

**We will start momentarily at 2pm ET**

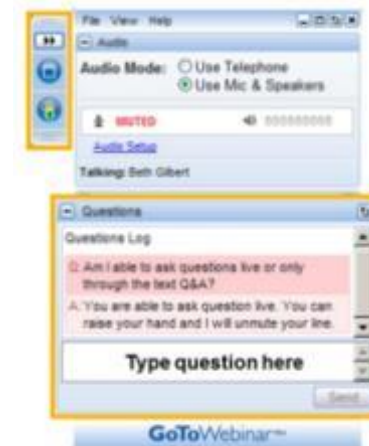


*Slides available now! Recordings will be available to ACS members after one week.*

[www.acswebinars.org](http://www.acswebinars.org)

Contact ACS Webinars<sup>®</sup> at [acswebinars@acs.org](mailto:acswebinars@acs.org)

# Have Questions?

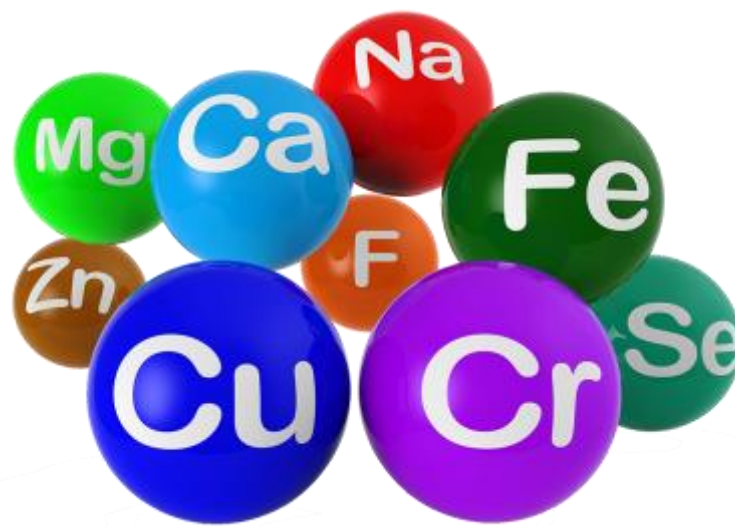


## “Why am I muted?”

Don't worry. Everyone is muted except the presenter and host. Thank you and enjoy the show.

Type them into questions box!

Have you discovered the missing element?



**[www.acs.org/2joinACS](http://www.acs.org/2joinACS)**

Find the many benefits of ACS membership!

## Benefits of ACS Membership



**Chemical & Engineering News (C&EN)**  
The preeminent weekly news source.



**NEW! Free Access to ACS Presentations on Demand<sup>®</sup>**  
ACS Member only access to over 1,000 presentation recordings from recent ACS meetings and select events.



**NEW! ACS Career Navigator**  
Your source for leadership development, professional education, career services, and much more.

[www.acs.org/2joinACS](http://www.acs.org/2joinACS)

Like us on Facebook!



 [facebook.com/acswbinars](https://facebook.com/acswbinars)

# How has ACS Webinars<sup>®</sup> benefited you?

“Today's webinar on transitioning from organic solvents was the best Webinar in which I participated both from the ACS and other organizations. It also gave me a genuine familiarity with the scope and benefits of green chemistry, which until now was something out there but to which I paid only modest attention.”

*Fan of the Week*

Steve Hirsch, Ph.D.





# Hungry for a brain snack?



“ACS Webinets™ are 2 minute segments that bring you valuable insight from some of our most popular full length ACS Webinars®”



See all the ACS Webinets at [youtube.com/acswbinars](https://youtube.com/acswbinars)

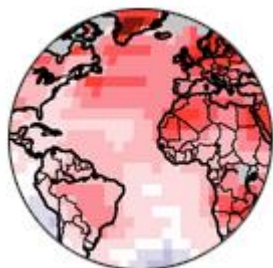


Beginning in 2014 all recordings of ACS Webinars<sup>®</sup> will be available to current ACS members two weeks after the Live broadcast date.

Live weekly ACS Webinars<sup>®</sup> will continue to be available to the general public.

