THE MIDLAND CHEMIST

Vol. 40, No. 7 October 2003

Vote!

Midland Section Candidates and Ballot, p. 2–10

59th ACS
Midland Section
Fall Scientific Meeting

October 17, 2003
11:00 a.m.–5:00 p.m.

Employee Development Center
The Dow Chemical Company
Midland, Michigan

Sci-Fest

Celebrate National Chemistry Week at Delta College, p. 52

THE MIDLAND CHEMIST

Volume 40, Number 7
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In this Issue ...

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Chair Column

Join Us at Midland Section Fall Activities!

Mike Owen, Chair
ACS Midland Section

Foremost among the activities this month are our Fall Scientific Meeting, Sci-Fest, National Chemistry Week, and the Central Regional Meeting in Pittsburgh—quite an October. Add the election for 2004 Midland Section officers, and you have quite a bit to attract your attention.

The program for the Fall Scientific Meeting is included in this issue of *The Midland Chemist* and is also available from the Section web site (http://membership.acs.org/M/Midl). This will be the 59th time we have held the Fall Scientific Meeting, and we are indebted to Wendy Flory and Dale LeCaptain for leading this activity a second year in a row. We are also indebted to The Dow Chemical Company for provided the meeting facilities and lunch for attendees. The theme is the very topical issue of “Green Chemistry.” Our keynote speaker is Richard Gross, Herman F. Mark Professor, Polytechnic University, New York. He is a Presidential Green Chemistry Award recipient.

Dave Stickles tells me this is about the tenth time we have held Sci-Fest. This is one of our events for kids of all ages. Approximately 1000 people attended last year—make sure you’re part of the fun this time around. Check out the flyer included in this issue of *The Midland Chemist*.

Finally, don’t forget to send in your ballot for the Midland Section election if you are a member of the Midland Section. The officers of the Midland Section spend a lot of time keeping your Section running and productive. Please spend a few moments deciding on the candidates you would like to vote for and send in your completed ballot.

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Exercise Your Rights! Vote!

Candidates for Midland Section offices are listed on subsequent pages by position and then alphabetically. These individuals are willing to spend their personal time working for you. ***Please respond by taking your time to vote for the candidates of your choice using the ballot on page 10.***

Candidates for Chair-Elect

Minghui Chai

After having held leadership positions in the Central Ohio Valley Section, I am pleased to join the Midland Section. The Midland Section is a vibrant section with many successful programs. For example, few sections are able to sponsor an annual scientific meeting. In addition, the section has several outreach activities that would be the envy of most sections. (This effort has been recognized by a number of ChemLuminary awards.) All these programs should be sustained and strengthened. In recent years, the Midland Section has responded to national priorities by establishing both a Committee on Minority Affairs and a Younger Chemists Committee. Both represent now thriving attempts to involve particular segments of Section membership.

Two areas which remain to be addressed are the formation of a Senior Chemists Committee (an increasing portion of Section membership is made up of retirees) and a Women Chemists Committee (the section membership contains many talented and energetic women professionals). Having served as a member of the Committee for the Advancement of Women Chemists, I am particularly aware of the concerns and ambitions of woman chemists. Consequently, I will have as a priority the establishment of a Women Chemists Committee (WCC) for the Midland Section. This will not only energize an important component of the membership but could enhance section efforts in the areas of public outreach, educational support, mentoring of younger members, networking activities, and several others. It is likely that members of the WCC can assume a number of leadership roles for the Section.

I look forward to working with members of the Midland Section and making a positive contribution to the functioning of the Section.

Educational Background: The University of Akron, Ph.D. (Analytical Chemistry), 2000; Yunnan University (PRC), M.S. (Organic Chemistry), 1988; Anhui Normal University (PRC), B.S. (Chemistry), 1985.
Professional Experience: Central Michigan University, Mt. Pleasant, MI, Assistant Professor, 2003–present; Marshall University, Huntington, WV, Assistant Professor, 2000–2003; The University of Akron, Akron, OH, Research Assistant, 1995–2000; Mount Union College, Alliance, OH, Visiting Professor, 1994–1995; Anhui University, Hefei, Anhui, PRC, Instructor, 1988–1994.
Activities in Professional Societies: ACS member, 1996–present; AX member, 2000–present; Chair-Elect, ACS Central Ohio Valley local section, 2003; Treasurer, ACS Central Ohio Valley local section, 2002; Secretary, ACS Central Ohio Valley local section, 2001; Proposal Reviewer and Panel Reviewer for NSF; Proposal reviewer for Cooperative Grants Program of the U.S. Civilian Research and Development Foundation (CRDF); Reviewer for the ACS Symposium Series; Reviewer for *Journal of Chemical Education*; A Member of COACh (Committee on the Advancement of Women Chemists)
Activities as Consultant: High Resolution NMR Services with Supelco Inc., Marathon Ashland Petroleum LLC, BASF, etc.

Pat Smith

Our Section has a lot to be proud of. It is active and creative, a model section for the ACS. The passion for the ACS, which I share with many in this Section, is to see it continue to offer the finest in scientific content to its membership. I have been active in the ACS because of its high-caliber scientific excellence and its relevance to my interests. We must be vigilant, as a local section, to maintain this scientific excellence, and we need to work hard to keep its content relevant to our membership. I especially like the idea of topical symposia and speakers for achieving this purpose. The "Green Chemistry" theme at the Fall Scientific Meeting is an example of the relevant scientific forums I would promote. I believe that membership in our section will correlate with our program's scientific excellence and relevance.

We have many retirees in our section who possess considerable untapped experience and talent. I believe that we should more actively target their needs such that we could benefit from their wisdom and participation. We should also continue our deliberate community outreach, as epitomized by our activities at the Midland County Fair this summer, Sci-

Fest, Project SEED, and National Chemistry Week.

Finally, we need to creatively provide career services to students and others looking for employment in the chemical industry. We should promote collaborative arrangements between local universities and industry, which play an important role in training and mentoring students for careers in industry.

Current Position: Scientist, Analytical Sciences Laboratory, The Dow Chemical Co., responsible for new business development for raw materials from renewable sources for chemicals and plastics.
Education: A.S., Flint Community Junior College, 1970; B.S., Chemistry, Michigan State University, 1972; M.S., Physical Chemistry, Michigan State University, 1974; Ph.D., Physical Chemistry, Michigan State University, 1978.
Work History: 2000–present, Analytical Sciences, Polymer Characterization Group, 1998–2000; Cargill Dow Polymers, 1978–1998; Analytical Sciences, 1976–1978; Michigan State University (Dow Scholarship), Ph.D., 1974–1976; Analytical Sciences. Co-author of over 400 Dow technical (CRI) reports, 70 external to Dow publications and 1 patent. An Adjunct Professor at Central Michigan University, a member of the American Chemical Society, Polymer Chemistry Division, and the Society of Plastics Engineers.
Awards: Midland Chapter Sigma Xi Award for Outstanding Research Publication, 1987; Midland Chapter ACS Award for Outstanding Achievement and Promotion of the Chemical Sciences, 1998; Dow Analytical Science's V.A. Stenger Award, 1984; Dow Michigan R&D Scientists' Award, 1994; Flint Community Junior College Freshman Chemistry Award, 1969.
Service to ACS: Joined ACS in 1974; Director, Midland Section, 2003; ACS Fall Scientific Meeting, Midland Section (1978–1989, 1998, 1999, 2002, 2003); Keynote Speaker Committee, 1982, 2002, 2003; "Green Chemistry" Symposium Co-Organizer, 2003; Toronto National ACS Meeting: Symposium Organizer on NMR Characterization of Macromolecules, 1998; National ACS Meeting, San Francisco, CA, NMR Symposium Organizer, 1997; Chair of ACS Committee on Continuing Education, 1991; Twenty-Second Central Regional ACS Meeting; Physical Chemistry Symposium Chairman, SVSU, 1990; Given courses on NMR spectroscopy at Central Michigan University (1990, 1992); Central Regional ACS Meeting (1990); and at Howard University (1985, 1986, 1987, 1988, 1990, and 1991).

Candidates for Secretary

Pamela R. Halpin

Ph. D. Chemistry, Northern Illinois University, 2001; B.S. Chemistry, Indiana University, 1996. Employed by Dow Corning since 2002; current position as Senior Analytical Chemist in Analytical Sciences. Served as student liaison, poster session chair, and board member at large of Chicago section of Society for Applied Spectroscopy (SAS), 1998–2001.

Debra A. McNett

Currently pursuing M.S. in Chemistry, Central Michigan University; B.S. Chemistry, Central Michigan University, 1991. Employed by Dow Corning since 1997, presently as Analytical Specialist in the Health and Environmental Sciences (HES) department. Previously employed at The Dow Chemical Company's HES group 1991–1997. Member of local ACS section for the majority of career both as a student and a professional in industry and would like the opportunity to make a contribution toward the success of our local ACS section.

Candidates for Treasurer

Doug Beyer

B.S., Chemistry, Michigan State University, 1974; M.S., Organic Chemistry, University of Wisconsin, 1975. Various research appointments, Dow Corning Corporation, The Dow Chemical Company, Swedish Forest Products Research Institute, 1969–1974. Held various research positions within The Dow Chemical Company, 1975–present. Current position: Research Associate, Saran Barrier Systems R&D. Volunteer, business, and finance advisor, Junior Achievement—Midland, company program, 16 years. ACS activities: Joined 2000, currently Midland Section treasurer (2001–03), served on various scientific meeting committees.

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Sheng Wang

Sheng Wang received his B.S in Chemistry in 1986 from Wuhan University in China. After he obtained his M.S. in Polymer Science from the Institute of Chemistry, Chinese Academy of Sciences, he worked 4 years as a research associate in the same institute. He then worked about 2 years at Max-Planck Institute for Polymer Research in Mainz as a visiting scientist. He obtained his Ph.D. in Polymer Chemistry in 2000 from Virginia Polytechnic Institute and State University under the supervision of Professor James E. McGrath. He has been employed by Dow Corning Corporation as an associate research specialist since 2000. He has been an active ACS member since 1998 and has presented his research work several times in the National ACS meetings and workshops. He has also be a member of other societies, such as MRS and Sigma Xi.

Candidates for Chair, Nominations and Elections Committee

Maneesh Bahadur

Ph.D. Chemistry, University of Vermont, 1991. Employed by Dow Corning Corporation since 1996; current position as Senior Development Associate in New Venture Business, Photonics Solutions Group. Served as chairperson for S&T seminar program for 2002–2003. Duties include: coordinating seminar activities globally for the Dow Corning Corporation. ACS activities: member of Polymer Division membership committee. 2002–present. Duties include increasing awareness of the polymer division and contacting ACS members for recruitment into polymer division.

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Greg Becker

Greg received a B.S. in Chemistry from Central Michigan University in 1999 after obtaining an A.A.S. in Industrial Chemistry Technology from Ferris State University in 1989. Greg has been with Dow Corning Corporation since 1998. His current position is chemist in the Science & Technology—Global Resin Technology Development group. He performs synthesis, characterization, and development of new materials for electronics applications. Before joining Dow Corning, Greg worked for The Dow Chemical Company in the Electronics Materials Development group from 1992 to 1998. He also worked several years for DowElanco in metabolism research. In the past Greg has been a member of the MMTG and also the Midland section of the ACS.

Candidates for Director

Steven P. Christiano

B.A., Chemistry from SUNY at Buffalo, 1978; Ph.D., Inorganic Chemistry from Michigan State University, 1983. Employed by Dow Corning Corporation since 1991. Current position; Senior Research Specialist. I have been a member of ACS 18 years and am a member of the ACS Colloid and Surface Chemistry Division. I think it is high time that I became involved in my ACS.

Andrew M. Chubb

Ph.D. Organic Chemistry, Iowa State University (Ames, IA), 2003; A.B. Chemistry (Minor: Classics), Washington University (St. Louis, MO), 1995. Assistant Professor of Chemistry, Saginaw Valley State University, 2002–present. Research interests include nerve-agent antitoxins, organosilicon and -germanium chemistry, and materials chemistry. Member, ACS (Organic Division), 1995–present. Member, Teaching and Learning with Technology Roundtable, 2002–present. Representative, Graduate Student-Faculty Liaison Committee, 1999–2001. Duties included meeting with faculty representatives to address issues related to program development, creating a graduate student "Survival Manual," and organizing seminars.

