibility of the PDMS component.

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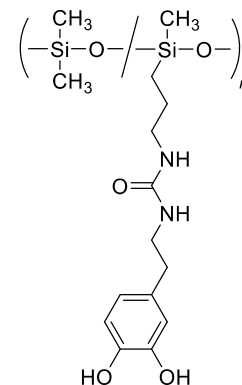


Figure 1. Structure of **PDMS/PS-Ph(OH)₂**.

Biodegradability of a Bio-based Coating (Epoxidized Sucrose Soyate) in Wastewater Environment

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Increasing efforts are being devoted to researching and developing bio-based materials that can effectively replace petroleum-based polymers in order to address the environmental concerns associated with their production, use and end-of-life. Epoxidized Sucrose Soyate (ESS) is a bio-based thermoset resin derived from sucrose and soybean oil that can be used in a wide range of applications such as adhesives, and coatings due to its high mechanical performance and enhanced functionalities. The extensive use of bio-based polymers urges understanding their behavior at the end of life, assessing the potential risk of bioaccumulation or leakage in the environment. We studied the biodegradability of ESS resin and ESS-based coating in wastewater (as their potential end-of-life scenarios) based on the biological oxygen demand of the material over time using a respirometer. The results show that ESS is readily biodegradable due to microorganisms' attack on ester linkages. However, biodegradation rate diminished for Cross-linked ESS.

Novel UV Curable Methacrylated Kraft Lignin Coatings

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Lignin is the most abundant source of renewable aromatic groups in nature. Lignin is underutilized as a feedstock is this is largely due to its heterogeneity. While this has been a hinderance in the past, using methacrylic anhydride has afforded a functionalized lignin. This functionalization generates methacrylic acid as a byproduct which allows the system to further functionalized by utilizing the acid functionality. The methacrylic acid also lowers the systems viscosity to prevent the need for solvents. The methacrylate functional groups can be polymerized through UV curing in the presence of ultraviolet light and photoinitiator. This solvent-free system produced a crosslinked, highly adhesive coating using methacrylate functionality. The coatings were very hard and had a high glass transition temperature.

Functional analysis of single-chain variable fragment antibodies that bind to *N*-glycolylneuraminic acid-containing sialyl Tn antigen

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Cancer cells express aberrant glycans, called tumor-associated carbohydrate antigens (TACAs), on their cell surface. TACAs are promising targets for developing anti-cancer antibodies and diagnostic markers. So far, several anti-TACAs antibodies such as anti-sialyl Tn and anti-sialyl Lewis A antibodies have been clinically used as diagnostic agents. Recently, *N*-glycolylneuraminic acid-containing sialyl Tn (Neu5Gc-Tn) antigen was found in human tumors^[1]. Since Neu5Gc should not be synthesized in humans due to a lack of genes for biosynthetic enzymes, Neu5Gc-Tn is a promising target for developing novel anti-cancer and/or diagnostic agents. Previously, we obtained three single-chain variable fragment antibodies (scFvs) that bind to sialyl Tn antigen using our original fiber type Sugar Chip^[2] immobilized with Neu5Gc-Tn and a phage display method (Figure 1). Here, we report their binding properties to liver cancer-derived HepG2 cell line, which is known to express sialyl Tn antigen^[3].

The binding properties of three scFvs were evaluated by ELISA, in which membrane proteins of HepG2 cells were coated on the plastic plate and anti-His tag (6xHis) antibody against 6xHis sequences in scFvs were used for detection. Three scFvs showed a dose-dependent binding. On the other hand, the scFvs that have no specificity to sialyl Tn antigen did not show binding potencies to the membrane proteins. To investigate the specificity of the three scFvs to glycans on the HepG2 cell membrane, an inhibition assay was performed using commercially available anti-Neu5Gc IgY or anti-sialyl Tn antigen IgG antibodies. The binding of three scFv to the membrane proteins was significantly inhibited. When the membrane protein was treated with *N*- and/or *O*-glycosidases, the binding was significantly decreased. These results suggest that three scFvs selectively recognize sialyl Tn antigen on HepG2 cell membrane proteins.

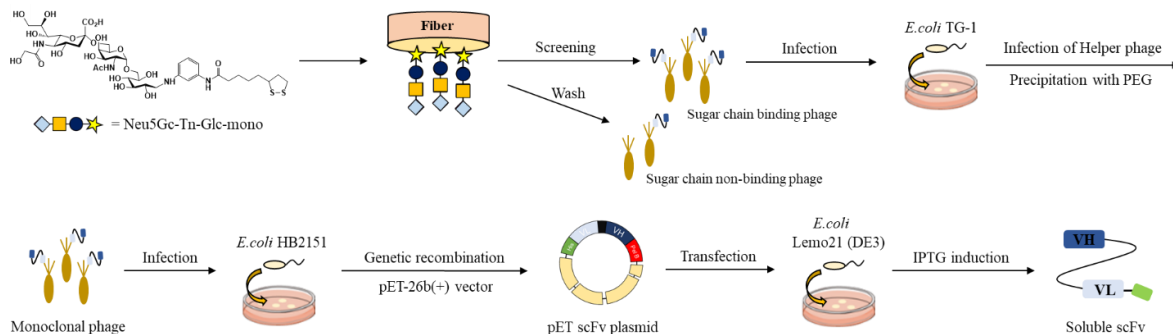


Figure 1. Preparation of the scFv that binds to Neu5Gc-Tn antigen

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Synthetic study on heparan sulfate partial structure partial structure

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Heparan sulfate (HS) is a heterogeneous sulfated polysaccharide classified in the glycosaminoglycan (GAG). HS universally exists on the cell surface and in the extracellular matrix in the form of proteoglycans covalently bound to the core protein. HS is constructed a disaccharide repeating unit consisting of glucosamine (GlcN) and uronic acid (glucuronic acid: GlcA or iduronic acid: IdoA). In the biosynthesis, HS is subjected to random enzymatic modifications such as *N*-deacetylase/sulfo-transferase, C5-epimerase, *O*-sulfotransferase, resulting in various glycan and sulfate patterns in the HS chain. In recent years, it is suggested that a certain microstructure of HS is involved in specific biological interactions. Therefore, the structural activity correlation (SAR) analysis is important.

To perform SAR analysis of HS, our laboratory has developed a disaccharide building block that can systematically synthesize hs partial Heparan disaccharide structures. In the GlcN-GlcA sequence, all 16 estimated disaccharide structures are synthesized^{1),2)}. In this study, to investigate HS biofunctions, we systematically synthesized HS disaccharide structures containing GlcNAc-IdoA sequence. The synthetic strategy for HS partial disaccharide structure is shown in Figure. So far, IdoA moiety 1 and GlcN moiety 2 were prepared from appropriate monosaccharides. Disaccharide building blocks 3 were prepared by glycosylation of monosaccharide moieties. HS partial disaccharide structure will be obtained from 4 by selective deprotection, sulfation, and global deprotection.

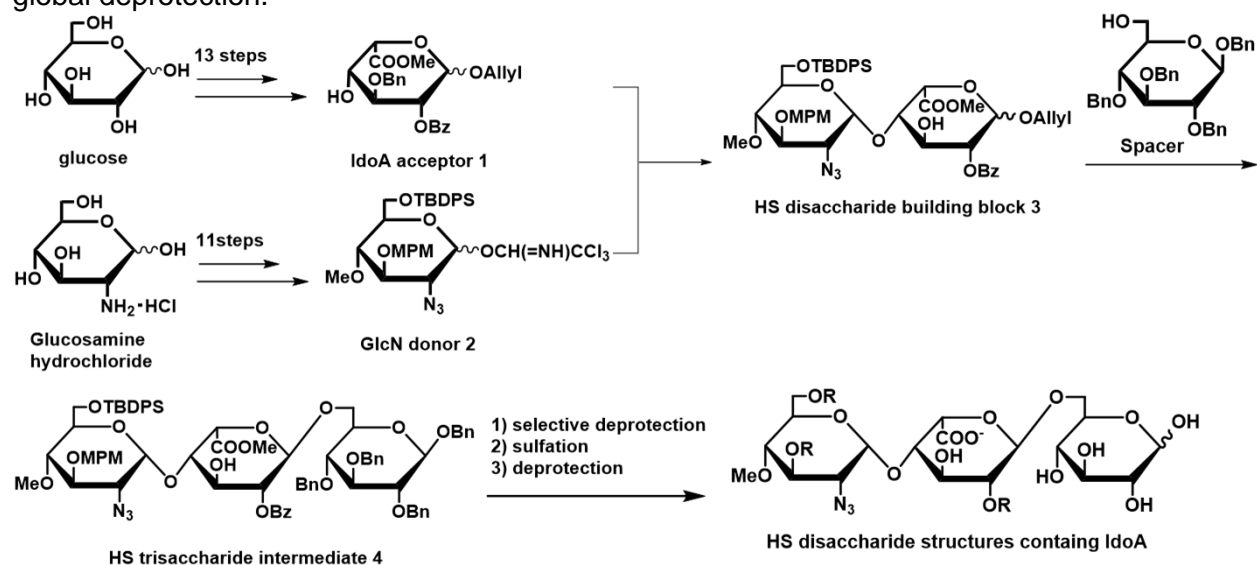


Figure. Outline for Synthesis of HS disaccharide partial structure

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Novel Bio-Based Reactive Diluents for Stereolithography

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Stereolithography (SLA) is an established and popular additive manufacturing (3D printing) technique that allows the fabrication of solid objects via photopolymerization of a liquid resin quickly with high precision and low material consumption. A typical SLA formulation consists of a relatively high-molecular-weight polymerizable resin(s) mixed with one or several low-molecular-weight reactive diluents that reduce the overall viscosity of the composition and copolymerize with the resin during the 3D printing process. Nowadays, petroleum-based acrylates constitute the majority of commercially available reactive diluents, however, the push for increased sustainability stimulates the development of new high-performance substituents from renewable raw materials. In the current work, the performance of a series of bio-based difunctional acrylates as reactive diluents was evaluated in a model SLA resin system. When compared to 1,6-hexanediol diacrylate (HDDA), a widely used petroleum-based difunctional diluent, the new bio-based diluents offer significantly improved mechanical properties (Young's modulus, tensile strength, as well as tensile and fracture toughness values) of the 3D printed parts, while maintaining the viscosity of the SLA formulation low. The use of new bio-based acrylates also increases the glass transition temperature of the 3D printed resin. This combination of properties makes the new difunctional acrylates promising candidates for use as reactive diluents in SLA resin formulations.