# Upcoming ACS Webinars

[www.acs.org/acswebinars](http://www.acs.org/acswebinars)



Thursday, March 12, 2015 at 2pm ET

## “Bringing CO<sub>2</sub> Monitoring to You: Communicating Atmospheric Chemistry”

**Alexis Shusterman**, PhD candidate, UC Berkeley  
2014 ACS Chemistry Champions Competition Runner-Up

**Dr. Darcy Gentleman**, Manager, Engagement and Science Communications,  
The American Chemical Society



Wednesday, March 18, 2015 at 11am CST

## “Panorama Energético en la Era de la Sustentabilidad: Energías Renovables y Dispositivos Emergentes”

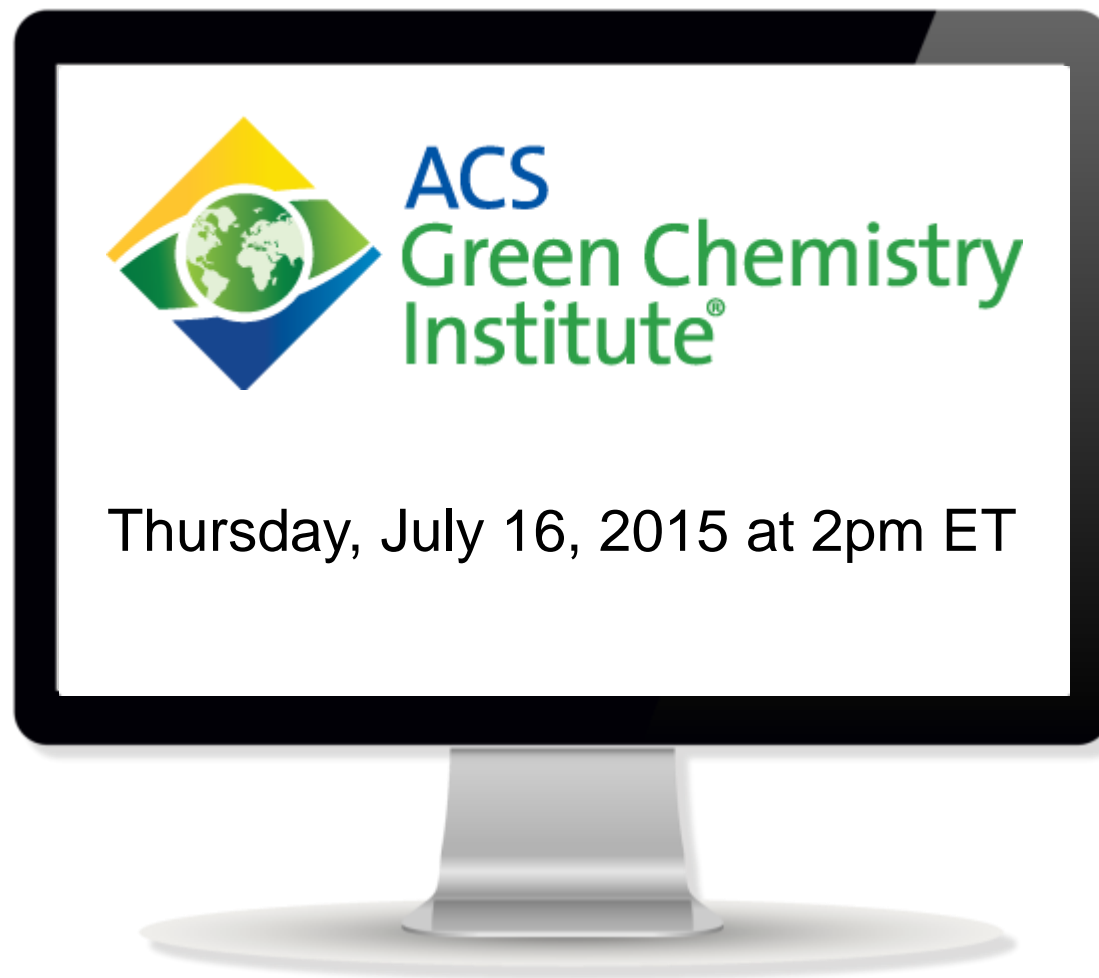
**Dr. Luis Echegoyen**, Profesor de Química, Universidad de Texas, El Paso

**Dr. Héctor D. Abruña**, Profesor de Química, Universidad de Cornell

**Dr. Ingrid Montes**, ACS Junta de Directores y Profesora de Química Orgánica, Universidad de Puerto Rico, Recinto de Río

Contact ACS Webinars ® at [acswebinars@acs.org](mailto:acswebinars@acs.org)

Join us for the next GCI ACS Webinar  
July 16<sup>th</sup> live from the Conference!