Jennifer Dingman

I am earning an M.S. degree from Central Michigan University (completion Dec., 2003) in Polymer Chemistry (Thesis: "Hydrosilation Catalysis Using New and Unique Platinum Complexes," presented at The Organosilicon Symposium, 2003) and my BS degree is in Biology from

Alma College (1996, Thesis: “Reconstruction of Pre-settlement Forest Patterns of the Bad River Watershed,” presented at the Michigan Academy of Science, Arts, and Letters). I have been employed by Dow Corning Corporation since November of 1998, and my current position involves working as an Industry Chemist in the Life Sciences AETS group focusing on helping our customers use silicones in the personal care market, as well as providing technical training to our national silicone distributors. From 1998–2002 I worked as an NMR Spectroscopist in the Dow Corning Analytical Sciences Department. Other work experience includes product development for Amway Corporation and product support for DowBrands. Served as Dow Corning Corporate Site Leader for United Way Campaigns and Fall Day of Caring for 2000–2003. ACS member since 1998.

Petar R. Dvornic

B.S., Chemical Technology and Metallurgy, 1972, University of Belgrade; M.S., Macromolecular Chemistry, 1975, University of Belgrade; M.S., Polymer Science and Engineering, 1978, University of Massachusetts, Amherst; Ph.D., 1979, University of Massachusetts, Amherst. Postdoctoral fellow in 1979–80 and a Visiting Scientist in 1985 at the Polymer Science and Engineering Department of the University of Massachusetts, Amherst, 1979–80. In 1980 joined the Institute of Chemistry and Technology of the University of Belgrade and went through the ranks from Research Scientist (1980–83) to Senior Research Scientist (1983–88) to the Head of the Polymeric Materials Department (1988–93). From 1985–93: Associate Professor of Polymer Chemistry at the Department of Chemistry of the University of Belgrade. Joined Michigan Molecular Institute, MMI, in 1993 and rose from Associate Scientist (1993–94) to Senior Associate Scientist (1994–95) to Research Scientist (1995–99) to Senior Research Scientist (1999–present). Appointed Professor of Polymer Chemistry at MMI in 1999, Adjunct Professor to Central Michigan University, Mt. Pleasant, MI, (1993–present) and Adjunct Professor Michigan Technological University, Houghton, MI, (1993–present). Member of ACS since 1977. Chair of the Midland Section Awards Committee 2003.

Sharyl A. Majorski-Briggs

M.A. Chemistry, Wayne State University, 1991; B.S. Chemistry, Central Michigan University, 1986. Employed by Central Michigan University since 1991; current position as Laboratory Coordinator. Served as secretary for Midland Section ACS during 2003. Served on the Chemistry Olympiad Program 2002–2003. Duties included conducting mailings, preparing necessary chemicals for the examination, overseeing the examination and presenting awards at recognition ceremony. Served as ACS faculty advisor to the student affiliates at CMU during 2002–2003.

Don Miller

B.S., Wayne State University, 1950; M.S., Central Michigan University, 1974; QC Chemist at Irwin Neisler Co., 1950–54; Polymer analysis, production, and environmental studies at The Dow Chemical Co., 1954–85; Vent sampling and analyis for both The Dow Chemical Co. (1986–88) and Dow Corning Corp. (1989–93); Volunteer work for Habitat for Humanity, Midland Recycling Center, Fun Zone, restoration of Midland Courthouse murals; Morningside Condominium Association Board of Directors (1995–99) as both secretary and president; volunteer work for Midland Center for the Arts, Hall of Ideas (2000–present).

ACS activities: Joined ACS in 1952; program committee, Midland Section ACS Meetings, 1959–60; ACS booth at Midland County Fair (1991–98); organized retirees to work daytime shift at ACS booth at Midland County Fair (1992–98); Midland Section Board (1995–99), director; instrumental in establishing Midland Section Career Services Program (1997); Career Services and Professional Committee (1997–present), chair (2001–present); 2000 Fall Scientific Meeting Committee (keynote speaker and panel discussion committees); ACS Kids & Chemistry Program (2000–02).

Charles W. Olsen, Jr.

Presently global fluorosilicone market specialist within Dow Corning's Silicone Elastomers Group. Olsen has worked as a manufacturing engineer and a senior materials and process engineer, spent seven years working on the space shuttle program solid fuel rocket boosters for Thiokol Corp. and developed and commercialized silicone polyurethane hybrid polymers for Allied Signal (Honeywell). He received a bachelor's degree in chemical engineering from the University of Washington in 1985, and a master's of science degree in management of technology from Stevens Institute of Technology. Olsen joined Dow Corning Corporation in 1996.

David L. Stickles

A.A.S. in Industrial Chemistry from Ferris State University, 1973; Employed by Dow Corning Corporation 1973–2002; Retired in 2002. Currently working as a contractor at Dow Corning. Served as Secretary for the Midland Section of the ACS in 2001, currently a Director of the Midland Section ACS, and Sci-Fest Co-Chair for the Midland Section of ACS from 1996–present. Member of Mid-Michigan Technician Group (MMTG) since its inception in 1990/1991, have served as Chair, Chair-Elect, Secretary, Elected Delegate, and Director for MMTG. Served as Secretary for the TECH Division of the ACS for 2002.

Ballot for Election of 2004 Midland Section ACS Officers

1. Vote for the candidate of your choice, selecting one for each office except as noted.
2. IMPORTANT: To maintain anonymity, **do not sign** the **ballot** or the **inner** ballot **envelope**.
3. Place the ballot in the ballot (inner) envelope. Place the ballot envelope in the return envelope and sign and print your name on the return (outer) envelope. You **must sign** your name on the **outer envelope** to have your ballot counted. See #4 below.
4. In order to vote, one must be a member or associate member in good standing with the ACS. Affiliates are ineligible to vote according to National ACS bylaws.
5. Ballots must be received at the address below **on or before October 24, 2003.**

Gary Kozerski, Chair
Midland Section ACS Nominations & Elections Committee
2200 W. Salzburg Rd. Mailstop DC 40A15
Dow Corning Corporation
Midland, MI 48686-0994

BALLOT

CHAIR-ELECT (vote for one)
☐ Minghui Chai ☐ Pat Smith

SECRETARY (vote for one)
☐ Pamela R. Halpin ☐ Debra A. McNett

TREASURER (vote for one)
☐ Doug Beyer ☐ Sheng Wang

CHAIR, NOMINATIONS & ELECTIONS COMMITTEE (vote for one)
☐ Maneesh Bahadur ☐ Greg Becker

BOARD OF DIRECTORS (vote for four)
☐ Steven P. Christiano
☐ Andrew Chub
☐ Jennifer Dingman
☐ Petar R. Dvornic
☐ Sharyl A. Majorski-Briggs
☐ Don Miller
☐ Charles W. Olsen, Jr.
☐ David L. Stickles

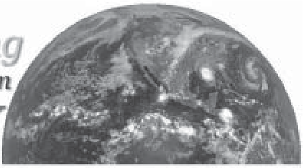
59th Midland Section ACS Fall Scientific Meeting Program

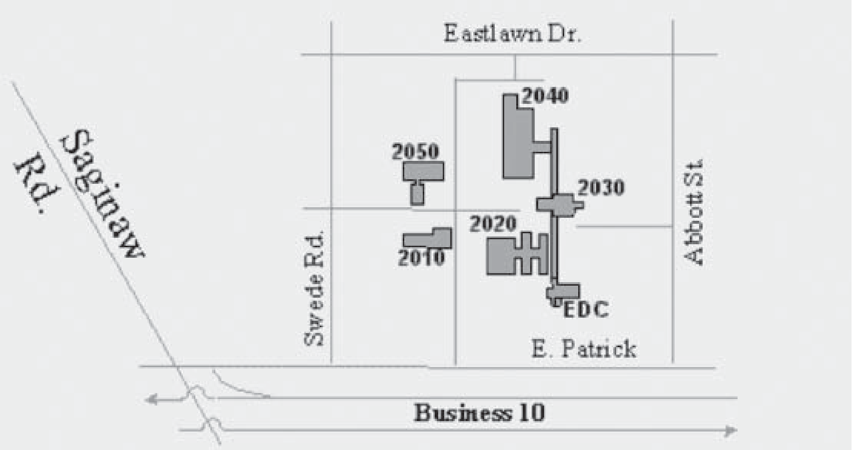
Workshops
Career Panel Discussion
Keynote Address
Symposia
Poster Sessions
Vendor Exposition
Post-Meeting Social

October 17, 2003
11:00 a.m.–5:00 p.m.

Employee Development Center
The Dow Chemical Company
Midland, MI

2003 Fall Scientific Meeting
American Chemical Society—Midland Section
GREEN CHEMISTRY





The Dow corporate center is easily accessible from west bound Business 10. East bound traffic on Business 10 should first exit to side streets <u>before</u> reaching the Saginaw Road overpass.

Welcome!

We welcome you to the 59th ACS Midland Section Fall Scientific Meeting. There is an incredible number of “Green Chemistry” options planned for the day, so please feel free to attend some or all of the events.

Even before the meeting starts we will present a workshop brought to us by the US Environmental Protection Agency and the ACS Green Chemistry Institute, “Green Chemistry Principles, Practice, and Economics.” The Fall Scientific Meeting itself gets underway at 11:00 a.m. with lunch, graciously provided by The Dow Chemical Company. There will be a workshop on Microsoft® Word 2002 and a panel discussion on career development taking place during the lunch hour. You’re welcome to take your lunch with you to these presentations. Also, the exposition will be in full swing. Please stop by the vendor booths and don’t forget about the prize baskets that will be given away. Also, don’t miss the poster session featuring exciting research from local universities and corporations.

The formal portion of the meeting gets underway at 1:00 p.m. with the welcome and awards presentation by the Midland Section of the ACS. We are honored to have the 2003 Presidential Green Chemistry Award recipient, Richard Gross of Polytechnic University, to deliver our keynote address. An excellent line-up of speakers follows in the areas of Renewable Materials and Green Processes. A post-meeting social will follow the meeting at Oscar’s with free appetizers and beverages. All are invited. This social is sponsored by our exposition vendors and is an excellent way to catch up with old friends, meet some new ones, and relax from the rigors of what will be an informative meeting.

Last but not least, it’s time to share the praise and gratitude to everyone who helped make this event possible. First to The Dow Chemical Company, especially Rick Gross for donating the use of these world-class facilities and for donating the superb lunch. A special thanks goes out to all of our vendors. The 2003 FSM organizational volunteers, listed below, did a wonderful job in organizing their venues. Please extend your personal gratitude to them as well. To the speakers, poster presenters, and vendors, thank you for providing the reason to meet. Finally, thank *you* for participating in the 59th Midland Section ACS Fall Scientific Meeting. We hope you find the meeting professionally and personally rewarding.

Sincerely,

Wendy Flory and Dale LeCaptain
Co-Chairs, 2003 ACS Fall Scientific Meeting

Committee Volunteers:

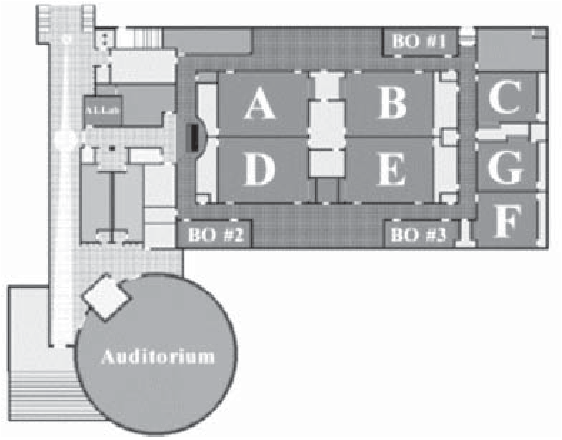
Speakers	Pat Smith, Whitney Conner, Mindy Keefe
Workshops	Gretchen Cole, Ann Birch, Don Miller, Gary Kozerski
Posters	Houxiang (Sean) Tang, Brad Fahlman
Locations	Becky Lorenz, Dan Dermody, Buford Lemon
Registration	Mike Johnson, Yang Cheng, John Tsavalas, Kate Austin, Maria Ngo, Kristin Prokopenko, Pamela Slavings, and Maria Ngo
Program	Ann Birch
Exposition	Wendy Klein, Pamela Slavings, Diana Mitchell, Gary Kozerski
Publicity	Carrie Briggs, Teresa Sanchez-Orvosh, Danielle Gingerich

Registration

The doors to EDC will be open beginning at 7:30 a.m. for those attending the Green Chemistry Workshop. Registration for the Fall Scientifc Meeting will begin at 10:30 a.m. However, we strongly recommend that you preregister at the ACS web site:

http://membership.acs.org/M/Midl

Click on the Fall Scientific Meeting banner and then on Registration. By doing so, we will have a name tag prepared for you and you will avoid the lines that form at registration the morning of the meeting. Preregistration ends October 10.