P-11

The molecular interaction of cyclodextran with a guest molecule using quantum chemical calculation and molecular dynamics simulation

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Cyclodextran (CI) is a cyclic oligosaccharide in which D-glucose forms a ring structure by α -1,6 glycoside linkage and forms an inclusion complex with various guest molecules. In this study, we conducted quantum chemical calculations and molecular dynamics (MD) simulations to analyze the molecular interaction mechanism of CI with a guest molecule. Calculations of cyclodextrin (CD), in which D-glucose forms a ring structure by α -1,4 glycoside linkage, were also performed for comparison. Here, coenzyme Q10 (CoQ10), a promising molecule for industrial application with CI, was chosen as a guest molecule.

Our quantum chemical calculation demonstrated that CD is a steric structure with a deep hydrophobic cavity. This characteristic is well-known and crucial for the ability to form an inclusion complex with guest molecules.⁽¹⁾ On the other hand, CI is a more planar structure without a deep cavity.

The MD simulation showed that both CI and CD had similarly large molecular fluctuations in the absence of CoQ10, based on the wide distribution of atomic distance and tilt angle. In the case that CoQ10 exists, the CD was found to form a rigid one-by-one inclusion structure, while CI does not.

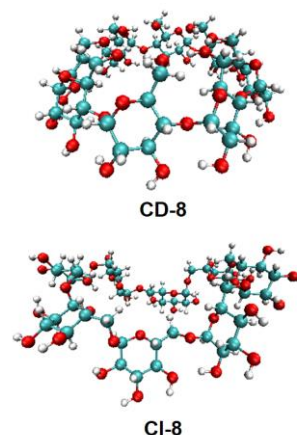


Figure 1: Energy minimized structures of CD-8 and CI-8

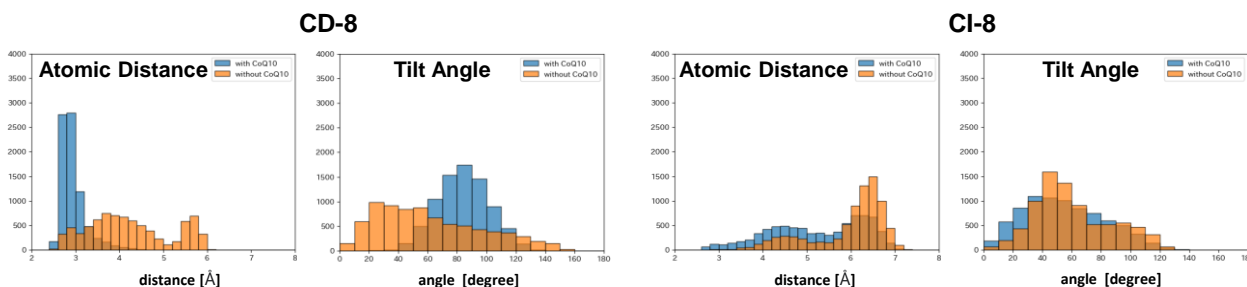


Figure 2: Distribution of atomic distance and tilt angle of the trajectory of the MD calculation for CD-8 and CI-8

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Bio-Based Imide Resins for Stereolithography

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Additive manufacturing (3D printing) is a technique that has begun to revolutionize many different production industries. It can be used to make a wide variety of items from body tissues to construction materials to art and beyond. Stereolithography (SLA) 3D printing uses photopolymerization of liquid monomers as the method to form parts. While acrylates and epoxy resins constitute the majority of commercially available monomers for SLA, other chemistries capable of forming high-performance polymer materials are also being explored. Polyimides, among others, show promise due to their exceptional thermal and mechanical properties, as well as chemical and corrosion resistance. Bismaleimides, in particular, are interesting starting materials for SLA resins due to their ability to undergo a variety of addition reactions like Alder-ene and Diels-Alder reactions in the post curing stage. In this regard, we studied the reaction between 4,4'-bismaleimidodiphenylmethane and a series of novel biobased diallyl monomers yielding aromatic imide resins. Furthermore, two formulations containing the synthesized imide resins were successfully printed, showing that the bismaleimide-diallyl monomer system has the potential to work as a 3D printable resin. Further testing is still required to determine the mechanical and thermal properties of each formulation and evaluate the overall effectiveness of the system.

P-13

Modeling Linseed Oil Autoxidation Through Global Analysis

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While the autoxidation of linseed oil has been extensively studied, the role of metal driers in catalyzing this process remains poorly understood. Previous studies have demonstrated that Fourier Transform Infrared spectroscopy (FT-IR) can be used to monitor the progress of autoxidation during linseed oil drying. Typically, studies have focused on a single absorption at 3010 cm^{-1} to determine the rate of autoxidation. In this study, FT-IR spectra of linseed oil during autoxidation were measured between 3800 and 700 cm^{-1} and fit to kinetic models using global analysis. This method revealed that the drier catalyzed autoxidation process is best modeled as an $\mathbf{A} \rightarrow \mathbf{B} \rightarrow \mathbf{C}$ type reaction, with \mathbf{B} corresponding to a cis-trans conjugated intermediate previously identified in model complex studies. These kinetic models further revealed that for three Co driers the rate constants for the $\mathbf{A} \rightarrow \mathbf{B}$ and $\mathbf{B} \rightarrow \mathbf{C}$ reactions are identical within experimental error, suggesting both reactions share a rate limiting step.

Synthetic study on heparan sulfate tetrasaccharide containing GlcNS3S6S-GlcA tandem structure

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Heparan sulfate (HS) is one of the sulfated polysaccharides classified in the glycosaminoglycan (GAG) family. It consists of a repeating structure of disaccharide units containing glucosamine (GlcN) and uronic acid (UroA, glucuronic acid: GlcA, or iduronic acid: IdoA). HS exists on cell surfaces and in the extracellular matrix and is involved in various biological processes. Recently, the microstructure in HS chains has been considered to regulate biological signals such as cell development, proliferation, and canceration, so that the structure-activity relationship analysis of HS at the molecular level has been conducted. Previously, we have constructed the HS library containing GlcN-GlcA disaccharide partial structures^[1,2], and have analyzed the interaction of HS disaccharides with various proteins by surface plasmon resonance (SPR) imaging sensors^[3]. As the result, we found that GlcNS3S6S-GlcA disaccharide structure was bound to Wnt-5b proteins.

In this study, to investigate the interaction of HS microstructure with Wnt-5b in more detail, we carried out the synthesis of tetrasaccharide structure including dimeric GlcNS3S6S-GlcA sequences. GlcN moiety **1** and GlcA moiety **2** were synthesized from appropriate monosaccharides, respectively. Disaccharide building blocks **3** and **4** were then prepared by the glycosylation of monosaccharide moieties. Pentasaccharide precursor **7** was obtained from glycosyl donor **5** and acceptor **6**. HS partial tetrasaccharide structure **8** will be obtained from **7** by selective deprotection, sulfation, and global deprotection.

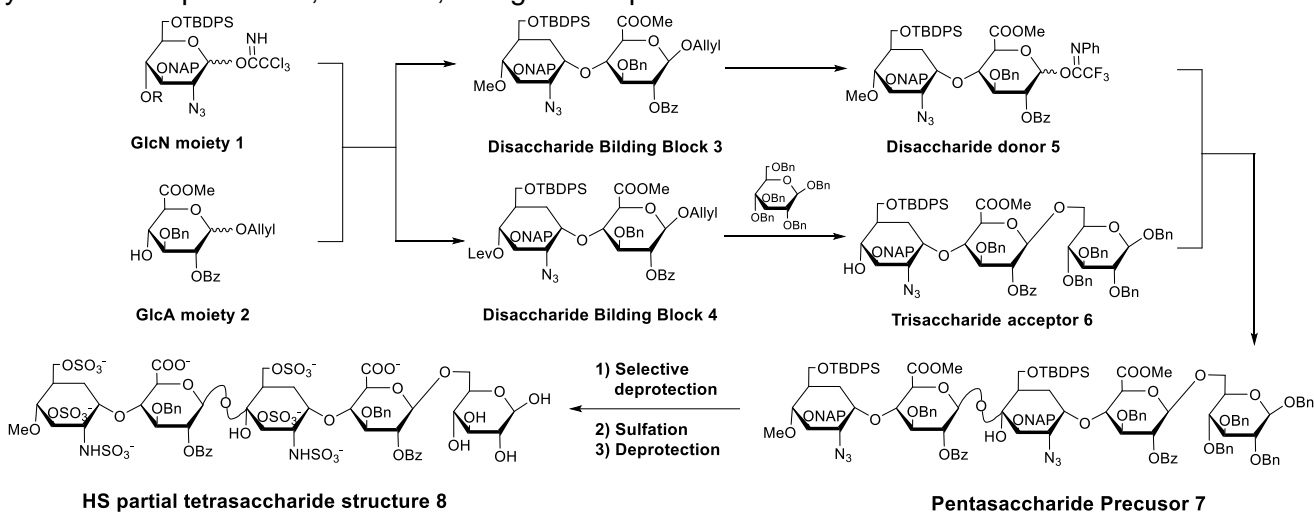


Figure. Synthetic outline for HS tandem GlcNS3S6S-GlcA tetrasaccharide structure.

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Preparation of amphiphilic ladder-like polymer in which hydrophilic polyether and hydrophobic polysiloxane chains are intramolecular cross-linked and stability of its nanoaggregate formed in water

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Nonionic amphiphilic polymers are widely used because of their characteristics such as stable nanoaggregate (e.g., micelle and vesicle) formation even in water containing salt. However, many nonionic amphiphilic polymers are known to have temperature-sensitive polyethylene glycol (PEG) chains in their hydrophilic segments, and only a few of them can stably form and micelles and vesicles under high temperature conditions.