<http://www.acs.org/content/acs/en/greenchemistry.html>

## ***“Making Plastic Greener Through Next Generation Polymers”***



**Dr. Marc Hillmyer**  
Director  
Center for Sustainable Polymers,  
University of Minnesota



**Dr. Joseph Fortunak**  
Professor of Chemistry,  
Howard University

***Slides available now! Recordings will be available to ACS members after one week.***

**[www.acswebinars.org](http://www.acswebinars.org)**

This ACS Webinar is co-produced with the ACS Green Chemistry Institute



Polymers are produced on the teragram scale. 1

---

---

---

---

---

---

---

---



The U.S. plastics industry creates nearly \$400 billion in annual shipments. 2

---

---

---

---

---

---

---

---



Polymer production is largely based on finite feedstocks. 3

---

---

---

---

---

---

---

---



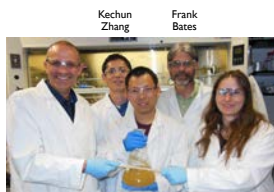
Polymer waste persists in the environment.

4

### Making Plastic Greener Through Next Generation Polymers

Marc A. Hillmyer

UNIVERSITY OF MINNESOTA  
Driven to Discover™



Kechun Zhang

Frank Bates

Mingyong Xiong

Debbie Schneiderman

C&E News June 2, 2014

5



Susan Freinkel



A Toxic Love Story

"In a world of nearly seven billion souls and counting, we are not going to feed, clothe and house ourselves solely from wood, ore and stone; we need plastics. And in an era when we're concerned about our carbon footprint, we can appreciate that lightweight plastics take less energy to produce and transport than many other materials. Plastics also make possible green technology like solar panels and lighter cars and planes that burn less fuel. These "unnatural" synthetics, intelligently deployed, could turn out to be nature's best ally."

New York Times 17 March 2011 6




---



---



---



---



---

lightweight	<p>Giant Molecules Time Life Books 1966</p>	moldable
protective		insulating
strong		disposable
transparent		inexpensive

8

---



---



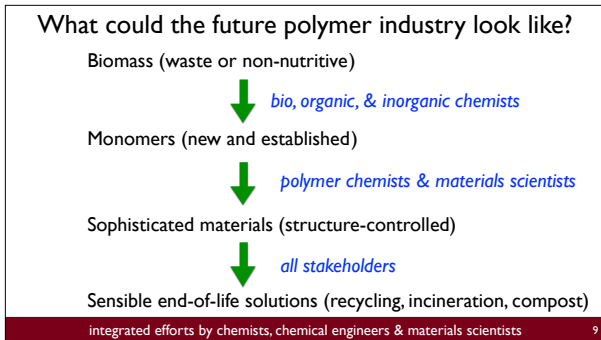
---



---



---




---



---



---



---



---

REVIEW

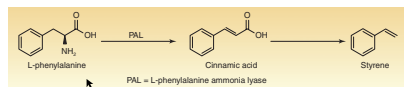
## Valorization of Biomass: Deriving More Value from Waste

Christopher O. Tuck,<sup>1</sup> Eduardo Pérez,<sup>2</sup> Ishán T. Horváth,<sup>2\*</sup> Roger A. Sheldon,<sup>2\*</sup> Martyn Poliakoff<sup>1\*</sup>

Most of the carbon-based compounds currently manufactured by the chemical industry are derived from petroleum. The rising cost and dwindling supply of oil have been focusing attention on possible routes to making chemicals, fuels, and solvents from biomass instead. In this context, many recent studies have assessed the relative merits of applying different dedicated crops to chemical production. Here, we highlight the opportunities for diverting existing residual biomass—the by-products of present agricultural and food-processing streams—to this end.

Waste constitutes an enormous potential resource: hundreds of megatonnes (Mt)/year across the world.

( $10^{11}$  kg or  $10^{14}$  g)



from fermentation of biomass

Tuck et al. Science 2012

10

How many billion kilograms in one teragram?