8:00–11:00 a.m.	Green Chemistry Workshop‡ (room A)		
10:30 a.m.	Registration Begins (entrance)		Vendor Exposition (rooms B&C) Poster Session (rooms D&E) Authors present from 11–1
11:00–11:25 a.m.	General Admission and Lunch* (AB and DE hallways)	MS Word Workshop‡ (room A)	
11:25–11:50 a.m.		MS Word Workshop‡ (room A)	
11:50 p.m. –12:50 p.m.		Panel Discussion: "Career Management" (room A)	
1:00–1:30 p.m.	Welcome/Section Awards (auditorium)		
1:30–2:15 p.m.	Professor Richard Gross (auditorium)		
2:15–2:25 p.m.	Break		
	Renewable Resources Session (auditorium)	Green Processes Session (room A)	
2:25–2:50 p.m.	Ramani Narayan	Tony Kingsbury	
2:50–3:15 p.m.	Greg Baker	John Nghiem	
3:15–3:25 p.m.	Break		
3:25–3:50 p.m.	Larry Drzal	Dilum Dunuwila	
3:50–4:15 p.m.	Dave Henton	Dennis Miller	
4:15–4:40 p.m.	Ray Cocco	Greg Zeikus	
5:00–7:00 p.m.	Social at Oscar's (140 East Main Street)		

‡Preregistration required, space limited.
**Provided by The Dow Chemical Company*

Workshops

Green Chemistry: Principles, Practice, and Economics

Mary Kirchhoff

Assistant Director, Green Chemistry Institute

Larry Koskan (invited speaker)

Green chemistry, the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances, is the most fundamental approach to pollution prevention. Green chemistry addresses the need to produce the goods and services that society depends on in a more environmentally benign manner. Life-saving pharmaceuticals can be produced while minimizing the amount of waste generated, plastics that biodegrade can be synthesized from plants, and reactions can be run in water rather than in traditional organic solvents by applying green chemistry principles to chemical products and processes. Green chemistry technologies have eliminated waste, improved safety, enhanced security, and saved industry money. This workshop will introduce the principles of green chemistry, provide industrial and academic examples of greener technologies, and highlight the economic benefits of adopting environmentally friendly processes. Please preregister for this workshop at http://membership.acs.org/M/Midl.

Using Microsoft® Word 2002 for Technical Documents

Ann F. Birch

Editech, Midland, MI 48640

What's new in 2002? Microsoft Word 2002, that is. Many technical professionals have just recently updated to MS Word 2002 from earlier versions. This 20-minute presentation explores the new features that benefit technical writers and offers advice on dealing with the features that they may not find helpful. Please preregister for this workshop at http://membership.acs.org/M/Midl.

Panel Discussion

Career Planning and Management

Don Miller

Panel Members: Bob Spears, Consultant, Right Management Consultants
Megan McHenry, Marketing Manager, Mid-Michigan Health
Deb Bergstrom, Vice-President of Operations, Dendritic Nanotechnologies

The panel will discuss:
- Career planning skills at both large and small companies
- Information for those considering alternate career paths (consulting, teaching)
- Tips on job searching (networking, interviewing, targeting the job market)

Come and hear strategies on how to take charge and manage your career, plus success stories of people who have been through major career changes.

Welcome

Wendy Flory and Dale LeCaptain

Co-chairs, 2003 Fall Scientific Meeting

Presentation of 2003 Midland Section Awards

Mike Owen

Chair, ACS Midland Section

Outstanding Achievement and Promotion of the Chemical Sciences

Each year the Midland Section honors an individual residing within the Section's geographical area who has demonstrated outstanding achievement and promotion of the chemical sciences. This award recognizes dedication and service to the chemical profession.

Outstanding Service to the American Chemical Society

The Section sponsors an annual award to a member to recognize outstanding service to the Midland Section of the ACS. This award recognizes achievement in the promotion of the goals of ACS.

Outstanding Chemical Technician

The Section presents an annual Outstanding Chemical Technician Award to an individual who has demonstrated an extremely high degree of professionalism as a chemical technician.

Fifty-Year Members

Robert Cierzniewski
Henry E. Hennis
Donald Ingebrigtson
Donald Petersen
Vernon Fauver
Robert L. Hotchkiss
I. Arthur Murphy
John Saam
Ted Selby

Don't Forget Post-Meeting Social!

Don't forget to join your colleagues at the post-meeting social at Oscar's Restaurant. Free appetizers and beverages will be available compliments of Midland Section—ACS and exposition vendors.

140 E. Main St., Midland
5:00–7:00 p.m., October 17

Keynote Address

Advances in Polyester Synthesis Using Lipase-Catalysis

Professor Richard A Gross
Polytechnic University, Brooklyn, NY

This lecture will focus on recent advances by our laboratory using *in-vitro* lipase-catalysis for lactone ring-opening and condensation polymerizations. Studies of the kinetics and mechanism of *Candida antartica* Lipase B (CALB) catalyzed e-caprolactone (e-CL) polymerizations were performed. The kinetic plot of Ln($[M]_0/[M]_t$) versus time is linear ($r^2 = 0.998$) indicating that termination did not occur and the propagation rate is first order with respect to monomer concentration.

Lipases can polymerize macrolactones that are otherwise difficult to polymerize by conventional catalysts. In fact, with immobilized CALB as catalyst, poly(PDL) with M_n up to 90 000 and >97% monomer conversion was obtained within 20 minutes. Poly(PDL) has hydrolyzable ester units as well as a T_m, T_g, and %-crystallinity of 97°C, -27°C, and 60%, respectively. Poly(PDL) forms hard-tough materials that elongate from 100 to 200%. Hence, poly(PDL) and its copolymers are a new set of materials made available by lipase-catalysis. The ability to substitute water with other initiators has allowed for the preparation of polyesters with various end-groups. Regioselective initiation of lactone-ring opening by carbohydrates was found to be a simple way to conjugate carbohydrates at the terminus of polyesters.

Soluble polymers from reduced sugars were synthesized with absolute molecular weights up to 117 000 (M_w), without chemical activation of the monomer acid groups or the addition of an organic solvent. Although highly polar reactants were used, they formed a monophasic liquid medium when gently mixed and heated without addition of a polar aprotic solvent. The lipase-catalyst (Lipase B from *Candida antartica* immobilized on Lewatit beads) suspended in the monophasic liquid was selective and highly active. Polyesters rich in hydroxyl functionality, such as poly(sorbityladipate), were prepared without the need to use protection-deprotection chemistry. While the lipase was highly selective for sorbitol polymerizations, it was promiscuous for glycerol copolymerizations. This promiscuity led to poly(1,8-octanoyladipate-co-glyceroladipate) chains that are rich in mono-substituted glycerol terminated branches. Thermal analysis of the sorbitol and glycerol copolymers revealed they are semi-crystalline, low melting, soft materials. The lipase-catalyzed polyol condensation synthetic strategy is anticipated to be broadly applicable to many natural and synthetic polyols.

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Gross, *J. Am. Chem. Soc.*, 124(9) (2002). R.A. Gross, A. Kumar, B. Kalra, *Chemical Reviews*, 101(7), 2097–2124 (2001). A. Kumar, R.A. Gross, *J. Am. Chem. Soc.* 122,11767–11770 (2000). A. Kumar, B. Kalra, A. Dekhterman, R.A. Gross, *Macromolecules*, 33, 6303–6309 (2000).

Biography: Dr. Richard Gross is the Herman F. Mark Professor at Polytechnic University, Brooklyn, New York. He received his Ph.D. in organic-polymer chemistry from Polytechnic University in 1986. He was awarded a postdoctoral fellowship at the University of Massachusetts Amherst, studying with Professor Robert W. Lenz. He was a professor at the University of Massachusetts Lowell from 1988 to 1998. He has been the Herman Mark Professor at Polytechnic University since 1998.

His research focuses on materials synthesis, particularly chemical methods and microbial and in vitro synthesis of biopolymers, and biodegradation testing. He is the president of the U.S. Society on Biodegradable Polymers and co-director of the Center for Enzymes in Polymer Science. He is the founder of the Journal of Environmental Polymer Degradation. The most recent of his awards is the 2003 Presidential Green Chemistry Award. Dr. Gross is the author or co-author of 73 publications.

Green Processes Symposium

Recovery of Glycols from Aqueous Solution via Reactive Distillation

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James E. Jackson

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A reactive distllation process has been developed for the recovery of ethylene glycol (EG) and propylene glycol (PG) from a mixture of chemical species in aqueous solution. The method involves the reaction of glycols with acetaldehyde or formaldehyde in a reactive distillation column to form cyclic acetals. These acetals form minimum boiling azeotropes with water and are removed from the reactive distillation column as they are formed, thus facilitating glycol recovery without having to vaporize all water present. The process is of particular interest for the recovery of EG and PG from the effluent stream of a carbohydrate hydrogenolysis process, where a feed material such as sorbitol is cracked to glycerol, EG, PG, and a mixture of C_2–C_5 polyhydroxylated compounds.

In the reactive distillation column, formation of acetals of EG (2-methyl-1,3-dioxolane) and PG (2,4-dimethyl-1,3-dioxolane) is catalyzed by strong cation exchange resins such as Amberlyst 15. Any acetals of heavier diols and polyhydroxylated compounds that are formed have boiling points higher than that of water, and are thus hydrolyzed in the lower section of the column, giving the aqueous solution without EG and PG as the bottoms stream. Downstream of the main acetal formation column, the acetals of EG and PG are separated from each other via conventional distillation and then hydrolyzed via reactive distillation with excess water to give high purity EG and PG. Acetaldehyde liberated in hydrolysis is recycled to acetal formation.

Experimental studies have been carried out in 3-m bench-scale and 6-m pilot-scale columns. Up to 95% recovery of PG from water has been obtained in the pilot-scale column. Hydrolysis of both acetals is rapid and nearly 100% recovery of high purity PG and EG can be achieved. Process simulations using AspenPlus simulation software, using thermodynamic VLE data collected for the acetals, accurately model pilot-scale column behavior is a rate-based model is implemented. Simulation illustrates that complete EG and PG recovery can be expected in a commercial-scale unit of modest size.

Biobased Industrial Products: Impact of New Succinic Acid Fermentation and Bioelectrocatalysis Technologies

J. Greg Zeikus

President Emeritus MBI International
Professor of Biochemistry and Molecular Biology
Michigan State University, Lansing, MI 48824

Biobased industrial products are enabling agriculture to expand into health, energy, chemical and materials markets in the twenty-first century. Examples of these products will be described including intermediary chemicals, pharmaceuticals, biochemicals, fuels, agrichemicals, bioplastics, and higher-value polymers and materials. Succinic acid as an intermediary commodity chemical derived from carbohydrate fermentation has the potential to supply over 2.7×10^8 Kg industrial products per year including: 1,4-butanediol, tetrahydrofuran, butyrolactone, adipic acid, n-methyl-pyrrolidone, and linear aliphatic esters. Although *A. succinogenes* strains can make succinate levels as high as 110g/L, chemical yields and productivities from glucose need to be improved to produce this commodity product at less than 25c/#.

The metabolic pathway for succinate production in *A. succinogenes* will be described with emphasis on key enzymes and genes. Improvements in succinate yields and productivities may be made by using a new genetic engineering system developed in this organism. The commercial potential of bioelectrocatalysis spans sensors, chemical diagnostic tools, energy generation and chemicals. Examples presented will include: electrical enhancement of succinate production; use of fumarate reductase as a sensor, fuel cell and synthetic catalyst; and electricity production from microbial degradation of organic waste waters.

Sustainable Plastics Recycling

Tony Kingsbury

Plastic Issues and Industry Affairs
2030 Building, The Dow Chemical Company
Midland, MI 48674

Over the past decade we have seen a huge increase in the amount of plastics being recycled. Most, if not all, of us have personal experience in recycling plastic packaging such as beverage bottles. We are now seeing new products such as computers and other durable goods being recycled in ever increasing quantities. Have you ever stopped to ask, is this sustainable recycling? Why do we recycle plastics? Are there opportunities to recycle more plastics and if so, should we recycle ever increasing amounts? In this talk I will address these and other aspects of this complex corporate, political and technical opportunity.

Renewable Materials Symposium

Plastics from Renewable Resources

Ramani Narayan
Department of Chemical Engineering & Materials Science
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(www.msu.edu/user/narayan)

Biodegradable plastics and biobased polymer products based on annually renewable agricultural and biomass feedstocks can form the basis for a portfolio of sustainable, environmentally responsible products. Two basic routes are possible. Direct extraction from biomass yields a series of natural polymer materials (cellulose, starch, proteins), fibers, and vegetable oils that can form the platform on which polymer materials and products can be developed. Alternatively, the renewable resources/biomass feedstock can be converted to bio-monomers by fermentation or hydrolysis and then further converted by chemical synthesis to biodegradable polymers like polylactic acid. Bio-monomers can also be microbially transformed to biopolymers like the polyhydroxyalkanoates. Surfactants, detergents, adhesives, and water-soluble polymers can be engineered from biomass feedstocks.