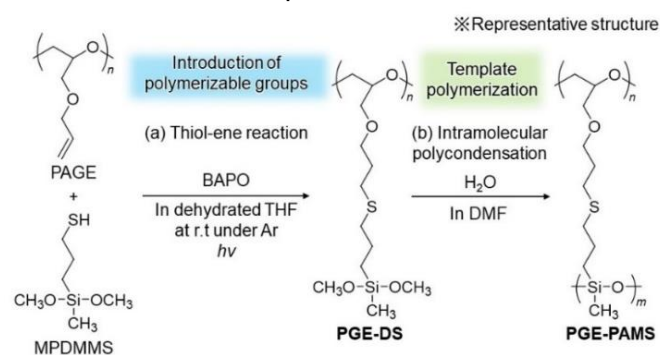
Recently, our group developed a ladder-like polymer (**PAAm-PAMS**), in which a hydrophilic polyacrylamide (PAAm) chain and a hydrophobic polyalkylmethylsiloxane (PAMS) chain were linked in parallel, as a new type of nonionic amphiphilic polymer.¹ **PAAm-PAMS** was prepared by intramolecular polycondensation (template polymerization) of PAAm containing dialkoxysilyl groups in the side chains as a precursor by heating in a dilute solution. Furthermore, it has been found that the **PAAm-PAMS** nanoaggregates formed in water were stably maintained without its collapse or formation of macroscopic aggregates even at high temperatures. However, because the hydrophilicity of **PAAm-PAMS** is rather weak, to prepare an aqueous solution, it is necessary to dissolve **PAAm-PAMS** in methanol, add water, and then evaporate the methanol.

In this study, for the purpose of developing a new amphiphilic ladder-like polymer, we prepared a ladder-like polymer (**PGE-PAMS**), in which a hydrophilic poly(glycidyl ether) (PGE) chain and a hydrophobic PAMS chain were linked in parallel. The preparation of **PGE-PAMS** was performed by introducing 3-mercaptopropyl dimethoxymethylsilane (MPDMMS) into the side chains of poly(allyl glycidyl ether) (PAGE) by a thiol-ene reaction (Scheme 1a), followed by water-catalyzed intramolecular polycondensation of dimethoxysilyl groups in dilute DMF solution (Scheme 1b). **PGE-PAMS** was soluble in water and organic solvents such as DMSO, methanol, ethanol, and isopropyl alcohol, indicating amphiphilic property.

PGE-PAMS formed nanoaggregates of ca. 60-100 nm in water at room temperature and maintained the formation of nanoaggregates when heated up to 90 °C. Moreover, the nanoaggregate formed in water can include hydrophobic tetraphenylporphyrin (TPP), and this inclusion state was maintained even at high temperatures such as 90 °C. From the above results, it was concluded that the nanoaggregate of **PGE-PAMS** formed in water was stable under high temperatures.

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Scheme 1. Preparation of (a) **PGE-DS** and (b) **PGE-PAMS**.

Development of glyco-nanoadjuvants using TLR9 ligand for adjuvant immunotherapies

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Immunotherapy has become a powerful strategy for treating infectious diseases and cancer in the past decade, and numerous researchers have been exploring a new class of immunostimulatory agents. Agonistic ligands of toll-like receptors (TLRs) that activate innate immunity are one of the promising candidates as adjuvants (immunostimulatory molecules) for antiviral or antitumor immunotherapies. So far, a lot of TLR ligands have been synthesized and investigated in clinical studies. Among various TLR ligands, TLR9 ligands which are oligodeoxynucleotides containing unmethylated CpG motifs (CpG ODN) are expected to be effective adjuvants. However, TLR9 ligands have several drawbacks such as low stability and low cell membrane permeability. Nanoparticles have been extensively employed as gene delivery system since they can protect DNA from nuclease degradation and promote cellular uptake. Previously, we developed glyco-nanoadjuvants that are gold-nanoparticles (GNPs) co-immobilized with purine-like synthetic small molecule TLR7 ligands and sugar chain and demonstrated that the potency of a small molecule TLR7 ligand is significantly enhanced by selective delivery to immune cells using sugar-chain immobilized GNPs as a carrier [1]. In this study, we examined α -mannose immobilized GNPs as a carrier for synthetic TLR9 ligands, CpG ODN to overcome the drawbacks of TLR9 ligands and investigated in vitro immunostimulatory activities of the novel glyco-nanoadjuvants using TLR9 ligands.

To immobilize CpG ODN onto the GNP surface, thioctic acid was conjugated to the 3' end of the CpG ODN. GNPs co-immobilized with CpG ODN and α -mannose (CpG- α Man-GNPs) were prepared according to the method described previously with slight modifications [1]. The hydrodynamic diameters measured by dynamic light scattering in phosphate-buffered saline of the resulting CpG- α Man-GNPs were approximately 8 nm. CpG ODN immobilized on GNPs was quantified using QuantiFluor ssDNA system (Promega) after degradation of GNPs using potassium cyanide. α -Mannose immobilized on GNPs was quantified by labeling with 4-aminobenzoic acid ethyl ester after hydrolysis with trifluoroacetic acid. The molar ratio of CpG ODN and α -mannose immobilized on GNPs was approximately consistent with that of the molar ratio in preparation. In vitro immunostimulatory activities of CpG ODN- α Man-GNPs were tested in mouse bone marrow-derived dendritic cells. Then, CpG ODN- α Man-GNPs showed higher induction of Interleukin-6 (IL-6) and IL-12(p40/p70) production than that of unconjugated CpG ODN, indicating that conjugating CpG ODN to α Man-GNPs enhances immunostimulatory activities.

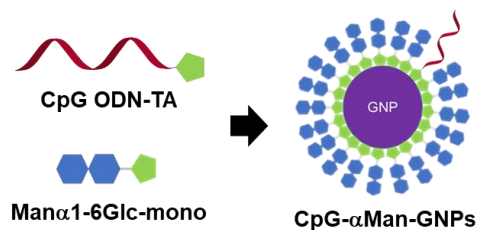


Fig. Illustrate for GNPs co-immobilized with CpG ODN and α -mannose.

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Preparation of antifogging films with hard-coating property by combining c functionalized POSS and polyvinyl alcohol

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Fogging occurs when water vapor condenses on a cold surface to form droplets large enough to scatter light. Coating the surface of the substrate with a hydrophilic material is currently the mainstream as antifogging technology. There are two types of these materials: inorganic material films such as TiO_2^1 and SiO_2^2 , and organic polymer films. Inorganic material films are required UV conditions and high temperature treatment. Therefore, the organic polymer films are expected as antifogging films due to their easy molding. However, there is a problem that the surface hardness is low and easily scratched.

Based on the above research background, “hybrids” and “inorganic polymers” that have the characteristics of both organic polymers and inorganic materials are expected as antifogging films with hard-coating properties. For example, organic-inorganic hybrid films in which inorganic nanoparticles such as silica were introduced as fillers into hydrophilic polymers such as polyvinyl alcohol (PVA)³ and polysilsesquioxane films prepared by hydrolytic condensation of silane coupling agents containing amino⁴ and glycidyl groups⁵ have been reported so far. Recently, we also reported the development of antifogging films with hard-coating property using a polymer linked polyhedral oligosilsesquioxanes (POSS) containing amino and carboxyl side-chain groups.⁶

In this study, carboxyl-functionalized POSS (POSS-C)⁷ with hydrophilicity and hard-coating property and PVA with hydrophilicity and film-forming property were combined to prepare antifogging films with hard-coating property.

First, POSS-C and PVA were mixed in water, and aqueous HCl solution was added as a catalyst for forming ester linkage. Then, the mixed solution was concentrated, applied onto the glass substrate, and heated to form the colorless and transparent cast films. It was found that the cast film prepared with the molar ratio of repeating units of POSS-C and PVA of 9:1 exhibited excellent antifogging and hard-coating properties.

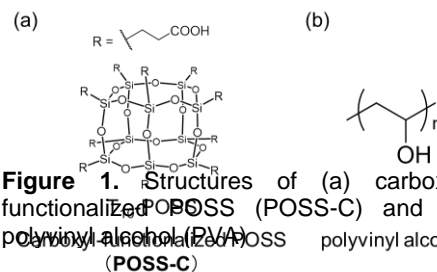


Figure 1. Structures of (a) carboxyl-functionalized POSS (POSS-C) and (b) polyvinyl alcohol (PVA).

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Preparation of polysiloxanes containing imidazolium component in their side chains and application to CO₂ separation membranes



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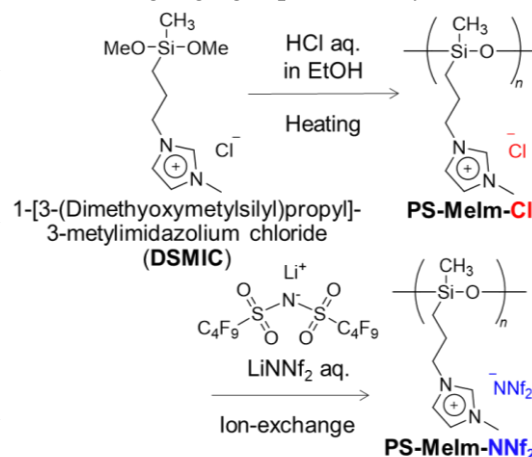
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The development of technology to solve global warming is an urgent issue. Among the conventional CO₂ capture technologies, the membrane separation is considered to be promising because of its low energy intensity, small foot-print, simpleness and hazardless process. However, because conventional gas separation membranes have low CO₂ permeability, a large pressure difference and wide area are required to separate low-concentration CO₂. Therefore, it has been considered virtually impossible to capture CO₂ gas by direct air capture (DAC) technology using membranes. Recently, Fujikawa et al. reported CO₂ separation (CO₂/N₂ selectivity: *ca.* 11) by a polydimethylsiloxane (PDMS) thin membrane that indicated excellent gas permeability and mechanical property.¹ This membrane may have the potential for CO₂ separation by DAC.

In this study, in order to enhance CO₂/N₂ selectivity while maintaining high gas permeability and mechanical property of PDMS, we prepared polysiloxanes containing imidazolium component in their side chains and applied these polysiloxanes on surface of the above PDMS membrane. Furthermore, gas permeance and gas selectivity of the resulting composite membranes were investigated.

The polysiloxanes (**PS-MeIm-X** [X = Cl and NNf₂]) were prepared by hydrolytic polycondensation of imidazolium-group-containing dialkoxysilane (**DSMIC**²) in ethanol using aqueous hydrochloric acid (HCl) as a catalyst, followed by converting Cl counterion to bis(nonafluorobutanesulfonyl)imide (NNf₂) anion. On the other hand, the surface of PDMS membrane was modified with α -thioglycerol (TG) (thiol-ene reaction) to improve the wettability between **PS-MeIm-X** and PDMS. Subsequently, composite membranes (**PS-MeIm-Cl/TG/PDMS** and **PS-MeIm-NNf₂/TG/PDMS**) were obtained by drop-casting methanol solutions of **PS-MeIm-X** on the surface-modified PDMS membrane. CO₂/N₂ selectivity of **PS-MeIm-NNf₂/TG/PDMS** was improved to *ca.* 15 compared with only a PDMS membrane (*ca.* 11). However, CO₂ permeability of this membrane was significantly reduced. We are currently considering these improvements.



Scheme 1. Preparation of **PS-MeIm-X** (X = Cl, NNf₂).

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P-19

Synthesis and characterization of novel biobased epoxidized sucrose cornate

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A novel biobased high functionality epoxy resin was synthesized from the epoxidation of sucrose cornate (SC), which was also synthesized. SC was synthesized via the esterification of corn oil methyl ester onto sucrose. The double bonds from the corn oil fatty acid chain were then converted to epoxy groups via a reaction with peracetic acid, generated from acetic acid and hydrogen peroxide in the presence of ion-exchange resin, to produce epoxidized sucrose cornate (ESC). The conversion of these double bonds was measured to be over 95%. Both the SC and the ESC were characterized via and nuclear magnetic resonance (NMR) spectroscopy and Fourier-transform infrared (FTIR) spectroscopy. Thermoset coatings were also prepared by crosslinking the ESC with 4-methyl hexahydrophthalic anhydride (MHHPA) in the presence of a zinc catalyst in varying epoxy-to-anhydride ratios. Chemical, mechanical, and thermal properties were investigated. Both SC and ESC have well-defined structures as a sucrose core with eight corn oil fatty acids. Each macromolecule has high epoxy functionality (8-15 epoxy groups). These reactive groups allow for further derivatization of ESC.

Sustainability assessment of lignin valorization into rigid foams

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Lignin is the second most abundant biopolymer on earth. The bulk of technical lignin produced is burned as a low-value fuel. Valorizing lignin into higher-value chemicals can create higher economic incentives for producers and potentially lower the environmental footprint compared to conventional chemicals. Lignin valorization can be achieved through multiple possible pathways including depolymerization, chemical modification, and macromolecular application. However, before recommending any valorization pathway, economic and environmental assessments are needed.

One application of lignin can be to produce rigid foams. The aromatic and aliphatic hydroxyl functional groups in lignin can be substituted with acetoacetate functionality to produce acetoacetylated lignin resin. This resin can be crosslinked with amines and a siloxane blowing agent to get foam. The advantages of this process are 1) the polyol used in the reaction mixture functionalizes with acetoacetate and acts as a reactive diluent while crosslinking the resin, and 2) the process is waste-free as no extra solvents are used in the process.

In this study, we perform an economic and environmental assessment of lignin-based foam. Techno-economic and life-cycle methods are used to perform the sustainability assessment. Our results show that lignin-based foam has a minimum selling price of \$6.48/kg compared to \$9/kg for rigid polyurethane foam. Uncertainty analysis shows lignin-based foam has the potential to be economically competitive with polyurethane foam under a variety of possible circumstances. Similarly, life cycle assessment shows lignin-based foam performs better in all impact categories except ozone depletion and fossil fuel depletion. For both economic and environmental analysis, tert-butyl acetoacetate (lignin functionalizing chemical) and amine crosslinker have the greatest contribution. Overall, the result showed that the mass-based comparison of lignin foam is better than polyurethane foam. However, when a different functional unit such as volume is used, then lignin foam may perform worse than polyurethane foam due to the higher density of lignin foam.

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Furanic Di(meth)acrylates Synthesis from Sustainable Biomass Diol as Diluents for UV Curvable Coatings

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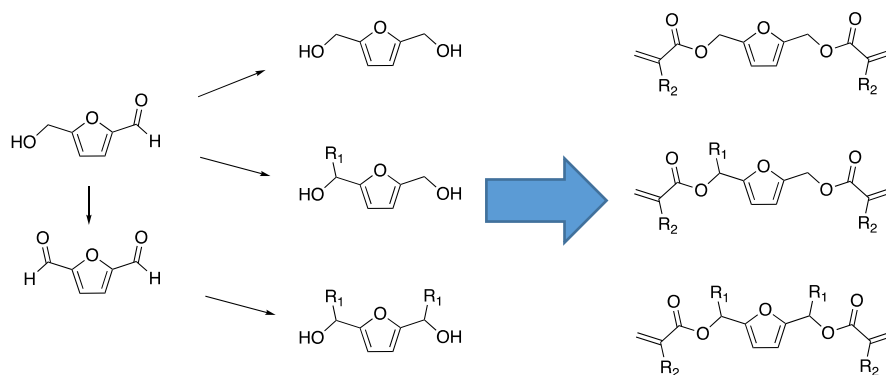
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UV curing is gaining popularity due to its distinct economic and ecological benefits, such as quick curing at room temperature, solid phase, low volatile organic compounds formulations, efficient energy consumption, and high-performance coatings.¹ Therefore, UV-curable coatings are frequently utilized for furniture, printing, plastic substrates, wood, optical fibers flooring, headlight lenses, and metal substrates.² 5-Hydroxymethylfurfural (HMF) is a promising biomass-derived compound with great potential for the synthesis of biofuels, polymers, solvents, pharmaceuticals, and other useful molecules. Bis-hydroxymethyl furan dimethacrylate was synthesized and used as a monomer to prepare polymeric materials via proton transfer polymerization.³ Thiol-Michael addition polymerization was utilized with diacrylate of bis-hydroxymethyl furan. Recently, our team developed a method for producing high yields of several symmetric and asymmetric diols derived from HMF.⁴ Here, we investigate the synthesis of the diols acrylation and methacrylate derivatives, which have potential uses in polymer applications.⁵



Scheme. Furanic Di(meth)acrylates Derivatives from HMF

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Study for development of the nasal vaccines against viral infectious diseases

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Nasal vaccines are modern attempts to elicit protective immune responses directly at the nasal mucous membrane (Figure 1). There are many advantages to nasal vaccines compared to conventional vaccines administered by intramuscular routes. Most importantly, nasal vaccines can induce protective immune responses at the mucosal nose, which is the major pathogen entry site, by producing pathogen-specific IgA and IgG antibodies. To date, very few nasal vaccines have been approved by U.S. food and drug administration for clinical use in humans. To develop novel effective nasal vaccines, adjuvants (immunomodulators) are essential components for promoting potent and persistent immune responses. In this study, we evaluated the immune-activating effects of the originally synthesized nano-sized adjuvant to develop a novel nasal vaccine.

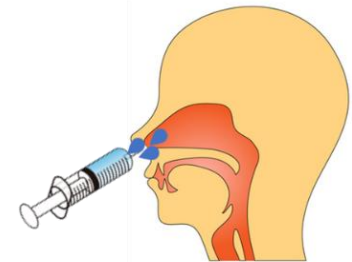


Figure 1. Image of nasal vaccine

To determine the optimal dosage of the adjuvant, ovalbumin (OVA) was initially used as a model protein antigen. The mice were intranasally injected with OVA and the nano-adjuvants (0.2, 2, or 20 nmol) once a week for three weeks, and nasal wash and blood were then collected 21 days after the first immunization. Antibody titers were estimated by ELISA method, and IgA and IgG titers specific to OVA increased in a dose-dependent manner of the nano-sized adjuvant both in the nasal mucosa and blood, indicating that nano-sized adjuvants effectively enhanced immune responses against specific protein antigen. Next, to evaluate the immune-activating effects of the nano-sized adjuvant with protein antigen of influenza virus, commercially available recombinant hemagglutinin (HA) and influenza HA vaccine (SEIKEN) were tested. The results showed that nano-sized adjuvant significantly enhanced induction of anti-HA IgA and IgG antibody production compared to that of adjuvant-untreated controls. These results suggest that our nano-sized adjuvant is an effective adjuvant for the nasal influenza vaccine.

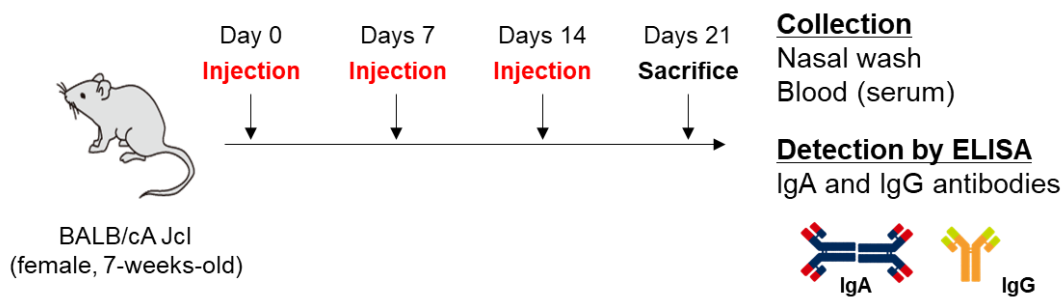


Figure 2. Immunization schedule of the vaccines

Model silicone elastomers containing silicone oils for reduced fouling and ice adhesion

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While silicone elastomers containing oil additives have been used to reduce adhesion of fouling organisms and ice adhesion, in order to clearly understand the role of the oils it is necessary to create well-defined and well-characterized model systems to control coating compositions and mechanical properties and link composition to performance. The purpose of this study was to investigate the influence of different free silicone oils on biofouling and ice release performance of silicone-based elastomer. Model elastomer systems were characterized using gel content, FTIR, DSC and TGA. After adding different silicone oils (e.g., phenylsilicone oils) to the model elastomers, water contact angle, surface energy, tensile strength, ice adhesion and adhesion strength of biofouling were used to evaluate the effect of silicone oils on silicone elastomer properties. The results showed that the incorporation of oils into the silicone elastomers improved the biofouling and ice release performance of silicone-based elastomers.