This presentation will focus on the manufacture of starch foam products, starch based thermoplastics, and vegetable oil based products based on ongoing work in our research group. The positive environmental benefits and sustainability of these products will be documented using life cycle assessment (LCA) methodology.

Cargill Dow's Polylactic Acid Products and Technology

David E Henton
Cargill Dow LLC
1707 Building, Midland, MI 48674

Poly(lactic acid), PLA, has been commercialized by Cargill Dow LLC, a joint venture between Cargill, Inc. and The Dow Chemical Company. PLA is a high molecular weight thermoplastic suitable for diverse application areas such as fibers and nonwovens, films, extruded and thermoformed containers, and extrusion coated paper. It is derived from corn via fermentation to first produce lactic acid followed by a solvent free process to prepare lactide and high polymer. Cargill Dow's NatureWorks™ process was awarded the 2002 Presidential Green Chemistry Award for its innovative and environmentally friendly characteristics. The chemistry of PLA, polymerization, materials science and applications will be presented. Life cycle analysis of energy and greenhouse gas production benefits compared to conventional oil based polymers will also be presented.

NatureWorks is a registered trademark of Cargill Dow LLC.

PLA Mimics of High-Volume Thermoplastics

Gregory L. Baker

Department of Chemistry and Center for Fundamental Materials Research
Michigan State University, East Lansing, MI 48824

Degradable polymers derived from renewable resources are “green” alternatives to materials now obtained from petroleum. Polymers based on lactic acid (PLAs) are now being commercialized as commodity materials, and there is intensive research interest in improving the properties of PLAs through synthesis and processing. Our strategy has been to replace the methyl group of lactic acid with various aryl and alkyl substituents to obtain polymers with properties substantially different from PLA. For example, replacing the methyl group of lactic acid with a benzene ring or an isopropyl group results in polymers that mimic polystyrene and polyethylene terephthalate, respectively. The synthesis and molecular characterization of these polymers will be described.

Structural Bio-Composites: Value-Added Opportunities for Biobased Polymers

Lawrence T. Drzal

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There is a growing urgency to develop and commercialize new bio-based “green” materials and innovative technologies that can produce a bio-based structural material competitive with current synthetic products and at the same time have the benefits of reducing dependence on foreign oil, enhancing national security, improving the environment, and creating new opportunities for the agricultural economy. The US Research and Development Act of 2000 along with Presidential Executive Orders 13134 and 13104 and the recent “Farm Bill” signed by President Bush on May 13, 2002, together provide a new impetus for the use of biobased materials and products as replacements for petroleum-based products. Ongoing research at Michigan State University has been exploring “biocomposites” made by embedding natural/biofibers such as kenaf, hemp, flax, jute, henequen, pineapple leaf fiber, corn-stalk fibers, and native Michigan grasses into petroleum-derived traditional plastics such as polypropylene, unsaturated polyesters, and epoxies and “green biocomposites” by embedding these biofibers into renewable resource-based bioplastics such as polylactides (PLA), cellulosic plastics, soy-based plastics, bacterial polyesters, and urethanes produced from vegetable oil based polyols.

A multidisciplinary approach has been developed to produce biocomposites with desirable mechanical properties which requires: (i) new and novel processing to combine biofibers with plastics; (ii) low cost but effective surface treatment of the bio-fibers; (iii) selection and design of a multicomponent blend of bast and leaf biofibers; (iv) and suitable matrix polymer modifications to optimize biocomposite strength and stiffness. Biofiber reinforced petroleum-based plastic biocomposites can at this time produce a structural material with a balance between ecology, economy, and technology. New and emerging renewable resource-based bioplastics are costly and energy intensive at this time but through reinforcements with inexpensive bio-fibers and through careful design and engineering, sustainability of the resulting products can be achieved. This presentation will give an overview of the present and future opportunities for biocomposite materials for automotive and building materials for the 21st century. Some examples that will be discussed include: cellulosic plastic based green composites with improved properties over polypropylene based biocomposites; reactive blending of soy-based plastics; novel hybrid plasticization of soy protein based plastic to produce a balance in stiffness-toughness.

This research is supported in part by grants from NSF (NSF-EPA Award #DMI-0124789; NSF-PATH Award # 0122108) and USDA (USDA-NRI Award # 2001-35504-10734)

WoodStalk™: An Environmentally Friendly Particle Board Composite

Ray Cocco

Engineering Sciences and Market Development
1319 Building, The Dow Chemical Company, Midland, MI 48674

On June 26, 2001, The Dow Chemical Company formed Dow BioProducts, Limited (DBP). DBP manufactures WoodStalk, a three-layer composite board made from wheat straw and pMDI. Unlike most other particleboards, WoodStalk is 100% formaldehyde free. In addition, WoodStalk meets or exceeds all M3 properties that represent high-quality particleboard, and WoodStalk is lighter, easier to machine and more moisture resistant than the competing wood particleboard products. WoodStalk is sold in several thickness including 3/4-, 5/8-, and 1/2-inch boards, and 1/4-inch underlayment. WoodStalk can be found throughout the United States and Canada in applications ranging from floor underlayment to shelving, furniture, windows, and doors. This presentation will explore the manufacturing process for WoodStalk and the environmental advantages of making such a product.

WoodStalk is a trademark of Dow BioProducts, Ltd.

Pretreatment of Biomass: The AFEX Process

Nhuan (John) P. Nghiem

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Biomass is a renewable resource, which is available in the U.S. in very large quantities. Typically at least 50% of the biomass consists of cellulose and hemicellulose, which are potential sources for fermentable sugars and fibers. Conversion of biomass by biological processes to fuels and chemicals is difficult both technically and economically mainly because of its recalcitrance. Therefore, biomass must be pretreated before it can be used in bioconversion. Many pretreatment technologies have been developed to improve the bioconversion of biomass. A good pretreatment process must a) Preserve all the available carbohydrates, b) Produce a highly reactive material, c) Generate no inhibitory compounds, and d) Have low processing cost. The Ammonia Fiber Explosion (AFEX) process meets all these requirements. In the AFEX process the biomass is reacted with anhydrous liquid ammonia at moderate temperatures (~90°C) and pressures (~300 psig) for a relatively short period (10–20 minutes). The reactor content then will be flashed into a large tank. The reaction of ammonia with the biomass and the resulting explosion will disrupt the fiber structure and make the biomass much more accessible to enzymatic or microbial attack. The AFEX process does not degrade available carbohydrates and does not generate compounds that are inhibitory to fermentation. The sugar hydrolysate can be used directly in a bioconversion process, for example, ethanol fermentation. After the pretreatment, greater than 95% of the ammonia can be recovered and recycled, thus significantly reducing chemical costs. In addition, in the AFEX process there is no requirement for neutralization, which minimizes wastes. This qualifies AFEX as an environmentally friendly process. At MBI we have a 300-mL AFEX reactor for process kinetics investigation and a 1-gallon reactor for scale-up study. Recent results obtained in our laboratory will be discussed.

Succinic Acid Fermentation

Dilum Dunuwila

Diversified Natural Products
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The most abundant potential source of feedstocks for chemicals and fuels is biomass. However, biomass-derived chemicals can’t compete with fossil-fuel-derived products due to the lack of integrated, cost-effective processes to convert biomass into products. However, use of inexpensive biological feedstocks and innocuous chemical conversions have paved the path for the development of cost-effective processes to convert biomass to useful chemicals. This approach is currently being pursued by Cargill Dow, LLC in the United States, Purac in the Netherlands, and Galactic in Belgium to produce lactic acid from a wide range of sugars ranging from beet sugars to starch derived from corn. These processes combine novel fermentation with chemical process steps to achieve economics that produce lactic acid at commodity prices. The next generation of biobased chemicals will come from succinic acid. The fermentation of sugars to produce succinic acid has been the subject of intense research and development worldwide. The U.S. Department of Energy (DOE), in particular, has invested in the development of succinic-acid-producing organisms. However, all commercially viable, succinate-producing microorganisms presently require neutralization of the fermentation to ensure that the pH does not become low enough to kill the microbes. Therefore, to obtain the acid, a cation elimination process is necessary, wherein the base cation needed to neutralize the acid in the fermentation is replaced by protonation. Michigan State University (MSU), with partial funding from Applied CarboChemicals of East Lansing, MI (currently, Diversified Natural Products, Inc.), developed a cost-effective separation and purification process that allows efficient conversion of succinate to succinic acid and regeneration and recycling of acid/base values. LEC TECH, Inc. (currently, Diversified Natural Products, Inc.) is integrating the separation process with fermentation with funding from the DOE. Such research has lead to a number of possible products including food ingredients, noncorrosive biodegradable deicers for runways, “green” solvents, detergent builders/chelators, surfactants, paper-sizing compounds, and several different polymers. This approach for the production of biobased succinic acid will be presented.

Posters

(1)

Colorimetric Nano-Sensors Based on Photo-Polymerizable Amphiphilic PAMAM Dendrimers

Abhijit Sarkar,[1] Paul S. Satoh,[2] Petar R. Dvornic[1] and Steven N. Kaganove[1]

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Synthetic studies aimed at the development of dendrimer-based colorimetric sensors that combine both sensory and reporter functionalities in nano-scaled macromolecular constructs are reported. Polydiacetylene segments function as colorimetric reporter units while dendrimer cores serve as structure-directing scaffolds. Because of their unique molecular architecture, high density of functionality and specificity, these sensors are expected to show enhanced sensitivity, good compatibility with analyzed media and facile fabrication and handling.

(2)

Synthesis and Characterization of Dendrimer Rods

Peter I. Carver

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The poly(amidoamine) (PAMAM) dendronized polymers (often referred to as dendrimer rods) were made from linear poly(ethylene imine) (PEI) cores that, in turn, were obtained by hydrolysis of the corresponding poly(ethyloxazoline) (PEOX) precursors. There was considerable difficulty in obtaining linear PEOX due to the branching that occurs during its synthesis by cationic polymerization of EOX. However, changes in the method of synthesis and cleaning procedure of the reagents allowed the successful preparation of moderately high molecular weight PEOXs of narrow polydispersity. The obtained products maintained their length even after exhaustive hydrolysis in aqueous hydrochloric acid and yielded linear PEIs of corresponding moderately high molecular weights and narrow polydispersities. The resulting linear cores were dendronized using the traditional divergent method of PAMAM dendrimer synthesis but with greater excess of ethylene diamine (EDA) in order to inhibit intermolecular cross-linking. Particular goals of this work were to characterize the dendronized polymer products for their chemical structure using ^{1}H and ^{13}C NMR, IR, and molecular weight characterization techniques, such as light scattering, and to use transmission electron microscopy (TEM) to visually evaluate the validity of the hypothesis that steric hindrance at large enough side-chain dendrons would cause the main-chain backbone extension resulting in a rod-like molecular conformation.

(3)

Synthesis of Dendrimer Derived from Naturally Occurring Amino Acids

Choon Y. Lee

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The objective of this research is to develop a novel protein-like dendrimer which can be used as a drug-delivery system. The building blocks for the dendrimer are glutamic acid, aspartic acid, and γ-aminobutyric acid (GABA). Because the dendrimer is made of naturally occurring amino acids, we expect that it is less toxic to the cell than other types of dendrimers. Another advantage of using a dendrimer in drug delivery is its spherical shape, which cannot bind to the active site of an enzyme allowing for the dendrimer to evade destruction by enzymes. To avoid enzymatic destruction of drugs, one can conjugate some therapeutic drugs onto the dendrimer. Because the drug-dendrimer complex is not destroyed by the liver, a lower dose is possible, thus extenuating toxicity and other inherent side effects from drugs. To avoid purification problems, solid phase synthesis is used to generate the dendrimer. On the surface of solid beads are grown dendrons (pie-shaped dendrimers) which are eventually connected to make bow-tie shape dendrimers. The novel dendrimers are analyzed using NMR, IR, UV, HPLC, MS, Raman spectroscopy, and gel electrophoresis.