Keywords: PDMS coatings; Silicone oils; Surface energy; Anti-icing; Anti-biofouling.

Stereostructural control of cyclic siloxanes with imidazolium and methyl side-chain groups

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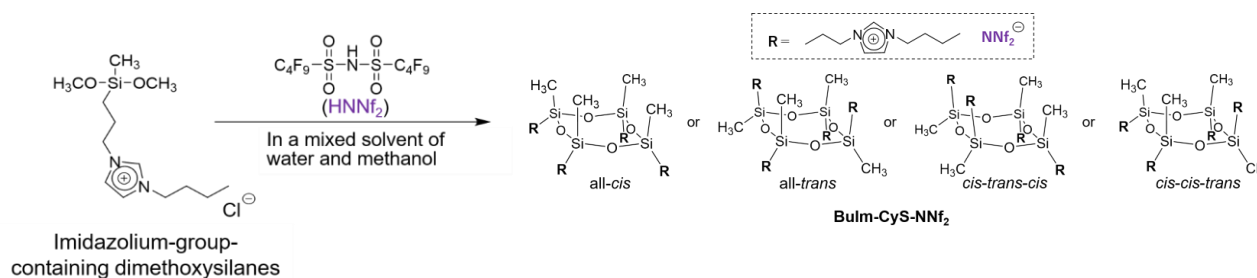
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Cyclic siloxanes are obtained by hydrolytic condensation of silane compounds containing two reactive groups (-Cl or -OR [R = CH₃, C₂H₅]) and two organic side-chain groups as the starting materials. However, the reaction of such silane compounds usually results in a mixture of cyclic and linear compounds with various molecular weights. Furthermore, in the case of use the silane compounds with different side-chain groups, the resulting cyclic siloxanes with same molecular weights have some stereoisomers. For example, cyclic tetramer have four stereoisomers. Generally, it difficult to selectivity prepare a single cyclic siloxane without stereoisomers.

Our group previously reported that a single (*cis-trans-cis*) cyclic tetrasiloxane containing propylammonium trifluoromethanesulfonate and methyl side-chain groups (Am-CyTS) was selectively prepared by the hydrolytic condensation of 3-aminopropyldiethoxymethylsilane (APDEMS) using aqueous CF₃SO₃H.¹⁾ However, use of the different starting materials (e.g. imidazolium-containing dialkoxysilanes)²⁾ and the catalysts (e.g. bis(trifluoromethane sulfonylimide): HNTf₂)³⁾ could not give the single cyclic siloxanes.

In this study, to prepare a new single cyclic siloxane without stereoisomers, we investigated hydrolytic condensation of bifunctional alkoxy silanes with various imidazolium and methyl side-chain groups using various superacid solutions as catalysts and solvents. Consequently, we found that a single cyclic tetrasiloxane (**Bulm-CyS-NNf₂**) was obtained by a hydrolytic condensation using an alkylmethyl dimethoxysilane with butyl group-containing imidazolium side-chain as the starting material and a bis(nonafluorobutane sulfonylimide) (HNNf₂) as the catalyst in water-methanol (1:19) mixed solvent (Scheme 1). The formation of a single cyclic tetrasiloxane was confirmed by the ¹H NMR, ²⁹Si NMR, and MALDI-TOF MS analyses. However, a stereostructure of **Bulm-CyS-NNf₂** has not yet been determined. We are currently investigating to prepare a single crystal for X-ray structural analysis.



Scheme 1. Preparation of a single cyclic tetrasiloxane (**Bulm-CyS-NNf₂**).

for X-ray structural analysis.

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Development of fluorescent nanoparticles immobilized with single-chain variable fragment antibody as an imaging probe

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A single-chain variable fragment (scFv) is a fusion protein of the variable region of heavy (V_H) and light chains (V_L) of immunoglobulins connected with a short linker peptide. It works like an antibody as a therapeutic, diagnostic, or analytical agent. To use scFv as an imaging probe, scFv is often labeled with fluorescent dye. In this paper, scFvs were immobilized on the fluorescent nanoparticles (FNPs). For FNPs, quantum dots (QDs) are ideal fluorescent dyes in view of optical properties, size, and functionality. However, many kinds of QDs are biologically incompatible because of containing toxic metal elements. To overcome the toxicity, we selected ZnS-AgInS₂(ZAIS)/ZnS^[1], which is a cadmium-free QD consisting of low toxic metal ions, and then optimized the preparation method of scFvs-ZAIS/ZnS conjugate (abbreviated as scFv-FNP). In addition, we investigated their function and binding potencies using cancer cells.

p-S1TSCFR3-1 was used as the scFv, which selectively bound to adult T-cell leukemia (ATL) cells^[2]. As shown in Figure 1, the surface ligands on ZAIS/ZnS QDs were replaced to TEG-mono and NTA-TEG-mono by the ligand exchange reaction. Then, p-S1TSCFR3-1 was immobilized onto ZAIS/ZnS through the interaction between Ni-NTA and 6×His (His tag) in the scFv to afford scFv-FNP. To examine the clustering effect of the scFv, one to five equivalents of scFvs were immobilized. The binding potencies of scFv-FNPs were evaluated by flow cytometry analysis using ATL cell lines (S1T, MT-2, and Su9T01) or non-ATL cell lines (MOLT-4). The binding potencies were cell dependent and increased with increasing the number of scFv on FNP, suggesting that the oligomerization of scFv on FNPs is effective for enhancing the binding interaction between the scFvs and antigens on the cell. Our developed FNPs system is a useful platform to fabricate fluorescent imaging probes of scFv.

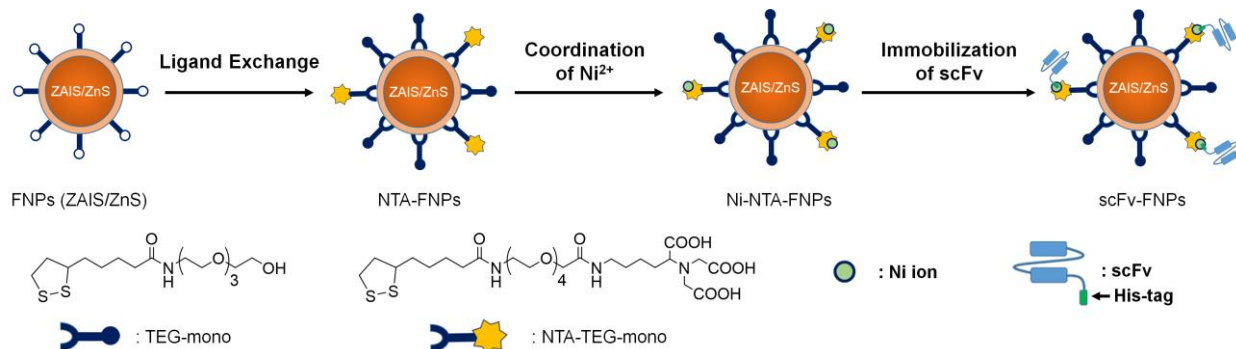


Figure 1. Schematic illustration for preparation of scFv-FNPs using ZAIS/ZnS QDs

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Synthesis of Bio-based Derived Monomers from the Vanillin & Eugenol



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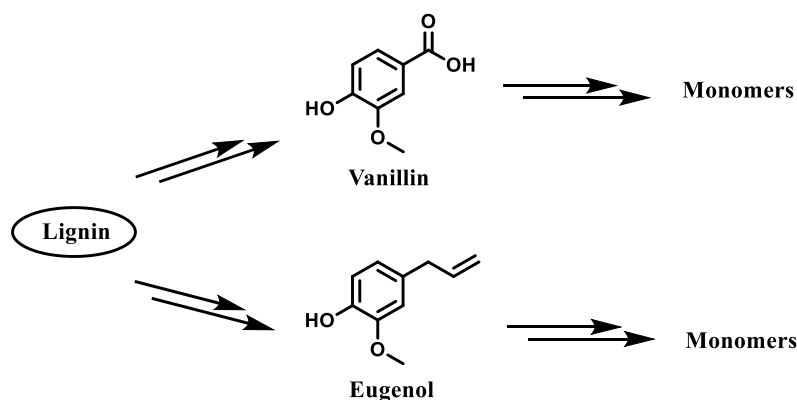
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Lignin, the 2nd most abundant natural polymer on Earth, is an aromatic biomacromolecule that holds a tremendous potential for the synthesis of biobased materials. The production of monomers and polymers from lignin has been investigated for years and keeps on-expanding, as proven by the flourishing literature.

Vanillin, an oxidation product of lignin, is one of the best investigated compounds.¹ The production cost of vanillin from lignin is lower than from any other substrate. It is currently the only aromatic molecule that is extracted from lignin on a commercial scale. This molecule is of high interest due to its multiple usages in a wide range of applications, such as flavoring agent (most demanded flavor after saffron) and polymer precursor.² The aromatic ring of vanillin has two important functionalities: a hydroxy and an aldehyde - so-called a phenolic aldehyde or *p*-hydroxybenzaldehyde.

Eugenol, can be obtained from lignin by thermo-chemical degradation or fast pyrolysis method.⁴ This aromatic compound possesses several crucial functional groups, such as hydroxy, methoxy, and allyl group along with the phenyl component.⁴ It shows different key activities, which makes it popular in medicinal applications, for example, it shows anti-inflammatory actions and can be used to produce local anesthesia for the dental applications.⁵ Apart from its medicinal applications, it can be used to produce different biopolymers, such as epoxy resins, benzoxazines, and other thermally stable polymers due to the presence of multiple functional groups for reaction. Due to the increasing awareness of the green chemical synthesis methods, in this study, I will be discussing the major research and synthesis of biomass-derived monomers from vanillin and eugenol.



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PREPARATION OF REPROCESSABLE COVALENT ADAPTABLE NETWORK FROM COTTONSEED OIL AND EVALUATION OF ITS MECHANICAL PROPERTIES

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The development of covalent adaptable networks (CANs) is gaining increasing attention in recent years, since this innovative polymer family fulfills the gap between thermosetting and thermoplastic materials. Having valuable properties of crosslinked thermosets, CANs can be reprocessed and reshaped as conventional thermoplastics. These unique abilities are imparted by the presence of crosslinks that become dynamic and undergo the exchange by either associative or dissociative mechanism under certain stimuli. The special type of CANs, which exhibit an Arrhenius viscosity-temperature relationship are known as "vitrimers". The main characteristic that distinguishes them from dissociative CANs is maintaining of the crosslinked network integrity during the dynamic bonds exchange process.

In this work, a study on the preparation of plant-oil based vitrimer from functionalized cottonseed oil was done. The acrylated-epoxidized cottonseed oil (AECO) was synthesized and then photopolymerized with difunctional reactive diluent: 1,6-hexandiol diacrylate (HDDA) and photoinitiator: 2-hydroxy-2-methyl-1-phenylpropanone (Omnirad 1173). The bonds exchange in AECO-based system was provided through dynamic transesterification, namely by incorporation of triazobicyclodecene catalyst in UV-curable formulation. The presence of this catalyst enabled the transesterification reaction between ester and hydroxy groups, presented in AECO, therefore, imparting the vitrimer properties. The vitrimer behavior of AECO resin was demonstrated by creep recovery experiments. The activation energy of dynamic transesterification was determined as 44.38 kJ/mol⁻¹. The thermomechanical properties of the AECO vitrimer were evaluated and its ability to reprocess was shown.

Bioplastic Proteopposite Films from Plant Proteins for Food Packaging Applications

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With increasing demand for alternatives to petrochemical based products in the food packaging industry, plant protein-based thermoplastics and thermosets become a perspective and attractive option. Soy protein bioplastics demonstrate good film-forming ability, decent flexibility, while oxygen barrier properties of soy-derived materials are promising. At the same time, such materials lack moisture resistance and toughness. Major corn protein Zein can contribute good moisture resistance and barrier performance, but films from Zein are exceptionally brittle and not adequate for food packaging materials. In this study, we combined Zein, soy protein and plasticizing additive, olive stone powder (OSP) to develop new bioplastic films and explore synergistic effects of soy protein's inherent film formation ability and Zein's higher strength. Incorporation of OSP helps additionally to plasticize and hydrophobize the resulted bioplastic films, as well as improve mechanical and barrier properties. As a result, strong yet flexible soy-Zein proteopposite films were prepared.

Overall, resulted novel bioplastic films are synthesized from all-natural ingredients, show competitive moisture resistance, mechanical properties, and improved barrier behavior.

Quinoidal Questions: Indophenine Monomers and Low Bandgap Donor-Acceptor Conjugated Polymers

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Indophenine, known since the late 1800's, is an intensely colored blue dye with a highly conjugated backbone.¹ The quinoidal nature of the backbone introduces significant rigidity, which limits the solubility of the indophenine monomer. As a result, applications of indophenines to conjugated polymer materials have been limited. Replacement of thiophene with 3,4-propylenedioxythiophene (ProDOT) allows for inclusion of solubilizing side chains resulting in more soluble materials to be synthesized. ProDOT-based indophenines (ProDOT-I) have been shown to possess deep HOMO levels, low-lying LUMO levels and band gaps of 1.4-1.5 eV.² ProDOT-I monomers are inherently quinoidal acceptors, which can aid in lowering the bandgap in resulting polymers. Polymerization of ProDOT-I with donors (i.e. thiophene, ProDOT) should result in traditional donor-acceptor frameworks, which can result in low bandgap systems. Additionally, ProDOT-I can be paired with the ambipolar unit thieno[3,4-*b*]pyrazine.³ Such ambipolar-acceptor pairings in the past have given low bandgap polymers with bandgaps of 0.97-1.12 eV.^{4,5} Synthesis of the ProDOT-I monomers, polymerization conditions, and characterization of the polymers will be presented.

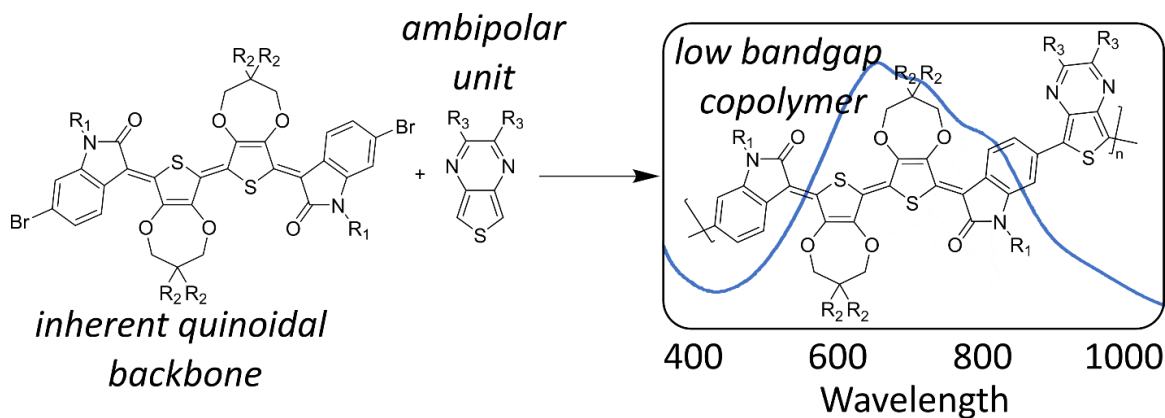


Figure 1. Synthesis of a low bandgap polymer of ProDOT-I and thieno[3,4-*b*]pyrazine.

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**Bio-Based Furanic acrylates and methacrylates as potential reactive diluents
for UV curable coatings: Synthesis and Coating Evaluation**

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A series of photocurable di(meth)acrylates from furan-based diols were prepared in good yields and evaluated for use as reactive diluents in UV-curable coatings. The furan-based di(meth)acrylates were found to have low viscosities and were used as reactive diluents with a commonly used urethane acrylate resin to prepare photopolymerizable coating systems. The coating formulations were cured using UV light, and properties such as solvent resistance, hardness, impact strength, and adhesion were evaluated. The thermal properties of the coatings were characterized using differential scanning calorimetry and thermogravimetric analysis. Dynamic mechanical analysis was used to determine the viscoelastic properties of the coatings. Nanoindentation experiments were performed to evaluate the modulus of elasticity and hardness of the coatings. In general, the coatings containing the furan-based (meth)acrylates had high hardness, elastic modulus, and glass transition temperature.

Analysis of Ground and Excited State Pair Spatial Localization Towards Understanding the Photodegradation in Polymers

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Photodegradation of polymers is a complex phenomenon that is influenced by both topological and electronic information.¹ Regarding the process of exciting an electron from ground to excited state orbitals for photodegradation to occur, it is known that various relationships need to exist between ground and excited states. Factors between the two states such as oscillator strength and transition energy have been investigated heavily and have shown influence.² Another factor that is believed to effect photodegradation is the spatial localization between the two orbitals relative to each other. To investigate the influence of spatial localization on photodegradation, we employ a cooperative approach between time dependent excited state molecular dynamics (TDESMD) and cheminformatic techniques where topological information is used to help describe the influential path of electron movements.³

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Photoluminescence and DFT simulation of conductivity of the p-type doped and charge-injected cis-polyacetylene of Cis-Polyacetylene Semiconductor Material

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Abstract

Photoluminescence (PL) is one of the key observables in experimental characterizations of optoelectronic materials, including conjugated polymers (CPs). Due to their tunable electronic and optical properties, semiconducting conjugated polymers (CPs) have shown great potential in organic solar cells and organic field-effect transistors (OFETs). A simplified model of *cis*-polyacetylene (*cis*-PA) oligomer is used to explain the mechanism of photoluminescence (PL) of the CPs. The photo-induced excited state dynamics were computed using a combination of the *ab initio* electronic structure and a time-dependent density matrix methodology. We explore the phonon-induced relaxation of the excited states. Here, the dissipative Redfield equation was used with the nonadiabatic couplings as parameters. The relaxation rate of the electron is found to be faster than the relaxation rate of the hole. The dissipative excited-state dynamics were combined with radiative recombination channels to predict the PL spectrum. The simulation revealed similarities in the absorption and emission spectra. The main result is that the computed PL spectrum demonstrates two mechanisms of light emission originating from (i) the inter-band transitions, corresponding to the same range of transition energies as the absorption spectrum and (ii) intra-band transitions not available in the absorption spectra. [1] The results can be used for improving organic semiconductor materials for photovoltaic and LED applications. Results on single oligomer serve as a basis for the computational predictions of electronic and optical properties of ensembles of *cis*-polyacetylene (*cis*-PA) multiple oligomers in two different forms (a) undoped *cis*-PA and (b) *cis*-PA doped by phosphorous fluoride via density functional theory (DFT) with hybrid functionals. The comparison of undoped *cis*-PA under the constraint of injected charge carrier and *cis*-PA doped by phosphorous fluoride shows that either doping or injection provides very similar features in electronic structure, optical properties, and conductivity. [2] These observations provide a better understanding and practical use of the properties of polyacetylene films for flexible electronic applications.

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Molecular insights into the hydration of zwitterionic polymers

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Abstract

Undesired Ice formation and accumulation on surfaces have always been a problem if water is present at low temperatures below freezing point. That phenomenon can cause catastrophe and can lead to economic losses and accidental casualties. One of the solutions is to use an anti-icing surface coating which can reduce ice adhesion. Herein, we used Density Functional theory (DFT) to study two zwitterionic polymers, polysulfobetaine (polySB) and polyphosphorylcholine (polyMPC), as prospective anti-icing coating polymers. We used DFT to get deep insights into the hydration of polySB and polyMPC zwitterionic polymers and to understand the interactions between the polymers and water molecules. The results show that water molecules tightly bonded to the polymers with negative adsorption energy, short bond length, and charge transfer from the polymers and adsorbed water molecules. Furthermore, the temperature effect was considered by calculating Gibbs free energy of the adsorptions. The Gibbs free energy of adsorption showed that water adsorption is a spontaneous reaction at all temperature degrees, which supports the strong hydrophilic nature of the studied zwitterionic polymers. In addition, we investigated whether or not the adsorbed water will form ice at a low temperature degree below the freezing point. Interestingly, we found that on both polymers large ice nucleation is inhibited, and only weak small ice clusters can form. Finally, both polymers showed good anti-icing properties. However, by comparing polySB with the anionic terminal group and polyMPC with the cationic terminal group, the second showed more anti-icing performance. Our findings suggest that polyMPC is an excellent candidate for anti-icing coating application.