(4)

Inorganic-Organic Polyamidoamine (PAMAM) Dendrimer-Polyhedral Oligosilsesquioxane (POSS) Hybrid Nanomaterials

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Eric J. Hill

Impact Analytical, 1910 W. St. Andrews Rd., Midland, MI 48640

The surfaces of polyamidoamine (PAMAM) dendrimers of various generations have been functionalized with polyhedral oligosilsesquioxane (POSS) species to prepare novel inorganic-organic hybrid nanomaterials. The structures of the obtained products have been fully characterized by MALDI-TOF mass spectroscopy, using trihydroxyacetophenone monohydrate matrix, and ^{1}H, ^{13}C, and ^{29}Si NMR and IR spectroscopy. Selected structure-property relationships across a range of dendrimer generations and percentage of their surface coverage with POSS have also been studied. Cross-linkable variants of these materials have been synthesized and some dendrimer-POSS compositions have been found to form robust and transparent nano-structured films. The dendrimer component of these films could be thermally degraded to create spherical voids and give a nanoporous material with potential application as a low dielectric coating, sensor, membrane or insulating material. Furthermore, the well-known ability of PAMAM-containing dendrimers to encapsulate electrophilic guest species opens up broad possibilities of tailoring still more complex nano-materials involving a variety of other inorganic, organic or organometallic species.

(5)

Investigation on Self-Assembly of Monobasic Acids on Dendrimer Templates

Michael Koivula, Dian He and Minghui Chai,

Department of Chemistry, Central Michigan University, Mt. Pleasant, MI 48859

Dendrimers possessing amphiphilic functionality are potential candidates for useful applications including molecular-scale reaction vessels, drug-delivery and gene-transfer carriers. Surface modifications can extend the inherent functionality of dendrimers through covalent or non-covalent interactions. The self-assembly process of poly(propyleneimine) (PPI) dendrimers (from the first to fifth generations) with long-chain monobasic acids, leads to the formation of noncovalently linked inverse micelles. Our study has shown the size of self-assembly can be tuned by controlling the molar ratio of monobasic acid to dendrimer. In a stoichiometric ratio, due to the aggregation of the self-assemblies, a gel or a powder precipitate is formed in a nonpolar or polar solvent, respectively. With twice the excess amount of acids for the self-assembly, a soluble complex (smaller size) can be formed for the self-assembly in a nonpolar solvent (benzene or toluene). Thus the excess acids can alleviate the aggregation of the self-assemblies. 1D NMR and T_1 relaxation studies were performed on the soluble complex, which clearly showed the acid-dendrimer self-assembly still effectively exists in the nonpolar solvent system. Further investigation through 2D NOESY (nuclear Overhauser effect spectroscopy) NMR and AFM (atomic force microscopy) was performed to understand how the excess acids help the solvation of the self-assemblies in the nonpolar solvent. Molecular dynamic modeling in this study further demonstrates, in the energy-minimized structure, the excess acids interact with the dendrimer-acid self-assemblies to segregate them from aggregation.

(6)

Dendrimer Templated Self-Assembly and Encapsulation

Minghui Chai, Aaron K. Holley, and Michael Koivula

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Monodisperse and cascade structures with multiple functional groups make dendrimers ideal building blocks and scaffolds for making self-assembled nanostructures. The nanosize voids inside dendrimers have been utilized to entrap small molecules for versatile applications. In this work, the stoichiometric amount of dibasic acid intramolecularly self-assembled with a poly(propyleneimine) (PPI) dendrimer to form a “interlocked” system through electrostatic interactions between the ammonium cation of PPI moiety and the carboxylate anion of diacid moiety. Small molecules like fluorescent dyes can be encapsulated within the voids of the PPI/diacid self-assembly. UV-VIS, fluorescence, and NMR spectroscopy were used to monitor changes for the dye in the presence of dendrimer and dendrimer templated self-assembly. Red shifts in the UV-VIS spectra of the dye, reductions in fluorescent emission, and decreases in ^{13}C spin-lattice (T_1) relaxation time indicated effective encapsulation of the dye within the self-assembly. NOE interactions have been observed between the dye molecule and the interior part of PPI dendrimer moiety of the self-assembly. Based on these experimental data, molecular modeling and dynamic simulation are performed to understand the unique properties and applications for the self-assembly and encapsulation of dendrimers.

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(7)

Electrophoresis of PAMAM Dendrimers & Conjugates

Dillip Mohanty, Ankur Desai, Riaz Ali, Ajit Sharma
Department of Chemistry, Central Michigan University, Mt. Pleasant, MI 48859

A simple, inexpensive, and rapid electrophoresis technique was developed for use as a routine tool for separation of polyamidoamine (PAMAM) dendrimers and their bioconjugates. A variety of factors influencing migration of generations 0–7 dendrimers on nongradient polyacrylamide gels were evaluated. The proposed method incorporates PAMAM dendrimer separation under basic and acidic conditions. Electrophoresis under acidic conditions gave increased resolution and sensitivity over separation at alkaline pH. Separation of bioconjugates of dendrimers was thus carried out under acidic conditions. Trailing generations and dimers could be clearly separated from parent dendrimer molecules thereby allowing the use of this methodology in evaluation of dendrimer purity during synthesis.

(8)

Intramolecular Photocycloaddition Reactions - (1) Total Synthesis of Ingenol, 2) Asymmetric Induction with Chiral Ester Tether Groups

Wendell L. Dilling
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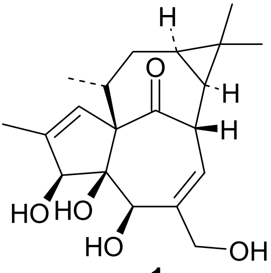
A CMU Organic Discussion Group seminar on the title subject presented earlier this year was based primarily on papers by Winkler (*J. Am. Chem. Soc.* **2002**, *124*, 9726–9728) and by Pete *(J. Org. Chem.* **2002**, *67*, 1061–1070) and their co-workers. In the first paper, racemic ingenol (**1**) was synthesized in 44 steps, the key of which was an intramolecular photocycloaddition. This synthetic target with its trans intrabridgehead stereochemistry, a tricky structural arrangement, had provided a difficult synthetic challenge for many years. In the second paper, intramolecular photocycloaddition of cycloalkenones with unsaturated side chains



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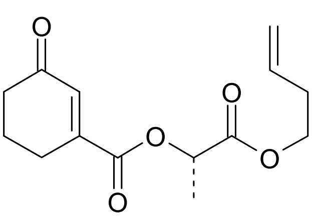

2

connected by ester linkages prepared from chiral, nonracemic, hydroxy acids, such as **2**, gave adducts with diastereomeric excesses as high as 94%. Part of this seminar involved a challenge to determine the *R* or *S* configuration of several chiral centers in the products from the latter reactions. Try your hand at it before you look at the answers.

(9)

Recent Organic Seminar Group (OSG) Presentations

Wendell L. Dilling (retired), David S. Allan, Mehmet Demirors, Robert P. Dion, Ray E. Drumright, Thomas E. Fisk, Jerry L. Hahnfeld, David E. Henton, Mladen Ladika, B. Robert Maughon, Dianne M. Maughon, Peter N. Nickias, Kevin D. Sikkema, David R. Speth, Edmund J. Stark, Daniel E. Verral II, John M. Warakomski, Rick A. Wolf

The Dow Chemical Company, Midland, MI 48686

Topics presented by members of OSG at group meetings over the last three years will be shown: Chemistry and Technology of Clay Materials; Why Sweat the Small Stuff: Chemical Analysis in Small Domains; Photocycloaddition Reactions of Fullerene-C_{60}; Recent Developments in the Application of Olefin Metathesis Chemistry in Organic Transformations; Multicomponent Reactions Using Isocyanides; Organic Synthesis on Soluble Polymer Supports; Drugs Used to Treat HIV; Advances in Selectivity in Hydroformylation; Diffusion of Reactive Organic Species; The Chemistry of Explosives; Anti-Oxidants, The Chemistry of Life; New Organometallic Approaches to Selective Hydrocarbon Functionalization; Would Wood Work?; Fire and Plastics; Water Tolerant Strong Acid Catalysis; DNA, Complementary DNA (cDNA), Oligonucleotides and the Search for the “Magic Bullet” to Cure Diseases; Asymmetric Autocatalysis; Making Sense of Antisense Oligonucleotides: Syntheses and Use.

(10)

Spring Research Project 2003: Developing Microscale Experiments for the Organic Chemistry Course

**Sara J. Barth, Marie J. Dulcos, Zachery T. Graham, Janet L. Kaminski,
Patrick M. Kendall, Kara A. Milbrandt, Jeremy J. Thaut and David Baker**
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A series of microscale experiments using pentaerythritol (**1**)[1,2] have been designed for the organic chemistry laboratory course. Undergraduates did all these experiments as part of a spring research project. These reactions illustrate many of the concepts and methods discussed in the organic chemistry lecture series. These reactions include chlorinations and esterifications of alcohols and the formation of diacetals. The experiments involve a variety of microscale techniques and skills. Initial observations suggest that the students enjoyed developing those experiments and seeing how functional groups can be manipulated and reacted.

(11)

Biocatalysis of Organosilicon Molecules

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Historically, conventional condensation catalysts and reaction conditions have limited the ability to control the structure of organosilicon materials. Under mild reaction conditions, enzyme-catalyzed reactions with organosilicon molecules were explored in order to study the feasibility of forming ester and amide bonds. The substrates were chosen to investigate the attributes of biocatalytic reactions during the preparation of relevant organosilicon monomer, macromer, and polymer systems.

Enzymatic routes for the synthesis of organosilicon polyesters, carbohydrates, and polyamides were discovered and reduced to practice. Lipase and protease enzymes catalyzed the formation of ester and amide bonds between various organosilicon and organic molecules including a regioselective reaction with a carbohydrate under mild reaction conditions. Various monomer, macromer and polymer materials were created to demonstrate the potential of the routes. In particular, pure organosilicon-sugar conjugates were prepared in a one-step reaction without performing any protection-deprotection steps. It was observed that the lipase-catalyzed reactions did not require activation of either the acid or alkyl ester groups. In comparison to organic materials, the hydrophobic organosilicon molecules were acceptable substrates and appeared to enhance the rate of condensation catalyzed by the interfacial enzyme. The ability to perform selective reactions under mild reaction conditions should enable the synthesis of structurally defined organosilicon molecules with a fully diversified set of functional groups and properties.

(12)

Comparative Reactivities of 2,4,6-Trihalopyrimidines with Sodium Phenoxide

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Previously we investigated the reaction of the four 2,4,6-trihalopyrimidines with sodium methoxide. We have now expanded these investigations to comparable reactions with sodium phenoxide. Not surprisingly, the halogens react readily with this anionic nucleophile in the general order of the halogens being displaced, namely F > Cl > Br > I. However, in contrast to the reactions of these halogenated pyrimidines with methoxide ion, the reactions with one equivalent of phenoxide ion did not stop at monosubstitution in all cases. We will describe the reactions involved and correlate the products obtained with the specific halogen atoms being displaced. The results have been obtained through a combination of proton NMR and gas chromatography.

(13)

Phosphorus Esters of 1,1,2,2-Tetraphenyl-1,2-ethanediol

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The reaction of 1,1,2,2-tetraphenyl-1,2-ethanediol with phosphorus trichloride or phosphoryl chloride has been explored as a possible approach to the preparation of strained phosphorus-containing compounds which might serve as radical initiators for polymerization. If effective as initiators the use of these compounds would lead to the formation of polymers containing phosphorus moieties in the main chain.

(14)

Development of a Technique to Monitor Polyurethane Reactions

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FT-IR technique offers a powerful means of studying chemical reactions in *in-situ* conditions [1-3]. Closed systems with infrared probes provide means of remote monitoring chemical reactions involving corrosive or toxic chemicals. Recent beneficiaries of such a capability include chemical, biotechnology, fermentation, and pharmaceutical industries. Insight gained from such studies is vital in new product development, improving current products, and in quality control/assurance. An analytical method was developed for monitoring polyurethane chemical reactions. This method uses the FT-IR-ATR technique. It is simple and easy to use. One mixes the ingredients rapidly in a hood and applies it to the crystal surface and records the spectra. Use of this technique to monitor consumption of certain ingredients, formation of new functional groups during a chemical reaction will be illustrated. When used in conjunction with complementary techniques such as NMR, GC-MS, GC one can get a deep insight into a chemical reaction.

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(15)

Newer Chromatographic Methods for the Characterization of Polymers

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The characterization of polymer structure and molecular weight represents an important analytical challenge. This is particularly the case for branched polymers. Chromatographic methods have long had an impact in this area. Newer chromatographic materials and techniques have now permitted significant improvement in the analysis of polymers of complex structure.

(16)

Synthesis of an Initiator for Mediated Radical Polymerization

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Poly(styrene) containing no head-to-head units may be prepared by nitroxyl mediated radical polymerization followed by reduction of the end groups. The construction of a suitable initiator for mediated polymerization of styrene at moderate temperature is based on *t*-butyl amine and involves several steps. Purification may be achieved using chromatographic techniques.