DNA-Wrapped Carbon Nanotubes Interaction: A DFT Analysis
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Abstract:

The interactions between single stranded DNA (ssDNA) and carbon nanotubes (CNTs) have been widely studied in recent years. Chemical reactions between ssDNA and semiconducting single-wall carbon nanotubes (SWCNTs) achieves covalent functionalization sites onto SWCNTs and create quantum defects on the CNTs surface that has the potential to improve the Photoluminescence (PL) effect. DNA molecules are able to wrap carbon nanotubes to build hybrid structure. Classical molecular dynamics simulations of the SWCNT-ssDNA wrapping process are performed. Then, we used DFT to optimize the coupled defect geometries and then compute photo-induced excited state dynamics using time-dependent density matrix methodology with a certain sequence of DNA at a SWCNTs. The noncollinear DFT includes spin-orbit coupling (SOC) between different spin-states and produces molecular orbitals. These orbitals are used to calculate the transition dipoles between electronic states, oscillator strengths, radiative transition rates, and emission spectra. Our simulation achieves an energy shift in the HOMO and LUMO energy levels for the hybrid structure due to the wrapping of ssDNA molecule. We have computed the PL decay for ssDNA-functionalized SWCNTs as a function of the sequence content of the ssDNA that dictates the red-shifting of their PL emission peaks relative to the band-edge exciton. The evaluation of the dynamics of photoluminescence (PL) from those quantum defects is important for understanding the nanotube electronic structure and helpful to the design of quantum light emitters. we correlate our results with previous experimental reports on CNTs-ssDNA complexes, providing complementary information to understand better their opto-electronic behavior.

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Electronic Structure of Janus Pbse/Cdse QDs Functionalized By Ru(II) N719 Dye and its Tunability via Dye Attachment and Solvent Polarity

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Colloidal quantum dots (QDs) represent a highly promising material for light harvesting, energy conversion, and light emitting devices. Additional control over the electronic and optical properties can be obtained through heterostructures, so called Janus QDs, where a half of the QD is made from one semiconductor (CdSe) and another half is from another semiconductor (PbSe) forming an interface along a specific crystalline direction. The charger transfer – the key processes for both solar-to-electrical and solar-to-chemical energy conversion processes – can be further improved via organic-inorganic interfaces by functionalization of the QD surface with dye molecules, such as derivatives of Ru(II) bipyridine. However, challenges remain in controlling complicated surface and interface chemistry of Janus QDs and the QD-dye interaction, which fundamental understanding is still far from completion. Using density functional theory (DFT) and linear response time dependent DFT (TDDFT) methods, we have studied the effect of the binding configuration of Ru(II) N719 dye on the electronic structure and optical properties of Janus PbSe/CdSe QDs of 2 nm in size. Calculations show that attachment of the dye to either PbSe or CdSe surface by two carboxylic groups leads to shrinking of the energy gap, compared to the attachment by a single carboxylic group. This is because the attachment via two carboxylic groups shifts the occupied dye's orbitals to the energy gap of the QD and provides favoring conditions for a hole transfer from the photoexcited QD to the dye. Additionally, the alignment of the dye's orbitals with respect to the QD's states is sensitive to the solvent media, with more polar solvent shifting the occupied dye's orbitals deeper inside in the QD's valence band. Also, non-polar solvent results in charge-transfer character of lowest energy optical transitions, where the hole is localized on the dye and the electron is localized on the CdSe part of the QD. Thus, our calculations confirm that the photophysics of Janus PbSe/CdSe QDs is adjustable by the dye attachment and media/solvent polarity allowing for favorable conditions for the hole transfer from the excited QD to the dye.

Investigation of Wood Windows Aging Using Thermal Desorption-Pyrolysis Gas Chromatography-Mass Spectroscopy

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Understanding wood window aging and resistance to weathering is essential for both manufacturers and users. Yet, fast mechanic and wet methods aiding to evaluate the performance of windows so they can withstand a 10-year warranty provide only a “yes-or-no” answer, lacking in chemical characterization, thus failing to determine and effectively troubleshoot the cause of the potential failure. Thermal desorption-pyrolysis gas chromatography-mass spectrometry (TD-Py-GC-MS) technique show the potential to be effective for determining wood preservatives and studying aging of wood-based materials without extensive sample preparation. This study introduces a new fast and effective TD-Py-GC-MS method for the quantitative determination of fungicides along with wood constituents. Various thermal desorption and pyrolysis temperatures and times were tested to quantitatively determine concentrations of various fungicides such as tebuconazole, propiconazole, permethrin, 3-iodo-2-propynyl butylcarbamate, chlorbufam, hexaconazole, and azaconazole in wood samples. The analytes' responses at different TD temperatures were compared and TD temperature of 275°C for 20 seconds was determined as the optimum for the analysis of wood preservatives. The pyrolysis from 275°C with ballistic heating to 500 °C & 20 s hold showed the effective determination of characteristic wood constituents. The combination of optimal TD and Pyr steps in TD-Py-GC-MS in both scan and selected ion monitoring MS acquisition methods will be applied in the characterization of aging in window-treated corner sections.

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Modification Of Hemicellulose With Grafted Polymers based on Acrylic Plant Oil Based Monomers

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Abstract:

Polymeric materials derived from renewable feedstock attract a lot of attention in recent years, targeting to replace currently used petroleum-based counterparts. In particular, naturally derived biopolymers, such as: cellulose, hemicellulose and lignin are studied extensively and demonstrate ability to undergo chemical/physical modifications due to the abundance of functional groups in their chemical structure.

Xylan, which is a polysaccharide that can be found in the cell walls of plants, can be derived from corncoobs, birchwood, beechwood and is currently considered an agricultural waste product. Due to its chemical structure, particularly the presence of multiple hydroxyl groups along the polymer backbone, its incorporation into plastic materials can improve material impact resistance, toughness and increase barrier properties. However, further chemical modifications are required for feasible applications due to xylan hydrophilicity and brittle nature. Previously, our group reported on one-step synthesis of plant oil-based acrylic monomers (POBMs) from a variety of plant oils with various unsaturation amount. The vinyl bond in the POBM undergoes free radical chain propagation reaction, while allylic bonds in the fatty acid chains remain intact and can be used for further post polymerization cross linking reactions. Incorporation of POBM fragments into the copolymer macromolecules facilitates internal plasticizing effect, increases water repellent properties. In this study, two POBMs differing in degree of unsaturation, derived from more unsaturated high oleic soybean oil and less unsaturated Babassu oil, are grafted to the xylan backbone using free radical polymerization approach. The purpose of the synthesis is to combine the individual benefits of xylan and POBM and develop a fully biobased plastics with superior flexibility, strength, and barrier properties. The desired application of the resulted xylan-g-POBM copolymers can be, in particular, modification of paper-based packaging materials to replace currently used petroleum-based protective coatings. To increase further barrier and mechanical properties of obtained polymeric material, it was blended with Carnauba Wax which is able to form packed crystalline domains within polymer matrix, thus better restrict water vapor permeation and provide extensive intermolecular interactions to favor polymer strength. Obtained results have shown that proposed fully-biobased, Xylan derived plastic material performs in a similar manner if to compare to petroleum-based Polyethylene which is currently the dominant material in food paper packaging in a role of protective liner.

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Study of stability/reactivity of lignin dimer compounds as model compounds in aqueous media

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Abstract:

Despite the fact that we pass through them unconsciously, trees, play an important role in humankind's life. We have been using conventional fossil fuels for many years, which are primarily made from trees. Now that we have faced environmental issues, we are doing much research for a substitute resource and finally ending up with trees again! Agricultural by-products have been identified as excellent feedstock for the fabrication of lignocellulosic biomass, because of their eco-friendliness, renewability, availability, low cost, and carbon-neutral characteristics.

Lignocellulosic biomass is highly abundant biomass in the world, consisting of cellulose, hemicellulose, and lignin. Lignin is an amorphous, highly branched polyphenolic macromolecule of complex structure with high molecular weight. Yet after decades of introducing lignin as a crucial biopolymer, its chemistry has remained in a cloud of ambiguity. For optimal and efficient usage of lignin in the subject of renewable feedstock material, the first step is understanding its structure and, consequently, its stability. In other words, lignin has great potential to be used as the replacement for fossil fuels as long as its stability/reactivity is understood. Nevertheless, the complexity of lignin and the variety of different feedstock prevents direct investigation, to enable the investigation of specific bonds and lignin structural features this study focuses on lignin-derived model compounds.

In this work, a target group of lignin samples including guaiacylglycerol- β -guaiacyl ether (G β 2) with aliphatic hydroxyl, methoxy, and β -O-4 (arylglycerol β -aryl ethers) functional groups and 4-formyl-2-methoxyphenyl benzoate (EST2) with carbonyl, ester dimer functional groups were used as lignin model compounds.

We have developed a simple, and sensitive method for the determination of G β 2 and EST2 by reverse phase high pressure liquid chromatography (RP-HPLC) analysis coupled with high resolution time-of-flight mass spectrometry (MS) with an electrospray ionization. The stability of the lignin model compounds was investigated at three different pH (3, 7, and 10) as well as in several biodegradation media. Finding demonstrate that pH variation has no effect on G β 2 responses in RP-HPLC-MS while it has some significant impact on EST2 responses. Based on the obtained results, the response of G β 2 against pH variation was low (<10%) in contrast, EST2 samples exhibit sustainable changes in basic media. In a nutshell, the EST2 response was reduced to approximately half of it in pH 3 and 7, and was almost negligible in pH 10 (<1%).