(17)

New Flame Retardants Derived from Melamine and Related Compounds

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Compounds containing both nitrogen and phosphorus as major structural components should function as superior flame retardants for polymeric materials. Melamine or aromatic amines may serve as convenient bases for the preparation of such compounds. Condensation with formaldehyde in the presence of diethyl phosphite affords phosphorus esters containing varying levels of nitrogen.

(18)

Lowering Ejection Force During Injection Molding of QUESTRA* Syndiotactic Polystyrene (SPS) Compounds

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QUESTRA syndiotactic polystyrene (SPS) is a semi-crystalline polymer that is useful as an engineering plastic, especially when compounded with glass-fiber reinforcement, and other additives, such as impact modifiers and flame retardants. With a melting point of 270°C, SPS compounds have excellent properties such as heat resistance, solvent resistance, low dielectric constant, insensitivity to moisture, low specific gravity compared to other semi-crystalline polymers, and dimensional stability.

During injection-molding operations, syndiotactic polystyrene compounds generally are ejected from the mold easily. In some cases, depending on the design and condition of the tool, improved demolding is desired. Ejection force can be decreased by up to 85% by adjusting molding conditions and adding mold release agents. We will describe a full factorial designed experiment from which we developed a predictive model for ejection force based on mold temperature, hold pressure, and melt temperature. We will also describe the effect of internal and external mold release agents.

*Trademark of The Dow Chemical Company.

(19)

Nitrogen-Bromine Compounds as Dual Functional Flame Retardants

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The demand for more effective, low-cost, environmentally friendly flame retardants for polymeric materials continues to increase. Dual functional compounds, i.e., compounds that display both solid-phase and gas-phase flame retardancy, offer strong potential to respond to this need. A number of compounds generated from variously brominated phenols and 2,4,6-trichlorotriazine contain both halogen (for gas-phase activity) and nitrogen (to promote char formation at the surface of the burning polymer).

(20)

Investigation on Copolymer Tacticity using Multidimensional NMR Spectroscopy

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Nuclear magnetic resonance (NMR) spectroscopy has been one of the most powerful tools for studying the structures and properties of chemically bonded molecules and noncovalently associated supramolecules. The tacticity and sequence of a specific copolymer chain affect the polymer's physical and chemical properties as well as its applications. So far, most studies on determining the tacticity and sequence of copolymers have relied upon 1D NMR spectroscopy and chemical-shift prediction, which can be complicated, inaccurate, and very ambiguous because of the heavily overlapped resonances of the copolymers. In this study, multidimensional NMR spectroscopy has been implemented to study the tacticity and sequence of copolymers and to resolve the overlapped resonances by dispersing the information into more dimensions. The multidimensional NMR experiments used include phase-sensitive HSQC-TOCSY (heteronuclear single quantum coherence-total correlation spectroscopy) and gHMBC (gradient heteronuclear multiple bond correlation spectroscopy). The copolymers used in this work are poly(methyl methacrylate-co-ethyl acrylate) and poly(ethyl methacrylate-co-methyl acrylate). The homopolymers include poly(methyl methacrylate), poly(ethyl methacrylate), poly(methyl acrylate) and poly(ethyl acrylate), which are also studied in comparison with the copolymers for NMR resonance assignments. It has been noticed that, in 2D NMR spectra of copolymers, delicate resonance patterns appear from complicated tacticity and sequence effects as more acrylate monomer units incorporate into the copolymer chain.

(21)

New Pathways for Modifying the Surface of High-Density Polyethylene: Chemically Benign Adhesion Promotion and Subsequent Functionalization

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Despite the engineering versatility of high-density polyethylene (HDPE), its pristine surface is nonpolar and has no inherent attraction to conventional paints as well as inorganic- or organic-based glues. The surface of HDPE was modified using a heterogeneous chemical reaction process patented by Beholz (U.S. Patents 6,077,913 and 6,100,343). HDPE panels were immersed in a heated solution of either aqueous NaOCl or $Ca(OCl)_2$ with either acetic anhydride, succinic acid, or acetic acid. The reaction was quenched with excess deionized water at room temperature. 1–10 mole percent chlorine heteroatoms were identified on the resulting HDPE surface using ESCA techniques. The polymer surface composition, surface tension, paint adhesion, and tensile adhesive strength were examined as a function of reaction time, stoichiometry, and number of repeated chlorination treatments. In contrast to the current methods used to render HDPE adhesive, this efficient, economical, and benign surface chlorination treatment produces relatively small handling and disposal risks as well as no apparent polymer surface degradation or bulk mechanical changes. Subsequent chemical functionalization reactions conducted on the chlorinated HDPE surface, which offer flexibility in ultimately tailoring surface interactions (i.e. hydrophilicity, polarity, compatibility, adhesion, and reactivity) will be detailed.

(22)

The Effect of Macromolecular Architecture on Functional Group Accessibility: Hydrogen Bonding in Phenolic Photoresist Polymers

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Macromolecular architecture-phenolic functional group accessibility relationships in linear and novel, branched poly(4-hydroxy styrene) (PHS) photoresist materials were investigated using the thermal properties and phase behavior of hydrogen-bonded polymer blends. Furthermore, PHS architectures were converted to poly(4-hydroxystyrene-*co*-5-vinyl salicylic acid) *via* electrophilic aromatic substitution and subsequent oxidation to increase hydrogen bonding as well as lithographic performance and breadth of applications. Branched PHS was also covalently tethered to uniquely surface functionalized high density polyethylene utilizing a scaffolding-type template polymerization in an effort to ultimately tailor inter-/intra-molecular interactions, compatibility, reactivity, and adhesion at the poly(α-olefin) surface.

(23)

Performance Benchmarking of Antifoams in Acrylic Based Binder Systems

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Acrylic binder systems cover a broad class of applications, including latex house paints, cement coatings, inks, and overprint varnishes, all with varying performance criteria. Even with their varying end applications they all have appearance as an important performance criteria. Defects such as craters and pinholes can appear in the final coating and are often caused by air entrapment in the formulation during mixing and processing; thus the need for an effective antifoam/defoamer. In this study, commercially available non-silicone and silicone-containing antifoams are benchmarked against developmental silicone antifoams to determine performance gaps and benefits. This study encompasses acrylic-based binder systems used in multiple-end applications to determine breadth of end-use applications.

(24)

O-Acetylation and Water Retention of Alginates

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It is well known that the only structural difference between algal alginate and bacterial alginate is that bacterial alginate contains O-acetyl groups attached to the mannuronic acid monomers.[1] In this research, the O-acetylated alginate will be chemically synthesized from an algal sodium alginate based on the procedure

described by Forsyth *et al.*[2] High temperature and multidimensional NMR will be used for the product characterization and the quantitation of the O-acetylation in the product. We think that it is a possibility that these acetyl groups play a role in preventing bacteria from dehydrating in an already dehydrated environment of the CF lung. The acetylated alginate acts like a sponge, soaking up the water as much as it can and holding the water close to the bacteria. ^{1}H T_1 tests have been used to determine if the O-acetyl groups cause the alginate to retain more water inside its gel system. Since the higher water retention means more water inside the gel system of the bacteria alginate, the retained water inside the alginate gives shorter T_1 relaxation because of its restricted motion compared with the "free" water outside the gel system. However, algal alginate has less water retention, which means more water outside its gel system. A longer T_1 relaxation has been observed for these water molecules. Because of the O-acetylation, the chemically acetylated alginate does have better water retention than its parent, natural algal alginate. Multidimensional NMR can be a powerful tool to probe how the O-acetylation can change the structure of these polysaccharides and makes them with higher affinity to water molecules.

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(25)

Curing Studies of Microwave Processed Biocomposites Made from Epoxy and Hemp Fibers

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There is considerable interest in the field of biofiber composites in structural application, but little research has been done on microwave curing of these composites. In contrast to conventional thermal ovens, microwave heating is volumetric and not restricted to the surface. As a result, materials can be processed more quickly in a microwave oven. Curing studies have been performed on hemp-reinforced epoxy (diglycidyl ether of bisphenol-A (DGEBA) with diaminodiphenyl sulfone (DDS) as crosslinking agent) composites. Samples were made using both microwave- and thermal-curing process for comparison. Differential scanning calorimetry was used to characterize the samples. The microwave-cured hemp and epoxy composite samples reached their full cure faster than the oven-cured samples.

(26)

Mechanical and Morphological Properties of Biocomposites from Microbial Polyesters and Natural Fibers

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"Green" composites are now emerging as the realistic alternatives to glass fiber reinforced composites. Bacterial polyesters have been produced in industrial quantities by fermentation and have been used commercially for cosmetic bottles, paper coatings, and medical applications. The cost of these bioplastics has been higher than petroleum-based plastics thus limiting their applications. Eco-friendly green composite materials have been fabricated from inexpensive chopped natural fiber and bacterial polyester, for example, poly (3-hydroxybutyrate, PHB), through extrusion followed by injection-molding processing. The formulation of the composite was changed through the addition of fiber in different proportions to obtain the desired properties. PHB grafted maleic anhydride was used as a compatibilizer in fabricating the composite materials. The composites have been tested for mechanical and thermal properties to evaluate their feasibility as a potential material for automotive applications. The composite mechanical properties have also been compared with the rule of mixtures. The fiber-matrix interfacial adhesion was also observed by environmental scanning electron microscopy. The modulus and strength of the composites increased with increase in the percentage reinforcement of hemp fiber as compared with that of virgin PHB. The heat deflection temperature (HDT) of the composites increased from 94°C to 145°C with hemp-fiber reinforcement. However, the impact strength did not change significantly with fiber reinforcement.

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(27)

Biodegradable Plastics from Polysaccharides, Protein, and Natural Fibers

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Oxidation, carboxymethylation, and acylation of polysaccharide-based materials, such as dried distiller's grain, corn-cob powder, sugar-beet pulp, and sawdust, followed by addition of soy protein previously resulted in hard solids with fracture strengths similar to some synthetic plastics such as polyvinyl chloride. Furthermore, the solids were susceptible to microbial attack when wet, indicating the ability to biodegrade. However, these materials were brittle and possessed little toughness. The focus of this work is to prepare and characterize composites made by including natural fibers in the processing steps of the aforementioned hard solids. Characterization of the products was performed with FTIR spectroscopy, differential scanning calorimetry, scanning electron microscopy, and diametral compression tests.

(28)

Sweet Silicones: Biocatalytic Reactions to Form Organosilicon Carbohydrate Macromers

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Historically, conventional condensation catalysts and reaction conditions have limited the ability to control the structure of organosilicon materials. Under mild reaction conditions, enzyme-catalyzed reactions with organosilicon molecules were explored in order to study the feasibility of synthesizing an organosilicon carbohydrate. The substrates were chosen to investigate the attributes of biocatalytic reactions.

An enzymatic route for the synthesis of organosilicon carbohydrates was discovered and reduced to practice. Immobilized lipase B from *Candida antarctica* (Novozyme 435®) catalyzed the formation of regioselective ester bonds between carboxylic acid-endblocked organosilicones and a C1-O-alkylated sugar under mild reaction conditions (i.e. low temperature, neutral pH, solventless). Specifically, the acid-endblocked organosilicones reacted with the primary hydroxyl group at the C6 position of α,β-ethyl glucoside during the regioselective esterification. The pure organosilicon-sugar conjugates were prepared in a one-step reaction without performing any protection-deprotection steps. It was observed that the lipase-catalyzed reactions did not require activation of the acid groups. In comparison to organic materials, the hydrophobic organosilicon molecules were acceptable substrates. Given the ability to perform selective reactions and maintain the integrity of the siloxane bonds, lipases appear to be useful catalysts in the efficient synthesis of structurally defined organosilicon carbohydrate bioconjugates.

(29)

Green Composites from Soy-Based Thermoplastic and Natural Fibers

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"*Green*" composites from soy-based thermoplastic and natural fiber have a huge potential to replace traditional fiber-reinforced petroleum plastic composites due to the fact that they have properties comparable to petroleum-based composites and are inexpensive and sustainable. As part of our ongoing project, "green" composites from soy-based bioplastic and natural fiber were successfully produced using conventional extrusion and injection molding processing methods. The influence of biofiber treatment on morphology and properties of "green" composites has been studied with ESEM and mechanical property measurements. It was found that after alkali treatment, the fiber was reduced in diameter due to the removal of the hemicellulose and lignin from the interfibrillar regions. Results will be presented showing that this alkali treatment produced a homogenous dispersion of fiber in the polymeric matrix and the mechanical properties of the biocomposites also improved. One possible reason is that the quantity and reactivity of hydroxyl groups on the surface of the fiber were enhanced after alkali solution treatment, which led to a better interaction between fiber and matrix. An additional benefit results from the increase in surface area and aspect ratio of the fiber.