Quantitative characterization of technical lignins by carbon-based analyses

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Plant biomass is comprised of three main components, cellulose, hemicellulose, and lignin. This marks lignin as the most abundant aromatic polymer on earth with the potential to serve as biofuel and/or renewable chemical feedstock in various applications. As a heteropolymer, challenges arrive in chemical characterization and continue through identification and quantification of breakdown products. A comprehensive quantitative and qualitative analysis of this heteropolymer would allow investigation into various degradation pathways. Therefore, this study aimed to characterize technical lignins with a suite of carbon-based analysis methods to derive their quantitative profiles and structural features. Three analytical methods were employed, including thermal carbon analysis (TCA), evolved gas analysis-mass spectrometry (EGA-MS), thermal desorption-pyrolysis-gas chromatography-mass spectrometry (TD-Pyr-GC-MS). These methods provided temperature fractions with unique abundances to distinguish volatile species evolving at thermal desorption temperatures and those of high molecular weight evolving at pyrolytic temperatures. It is seen that evolving compound variation is largely impacted by lignin type and manufacturing processes. The previously developed TCA provided quantitative profiles for TD and pyrolytic temperatures, allowing one to differentiate the abundance of volatile components and those of higher molecular weight. EGA-MS provided general structural information based on common MS ions. Finally, TD-Pyr-GC-MS enabled detailed speciation within certain temperature fractions, using the combination of the retention time and mass spectra for identification.

Thermal decomposition and stability of anthropogenic waste

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Pyrolysis, the thermochemical breakdown of compounds in an inert environment, has potential to get rid of two prevalent pollutants: poly- and perfluoralkyl substances (PFASs) and plastic waste. Pyrolysis is often understood as chemical recycling allowing for polymeric compounds to either be broken down into their original monomers and further reused and repurposed, or break them apart completely into basic components.

PFAs are man-made compounds with a variety of uses in cookware, food packaging, fabrics, etc. Because of their widespread use they are prevalent in the environment, and as a result, most people have been exposed to PFAs leading to possible health issues. Combination of two methods – evolved gas analysis (EGA) and thermal desorption – pyrolysis – gas chromatography with mass spectrometry (TD-Py-GC-MS) – can be used for compound volatilization, breakdown and subsequent identification and quantification. EGA serves as a screening method providing information about volatilization and breakdown conditions. TD-Py-GC-MS can be used to focus on specific conditions allowing compound separation and identification. With example of Perfluorooctanoic acid (PFOA), combination of EGA-MS and TD-Py-GC-MS enabled determination of the breakdown temperature in a range of 200-300 °C and the main product of this breakdown as perfluoro-1-heptene.

Pyrolysis is also a promising tool to recycle otherwise unrecyclable plastics. Single-plastic streams have been heavily studied, but the mixed plastic waste leftover from recycling facilities has not. This leaves a novel opportunity to study the interactions between plastic types when co-pyrolyzed. Using pyrolysis-GC-MS, product distributions are analyzed to observe changes based on plastic feedstock composition. Polypropylene-polystyrene mixtures showed variation in composition: for polypropylene-derived compounds up to 30% and polystyrene products up to 15%. These micro-pyrolysis experiments will be extended and compared to bench-scale reactors and further experiments will be performed to construct a kinetic model of pyrolysis of plastic waste.

Development of predictive QSAR models to assess the corrosion inhibition efficiency of different classes of organic compounds and experimental determination of corrosion rate of steel in the presence of different organic corrosion inhibitors

Abstract:

Most molecular discoveries today are the result of an iterative, three phase cycle of design, synthesis, and testing. Analysis of the results from one iteration provides information and knowledge that enables the next cycle to be initiated with further improvements to be achieved. A common feature of this analysis stage is the construction of a mathematical or statistical model which enables the observed activity or the property to be related to the molecular structure. Such models are often referred to as Quantitative Structure-Activity Relationships (QSARs) or Quantitative Structure-Property Relationships (QSPRs). In this study, preliminary QSAR models have been developed correlating the corrosion inhibition efficiency and the molecular structure of different classes of organic corrosion inhibitors. The synthesis and selection of corrosion inhibitors are still based on trial-and-error experimentation. Therefore, it is urgent to investigate the corrosion inhibition mechanism and the influence of the structure of an inhibitor on the inhibition efficiency as it will provide theoretical guidance for the design of effective corrosion inhibitors. Many organic compounds containing hetero atoms, such as O, N, or S, with free electron pairs which are readily available for sharing, are found to be effective corrosion inhibitors for many metals and alloys. It has been investigated that coordinate covalent bonds are formed between the organic compound and the metal surface during the adsorption process forming a protective layer on the metal surface. Imidazoles, thiadiazoles, and other nitrogen containing compounds and their derivatives can act as corrosion inhibitors as they can form a protective film on a transitional metal surface instantaneously which in turn reduces the corrosive attack in acidic media. The QSAR models developed in this study to predict the corrosion inhibition efficiency are found to be correlating with specific physical and chemical properties of organic compounds, and with further improvement, can play an important role in effective assessment of potential corrosion inhibitors. Experimental determination of corrosion rate of steel in the presence of different corrosion inhibitors has been carried out by using Linear Polarization Resistance (LPR) testing and the weight loss technique. Linear Polarization Resistance (LPR) method is an electrochemical technique which can be used to assess the corrosion rate of a metal substrate in an electrolytically conductive liquid. Weight loss test is a gravimetric method used to determine the corrosion rate of a substrate.

Biography:

Chameli Samarawickrema graduated with a bachelor's in chemistry & Molecular Biology from the University of Peradeniya, Sri Lanka, and then with a Master's in Applied Organic Chemistry from the University of Colombo, Sri Lanka. She joined the Department of Coatings & Polymeric Materials at NDSU in Fall 2021 to pursue her doctoral studies and is currently working under the supervision of Dr. Bakhtiyor Rasulev.

Plant Oil-Based Acrylic Latexes towards Multisubstrate Bonding Adhesives Applications

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Abstract: To investigate the utility of acrylic monomers from various plant oils in adhesives manufacturing, 25–45 wt. % of high oleic soybean oil-based monomer (HOSBM) was copolymerized in a miniemulsion with commercially applied butyl acrylate (BA), methyl methacrylate (MMA), or styrene (St). The compositions of the resulting ternary latex copolymers were varied in terms of both “soft” (HOSBM, BA) and “rigid” (MMA or St) macromolecular fragments, while total monomer conversion and molecular weight of copolymers were determined after synthesis. For most latexes, results indicated the presence of lower and higher molecular weight fractions, which is beneficial for the material adhesive performance. To correlate surface properties and adhesive performance of HOSBM-based copolymer latexes, contact angle hysteresis (using water as a contact liquid) for each latex-substrate pair was first determined. The data showed that plant oil-based latexes exhibit a clear ability to spread and adhere once applied on the surface of materials differing by polarities, such as semicrystalline polyethylene terephthalate (PET), polypropylene (PP), bleached paperboard (uncoated), and tops coated with a clay mineral paperboard. The effectiveness of plant oil-based ternary latexes as adhesives was demonstrated on PET to PP and coated to uncoated paperboard substrates. As a result, the latexes with high biobased content developed in this study provide promising adhesive performance, causing substrate failure instead of cohesive/adhesive break in many experiments.

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Amphiphilic Invertible Polymers. Characterization and application as targeting drug delivery systems in cancer cell treatment.

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Abstract:

In this study we used Amphiphilic Invertible Polymers (AIPs) for encapsulation of ERKi and Gemcitabine molecules and their delivery into tumor cells. AIPs are class of environment-responsive polymers, owing their unique properties to the presence of both alternating hydrophilic (PEG) and hydrophobic (PTHF) blocks within polymer backbone. Polarity of surrounding medium controls mutual orientation of these blocks, where presence of ester bonds allows macromolecules to undergo conformational changes as a respond to polarity changes. Being introduced into polar water medium, AIPs undergo self-assembling process driven by solvophobic interactions and form Invertible Micellar Assemblies (IMAs). Hydrophilic PEG fragments of these IMAs are directed towards external polar phase, while PTHF fragments are packing into micellar core and provide environment that can facilitate poorly water-soluble via hydrophobic interactions. Upon contact with cell membrane surface of lower polarity, AIPs exhibit their environmental-sensitive properties, disassemble and allows direct pathway for cargo into the cell membrane core. Negative charge on IMAs -water interface due to presence of carboxylic groups in AIPs, allows utilize it for surface modifications, introducing layers of polyelectrolytes by L-b-L technique. Taking advantage of this AIP's feature, micellar assemblies made of them were layered with poly-L-lysine and Hyaluronic Acid (HA). Presence of (HA) on surface of delivery systems provided targeted delivery of encapsulated drugs to pancreatic tumor cells, thus increasing therapeutic efficiency of Gemcitabine and ERKi as well as avoiding side toxicity which these drugs can cause for healthy cells.

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Photo-physics of Cu (I) Dipyrrin Complexes: Effect of Substituting Groups and Side Linkages

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Most photo-active transition metal complexes (TMCs) are made from precious metals with very low natural abundance in Earth's crust. Additionally, development of highly efficient near infrared (NIR) emitting TMCs has been under-pursued to date due to our limited understanding of the interplay between radiative and non-radiative relaxation processes leading to extreme variations in photoluminescence quantum yield (PLQY). We use density functional theory (DFT) and time-dependent DFT (TDDFT) to investigate the photo-physics of Cu (I) dipyrrin complexes and Redfield-based non-adiabatic molecular dynamics (NAMMD) to compute PLQY. Calculations show a low-energy absorption peak appearing in the red-to-near infrared (NIR) regions (~700 nm) tunable by substituting electron withdrawing (CN, NO₂) and electron donating groups (OCH₃, NPh₂), as well as changing the π -conjugation via side linking groups (H, -CH₂CH₂-, -CH=CH-). The substituent groups change the charge transfer character of the low-energy excitons which is expected to have a large influence on the resulting PLQY, while the side linkages (conjugated connectors) increase the degree of delocalization of the excitons. When non-adiabatic couplings are computed with PBE functional, the splitting between energy levels, including the HOMO-LUMO gap, is smaller, compared to hybrid PBE0 functional. Therefore, PBE likely overestimates non-radiative recombination rates. However, systematic comparison across all models shows that the PLQY increases with the strongest electron-withdrawing group, as well as with enhancement of structural rigidity caused by π -conjugated side linking. Further work will involve computing non-adiabatic couplings with a hybrid functional to improve accuracy of NAMMD calculations.

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