Support from USDA-NRI (Grant No. 2001-35504-10734) is gratefully acknowledged for this research. Authors also thank to ADM (Decatur, IL), Bayer Corp. (Pittsburgh, PA), and Smith, Adams & Associates LLC (East Lansing, MI) for supplying soy flour, polyester amide, and grass fiber, respectively, for this research.

(30)

'Green' Nanocomposites from Bacterial Polyester and Organically Modified Clay: Thermomechanical and Morphological Properties

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Polyhydroxybutyrate (PHB) is one of those few naturally occurring linear thermoplastic bacterial polyesters that is fully biodegradable and biocompatible. This property of PHB makes it very desirable for applications such as artificial bone and biodegradable polymeric composites. Although the mechanical properties of PHB are reported to be equal or even better than traditional thermoplastics, its brittleness, high crystallinity, and low strength restrict the range of its applications. Additionally, improving its thermomechanical and barrier properties would make it the most versatile biodegradable polymer for commodity applications. In the present investigation we fabricated PHB clay nanocomposites by reinforcement with 4–10 wt % organophilic-modified layered silicate clay. This nanocomposite was processed in a twin-screw miniextruder with screw speed

varied from 50–150 rpm, residence time maintained between 60–240 seconds and the polymer processing temperature set at 190–172°C. A maleated PHB was synthesized as a compatibilizer and the effect of the reaction parameters was studied for changes in the thermo-mechanical and morphological properties of the resultant PHB clay nanocomposites. Addition of 5 wt% of the maleated PHB helped to achieve good intercalation of 9 wt% clay, which was otherwise not possible. Addition of 5 wt% clay in presence of 5 wt% of maleated PHB led to complete exfoliation as observed in the XRD spectra and by TEM images. The impact and tensile strength of the PHB with clay reinforcement improved up to 22%. However, the flexural modulus showed only a small improvement of 15%. The heat distortion temperature increased from 94°C for neat PHB to 103°C with 5% clay reinforcement. Moisture absorption in these nanocomposites carried out at 40°C and 90% relative humidity was not detectable for the times studied. Research to enhance the properties of PHB clay nanocomposites is still underway.

(31)

Injection-Molded Eco-Friendly Natural Fiber and Cellulosic Plastic Biocomposites

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Biocomposites are emerging as a viable alternative to glass-fiber-reinforced composites especially in structural and automotive applications. By embedding inexpensive natural cellulosic fibers into biopolymeric matrices, 100% biobased composite materials (biocomposites) can be made. Cellulose esters, e.g. cellulose acetate plasticized with 30 wt.% citrate plasticizer, has been successfully reinforced with chopped hemp fiber as a potential alternative to glass-fiber-based composites for automotive applications. Extrusion processing followed by injection molding has been adopted in fabricating biocomposites with 30 wt% of hemp. An enhancement of flexural strength of ~75% and modulus of elasticity by ~250% was measured over the neat plastic properties. The intimate mixing resulting from the high shear forces in this type of processing is necessary to produce superior strength biocomposites. Environmental scanning electron microscope images of fractured impact samples indicates less fiber pullout indicating better adhesion between hemp fiber and CA matrix under these processing conditions. The cellulosic plastic under investigations appears to be matrix with performance at least equal to polypropylene (PP) for natural fiber reinforcements.

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Environmentally Benign Nanocomposites from Cellulose Ester and Layered Silicates

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Renewable cellulose esters are a potential biopolymer. Injection molded "environmentally benign" nanocomposites have been successfully fabricated from cellulose acetate, triethyl citrate plasticizer and organically modified clay. The effects of the amount of plasticizers on the performance of these nanocomposites have been evaluated. The cellulosic plastic with 85–60 wt. % pure cellulose acetate and 15–40 wt.% triethyl citrate plasticizer with or without organoclay Cloisite 30B was used as the polymer matrix for nanocomposite fabrication. The morphologies of these nanocomposites were evaluated through X-ray diffraction (XRD) and transmission electron microscopy (TEM) studies. The mechanical properties of nanocomposites have been correlated with the XRD and TEM observations. Cellulosic plastic-based nanocomposites with 20 wt% TEC/5 wt% organoclay showed a better exfoliated and intercalated structure than their counterpart having 30 or 40 wt% plasticizer. The tensile strength and modulus of cellulosic plastic reinforced with organoclay improved with decreasing plasticizer content. The nanocomposite thermal stability and water vapor absorption was improved as well, but the impact strength was decreased.

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(33)

Laser Induced Breakdown Spectroscopy (LIBS) for Chemical Process Analysis

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The analytical ability to perform *in situ* and multi-element analysis without direct sample contact is desired to monitor industrial processes and environmental samples.[1] The LIBS technique uses a ND:YAG laser beam to strike the sample (solid, liquid, or gas) and completely ionize the sample by creating a microplasma, which causes atomic emission that is detected by an ICCD and analyzed. The little or no sample preparation and spectroscopically transparent sampling chambers make LIBS useful for solid, liquid, and gas analysis. Air analysis,[2] aerosols,[3] solid samples,[4] pharmaceuticals,[5] and quantitative and qualitative measurement of pollutent atoms (fluorine, chlorine, sulfur, and carbon) at atmospheric conditions[6] indicates the sample versatility of the technique. It has also been demonstrated in the use of spatial analysis in a flame[7] demonstrating its robust applicability.

We will present some of these results as well as our modular equipment design employing fiber-optical laser source and the emission detection equipment.

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SMC Bio-composite Housing Panels and their Properties

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The purpose of this work is to produce low-cost green materials (biocomposites) for use in various housing panel applications. Biocomposites have been traditionally made using extrusion, injection molding, compression molding, and pultrusion processing techniques. Under this project, a novel high-volume processing technique called a "bio-composite stampable sheet molding compound panel" (BCSMCP) manufacturing process was developed to mimic the continuous sheet-molding compound (SMC) currently used in making glass fiber-polyester resin composites. This process yields continuous production of biocomposites on a large scale, and can be easily adopted in durable goods industries. The prepregs from the SMC line were matured for the desired time and then compression molded. The molded samples were tested for various mechanical and thermal properties, in accordance with ASTM procedures. The natural fibers investigated included flax, big blue stem grass, hemp, jute, henequen, and kenaf, which were combined with an unsaturated polyester resin matrix. The effect of surface treatment of the biofibers on the thermo-mechanical properties was also investigated. Grass-fiber-reinforced polyester SMC biocomposites show very promising results.

In particular, after treatment with 1% methacryloxypropyltrimethoxy silane, the bending strength and modulus of elasticity of big blue stem grass fiber-based SMC biocomposites increased by 15% and 20% respectively as compared to untreated grass fiber biocomposites. This research was supported by PATH (Partnership for Advancing Technologies in Housing) for future American housing.

The authors are highly grateful to NSF- PATH 2001 Award #0122108, for financial support and Flaxcraft Inc. and Kemlite Inc. for supporting this project.

(35)
Biobased Epoxy Matrix for Clay Nanocomposites

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The importance of environmentally friendly natural products for industrial applications is increasing with increasing emphasis on environmental issues, waste disposal, and the depletion of nonrenewable resources. There is a growing urgency to develop and commercialize new biobased products and other innovative technologies that can reduce the dependence on fossil fuel. Renewable resource-based polymers can serve as a new platform to provide an alternative to petroleum-based polymers if they can be innovatively used while maintaining a favorable cost-performance ratio. Functionalized vegetable oils, increasingly used as coatings and plasticizer additives, are now commercially available. The petroleum-derived epoxy resins are known for their superior tensile strength, high stiffness, and exceptional solvent resistance. The blending of nanoscale reinforcements, such as organically modified clay, and bio-based epoxy resin could result in advanced materials applicable for automotive and aeronautic structures. In this study, thermophysical properties of bio-based epoxy/clay nanocomposites were investigated by dynamic mechanical analysis (DMA) and the microstructure of the clay particles in these nanocomposites was observed by transmission electron microscopy (TEM) and wide angle X-ray scattering (WAXS). Results indicate that the petroleum-based content of epoxy resins can be reduced by the addition of biobased vegetable oils with little change in performance.

(36)
Solubility and Decomposition Studies of Carbon Tetrachloride in Supercritical Carbon Dioxide

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Carbon-clustered species are of particular interest to materials scientists and have contributed much to the rapidly expanding research conducted within nanotechnology. Metal-catalyzed chemical vapor deposition (CVD) is now the method of choice for growth of carbon nanotubes (CNTs). However, temperatures on the order of 700–1000°C are necessary, which precludes the use of temperature sensitive substrates. This research group is investigating the formation of CNTs at low temperatures using carbon halide precursors and high-pressure con-

ditions. We present decomposition and solubility models of carbon tetrachloride at varying temperatures and pressures within supercritical carbon dioxide.

(37)

Methylmethoxysilane Hydrolysis by Raman Spectroscopy

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A study was conducted to determine the feasibility of using Raman spectroscopy to detect the presence of organosilicon molecules and their intermediate hydrolysis products in aqueous and biochemical matrix environments. Raman spectra were collected on a series of methylmethoxysilanes. The hydrolysis reactions of methylmethoxysilanes in solutions of varying ionic strength were followed by Raman spectroscopy in order to identify the silanol products. A strong Raman peak in the 600–700 cm^{-1} region is a marker for the Si—C/Si—O symmetric stretching vibration in silanols. Relative detection limits were determined on the hydrolysis products of phenylmethyldimethoxysilane, which is more stable in aqueous environments than methylsilanols.

(38)

Chemical Vapor Deposition of Metal Oxide Thin Films: Design of Actively Protective Clothing Against Chemical Warfare Agents

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With the constant threat of terrorist attacks, much attention has been focused on the development of materials that will protect both military personnel and civilians against the release of chemical and biological warfare agents. Solid metal oxides, such as aluminum oxide, have been shown to adsorb and decompose organophosphorus-based chemicals at temperatures not far removed from ambient.[1] The deposition of thin films of these materials onto substrates such as clothing fibers and fabrics would allow the facile fabrication of actively-protective clothing, for both military and civilian use. Toward this end, aluminum oxide and aluminosilicate thin films were deposited onto carbon fibers using chemical vapor deposition. The liquid precursor for aluminum oxide was dimethyl aluminum isopropoxide, prepared from trimethyl aluminum and aluminum isopropoxide. Aluminosilicate films were prepared from a 1:1 solution of the aforementioned aluminum precursor and tetraethoxysilane. Characterization of the fibers was carried out using tandem energy dispersive spectroscopy/scanning electron microscopy (EDS/SEM). Cross-section SEM images and elemental dot mapping show a conformal coating of aluminum oxide and aluminosilicate on the surface of individual carbon fibers. NMR studies of aluminum oxide coated fibers in contact with a nerve agent stimulant, dimethyl methylphosphonate (DMMP), show peak broadening which is consistent with adsorption of the chemical onto the oxide layer.

1. Sheinker, V. N.; Mitchell, M. B. *Chem. Mater.* **2002**, 14(3), 1257.

(39)

Polymers Grown from Silica Particles

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The surface of silica particles may be modified by covalent attachment of compounds which may be utilized as initiation sites for atom transfer radical polymerization (ATRP). Polymers of fixed size may then be grown from the surface. The resulting polymeric structures may have a variety of applications including the preparation of novel chromatographic systems.

(40)

Fullerene-Coated Materials as Reusable Catalysts

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Polymer resin beads coated with C60 have been used to oxidize various compounds with 1O2 and UV light. Subsequent layers added to the basic C60 catalyst can stereo selectively oxidize many compounds. Several different catalysts were made. These catalysts were used to oxidize a variety of compounds. These reactions were analyzed by ^{1}H NMR spectroscopy and, in the cases where chiral catalysts were used, HPLC.

(41)

Supercritical Fluid Facilitated Growth of Copper and Aluminum Oxide Nanoparticles

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Although supercritical fluids have long been exploited for homogeneous catalysis and extraction applications, there is only recent interest in this “green chemistry” medium for materials synthesis. Nanoparticles of copper and aluminum oxide were formed using a variety of procedures and particle diameters were characterized using transmission electron microscopy (TEM). While particles of aluminum oxide were found to average 100 nm with sufficient aggregation, the copper nanoparticles were much smaller in diameter, with less agglomeration. A discussion of other techniques that will be attempted to further reduce particle size and aggregation will be provided.

(42)

Short-Term Variability of Physical and Chemical Parameters in Suboxic/Anoxic Bottom Waters of the Chesapeake Bay During Late July 2002 and 2003

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The Chesapeake Bay experiences widespread seasonal anoxia due to water column stratification and microbial decomposition of organic matter. A combination of CTD casts, discrete bottle sampling and *in situ* voltammetric microelectrode profiling was used to examine redox conditions over several days. Sampling was done in late July of 2002 and 2003. During the 2003 cruise, the water column experienced the largest anoxic zone on record. Vertical profiles of physical and chemical parameters were measured each day, including temperature, salinity, density, dissolved oxygen, sulfide, nitrate/nitrite/ammonia, and dissolved Mn and Fe(II). Nitrite varied from <0.01 to 0.4 μM. Highest values occurred above the suboxic zone, at oxygen concentrations of $\sim$40–70 μM. Nitrite varied from < 0.01 to 0.4 μM. Fe(II) was detected only at oxygen levels <5 μM, with concentrations in the deep waters ranging from $\sim$0.2 to 1.4 μM. Plotting the chemical data versus salinity rather than depth decreases the scatter due to tidal variation and displays a clear separation between the onset of Mn and Fe reduction. This study illustrates the dynamic, rapidly changing nature of water-column anoxia in the Chesapeake Bay. The depth of oxygen penetration, the thickness of the suboxic zone and the concentration of sulfide in the deep waters fluctuate in response to tidal oscillations and to the passage of storm events. Real-time measurements are necessary to document these short-term variations.

(43)

Sequestering Metal Cations from Aqueous Solution with Natural Polysaccharide and Protein-Containing Materials

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We have studied the interactions of metal cations with polysaccharides and proteins in raw and oxidized natural materials. Cation binding affinity was measured for numerous metals with varying oxidation states. Our results indicate that binding affinities are strongly dependent on cation radii with large cations being bound more strongly than small. This may correspond in part to steric strain be-

tween coordinated water molecules on the cation (Lewis acid) and the Lewis bases in the natural materials. Cation binding affinity also correlated loosely with the ionicity of the metal-ligand bond (degree of hardness). As expected, solution pH strongly affected the binding equilibria. The extent of cations removed from solution was determined using ICP-MS. The amount of metal cations sorbed onto the natural material was determined by digestion into solution followed by measurement with ICP-MS. The materials were further characterized by FTIR spectroscopy and titration in order to estimate the relative abundance of functional binding sites between raw and oxidized materials.

(44)

Comparison of Series 5 (5% phenyl methyl silicone) GC Column Performances from a Variety of Manufacturers for Separation of Chlorinated Dibenzo-p-Dioxins and Dibenzofurans by HRMS

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Current EPA methods for polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) analysis have been developed based on J&W DB-5 GC column performance. However, there are several other Series 5 (5% phenyl methyl silicone) GC columns available on the market from a variety of manufacturers including Chrompack CP-Sil-8-CB-MS, Phenomenex ZB-5UMS, Agilent HP-5MS, Restek Rtx-5MS, Supelco Equity 5, and J&W DB-5MS. In this study, seven GC columns have been evaluated for separation of International Toxic Equivalent Factor (I-TEF) isomers (tetra- through octa- chlorinated at 2,3,7,8 positions only) from closely co-eluted isomers. The data expressed in this series of GC mass chromatograms are the most comprehensive to date with regard to separation of 2,3,7,8-substituted isomers and provide a valuable addition to the standard EPA method 1613b.

All GC conditions were kept consistent and as close as possible to EPA method 1613b for all columns tested, and no specific effort was made to optimize GC conditions (temperature program in particular) to maximize resolution of I-TEF congeners for any specific column. In some cases, columns exhibited differences in isomer resolution; e.g., isomers co-eluting on the column from one manufacturer were found to have some degree of separation on a column from another manufacturer. Sometimes, elution order of isomers of interest might be different. Equity-5, HP-5MS, and Rtx-5MS columns have isomer elution orders identical to DB-5 column performance. DB-5MS, SP-Sil-8-CB-MS, and ZB-5UMS show differences in isomer resolution in some cases compared to DB-5 type columns and with respect to each other. For example, DB-5, HP-5MS, Rtx-5MS, and Equity-5 60m columns could separate most of I-TEF isomers excluding 1,2,3,7,8,9-HxCDD, 2,3,7,8-TCDF, 2,3,4,7,8-PnCDF, and 1,2,3,4,7,8-HxCDF from the other closely eluting isomers tested. On another hand, DB-5MS, SP-Sil-8-CB-MS, and ZB-5UMS columns with the same length could not resolve well 1,2,3,7,8-PnCDD, 2,3,4,7,8-PnCDF, 2,3,4,6,7,8-HxCDF, and 1,2,3,7,8,9-HxCDF from other isomers. For those three MS columns, it is worth mentioning that the I-TEF isomer of 1,2,3,7,8,9-HxCDD elutes after its “window-defining standard” required by EPA methods to demonstrate column performance.

All seven GC columns tested for this study can be used for PCDD/PCDF analysis. The relative performances of these columns were compared on the basis of separation of 2,3,7,8-substituted isomers of PCDD/PDCFs. None of the columns tested were able to separate all 17 I-TEFs from other co-eluted isomers. In comparing isomeric data from different analytical studies, care should be taken to insure that these subtle differences in isomeric separation are taken into account.

(45)

Studying the Chemical Structure of Bone through Raman Spectra of Model Materials

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Bone chemical structure and changes in response to age, stress and disease are key issues in human health. The primary mineral in bone is calcium phosphate in an arrangement similar to the hydroxyapatite mineral $Ca_{10}(PO_4)_6(OH)_2$. But, in bone, the ions Na^+, Mg^{2+} and K^+ and the anions CO_3^{2-}, HPO_4^{2-}, Cl^- and F^- are also present. The substitution pattern of these ions into the apatite matrix causes small changes in the phosphate vibrations. In order to understand how the structure of the biological samples causes variations in the Raman spectra, hydroxyapatites have been prepared as model bone.

Substituted apatites were prepared by aqueous precipitation with a variety of concentrations of carbonate, sodium, magnesium, and chloride. The samples were fully characterized by AA, IR, visible absorption, and powder x-ray diffraction. Raman spectra of the substituted apatite samples were collected and correlated with the substituted ion concentration. The effect on the phosphate spectra was observed as changes in peak wavenumbers, bandwidths, and relative intensities of many peaks.

The Raman spectrum of apatite was also modeled through density functional theory (DFT) calculations on small clusters of ions. The theoretical models allow us to investigate the effects of position and orientation of ions on apatite Raman spectra. Linear arrangements of two phosphates or carbonates and up to three calcium ions were tried as well as arrangements derived from the crystal structure of hydroxyapatite and B-type carbonated apatite.

(46)

Regeneration of Ammonium Bisulfate from Ammonia using Thermal Cracking and Raman Spectroscopy

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The much anticipated and currently desired next generation of chemical production will utilize renewable nonpetroleum-based resources. The project deals with minimizing the salt byproduct, thus making the entire process “greener”. The regeneration of acid (ammonium bisulfate) and base (ammonia) from the salt (ammonium sulfate) for “green” production is possible through thermal cracking. Different parameters are being studied in order to develop this method to generate ammonium bisulfate from ammonium sulfate. Work done to date shows the production of ammonium bisulfate and enhancing the yield of acid and base values can be obtained through varying different parameters, such as the method of sample injection, temperature, and method of heating. This work also demonstrates the application of Raman spectroscopy and various other analytical methods for the study of an economically feasible, energy efficient and environmentally friendly regeneration and recycling of acid and base values as part of the production of green chemicals.

(47)

Structural Characteristics of Oligomer-Metal Compounds from Molecular Modeling

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The structural features of several metal compounds derived from amino-terminal or carboxyl-terminal oligomers have been examined using molecular modeling techniques. An initial focus has been compounds containing platinum or palladium as the metal and *cis*-1,2-diaminocyclohexane or chloride as the non-oligomeric ligands.

(48)

Syntheses and Volatility Assessments of Novel Group 13 Complexes: Toward Aluminum and Gallium Oxynitride Thin Films

Duston O. Miller and Bradley D. Fahlman

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As device size continues to shrink in common microelectronic devices, there will be a need for new dielectric alternatives to silicon-based materials. A new material, aluminum oxynitride, has been recently reported to feature intermediate properties of both the oxide and nitride, resulting in an optically translucent ceramic material, with high hardness and excellent high-temperature resistance. Thin films of these materials, as well as other Group 13 analogs, have not been synthesized to date, and would have a variety of applications for microelectronics, sensors, and protective coatings. Toward this end, Group 13 bis(acetylacetoneethylenediimine) complexes, containing both metal-oxygen and metal-nitrogen linkages, are being considered for single-source precursors for metal oxynitride thin films. We submit syntheses, characterization and volatility studies for these compounds.

(49)

Organoplatinum Compounds Derived from Amines and Carboxylic Acids

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Organoplatinum compounds containing two inert cis ligands and two labile ligands constitute a class of very effective antitumor agents. The inert ligands are most typically amines with *cis*-1,2-diaminocyclohexane being a common amine ligand. Labile ligands are typically chloride or carboxylate. Either inert or labile ligands may be polymer based.

(50)

Synthesis, Characterization, and Volatility Studies for Group 13 Amidinate and Triazenide Complexes

Jason K. Vohs, Duston O. Miller, and Bradley D. Fahlman

Department of Chemistry, Central Michigan University, Mt. Pleasant, MI 48859

Group 13 amidinate and triazenide complexes are of increasing interest as possible single-source precursors for nitride thin film materials. This research group has recently studied a number of such ligand systems for their potential utility in the chemical vapor deposition of aluminum and gallium nitrides, as well as Fe/Al and Fe/Ga bimetallic thin films. Herein are reported the syntheses, characterization, and volatility studies for a number of complexes.

(51)

Roof Insulation for Sustainable Buildings

**Joann Surma[1], Jerry Williamson[1], Mike Kontranowski[2],
Mike Ennis[1], and David Greeley[1]**

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Today's environment is changing, and so is the way we design our buildings. Our future growth, with respect to the environment, will rely on our knowledge of how to design, construct, and reap the reward of a sustainable building. With the conservation of energy and rising energy costs, there has been increasing concern and demand for energy-efficient roofing assemblies. One area with little discussion, but of high importance to the roofing assembly is the use of insulation. This presentation will cover the roles of rigid insulation in the sustainability of buildings, which include optimization of energy performance, construction waste management, re-use warranties, local /regional materials, recycle content and availability of multiple roofing systems. Why insulation should be used, how insulation works, and the sustainability features and issues for both Styrofoam* extruded polystyrene rigid insulation and polyisocyanurate rigid insulation will also be addressed.

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In Past Issues of *The Midland Chemist*

By Wendell L. Dilling, Midland Section Historian

- **30 Years Ago This Month**—Councilor David C. Young reported that the nearly all-day council meeting at the August ACS National Meeting in Chicago was hot and heavy, much like the weather there. One of the proposals adopted was a special kind of preferential ballot procedure to use if there are three candidates for president-elect or for regional director, and requirement for a runoff election if there are four or more candidates and none receives a majority of the votes on the first ballot.
- **20 Years Ago This Month**—Herbert D. Doan will give the keynote address at the 39th ACS Fall Scientific Meeting on "Thoughts on Technology." In the abstract of his address he states, "It's no secret that the U.S. is not doing as well as it used to, relatively speaking….But fortunately, the solution is at hand….it involves reemphasizing our traditional pluralistic and individualistic approach to solving problems, as opposed to going for government-made solutions."
- **10 Years Ago This Month**—The 49th ACS Fall Scientific Meeting will be held at Delta College on October 23, 1993. Brad Lienhart, Managing Director of the Chlorine Chemistry Council, will present the keynote address, "A World Without Chlorine: Will an Element be Banished?"

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Important Dates on the ACS Midland Section Calendar

Oct. 6	CMU Chemistry Faculty, “A Sampling of CMU Faculty Research Projects, Dow 175, 3:00 p.m. (Anton Jensen, 989-774-3125).
Oct. 13	Prof. Claudio J. Margulis, University of Iowa, “Computational Study of Hydrophobicity at Small and Large Length Scales, or What’s the Trouble Bubble?” CMU Seminar Series, Central Michigan University, Dow 175, 4:00 p.m., reception preceding in Dow 264 at 3:30 p.m. (Anton Jensen, 989-774-3125).
Oct. 13	Midland Section board meeting, Delta College Midland Center, Rm. 12, 7:00 p.m.
Oct. 17	Green Chemistry Workshop, The Dow Chemical Company, Employee Development Center, 8:00 a.m.–11:00 a.m.
Oct. 17	Fall Scientific Meeting, The Dow Chemical Company, Employee Development Center, 11:00 a.m.–5:00 p.m.
Oct. 18	Sci-Fest, Delta College, Pioneer Gym, 10:30 a.m.–2:30 p.m.
Nov. 3	Deadline for December issue of *The Midland Chemist*.
Nov. 10	Midland Section board meeting, Delta College Midland Center, Rm. 12, 7:00 p.m.

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