- (a) 1
- (b) 10
- (c) 100
- (d) 1000

11

### Center for Sustainable Polymers

NSF Center for Chemical Innovation

UNIVERSITY OF MINNESOTA | Cornell University | Berkeley

- Established at UMN in May 2009
- Phase I NSF CCI September 2011
- Phase II CCI from the NSF August 2014

SciGirls | A World of Opportunities | Managing Director | Director of EO&D

Laura Seifert | Jennifer Henderson | Bai Tolman | Dean Tosse | Jane Wisinger | Kechun Zhang

@UMN\_CSP | csp.umn.edu

12



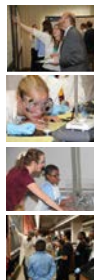
## CSP Grand Challenge

Discover efficient and precision conversions of renewable raw materials into innovative polymeric products that outperform the current suite of non-sustainable polymers from performance, environmental, and cost perspectives.

13

## Integrative elements

- Center management  
*Streamlined & lean approach that fosters creativity*
- Innovation  
*Effective engagement and partnerships with industry*
- Education and Professional Development  
*Train tomorrow's leaders in sustainable science and technology*
- Informal Science Communication  
*Capture the attention of kids and adults on a grand scale*
- Broadening Participation  
*Actively encourage diversity as a critical ingredient for success*



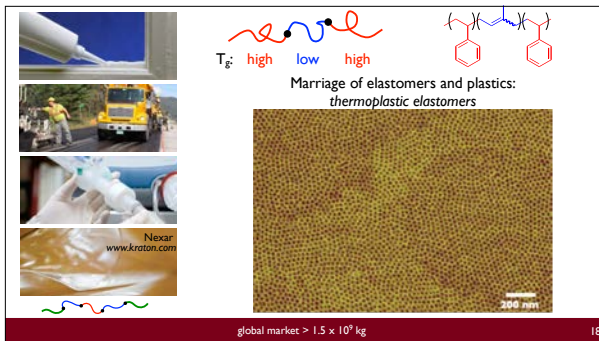
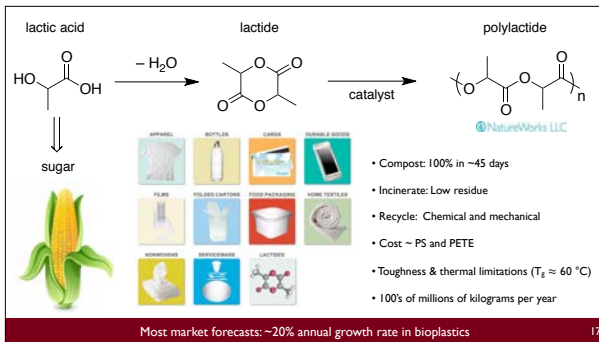
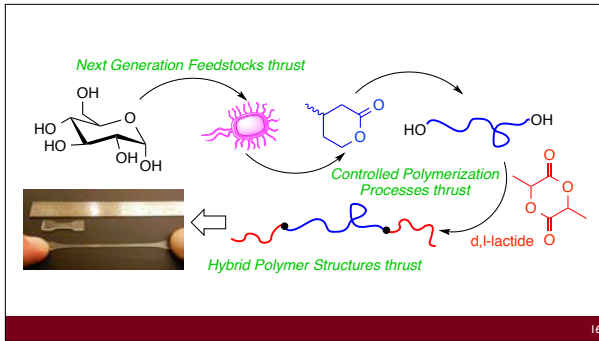
14

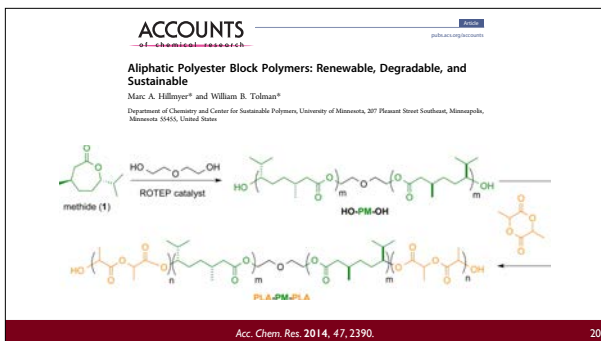
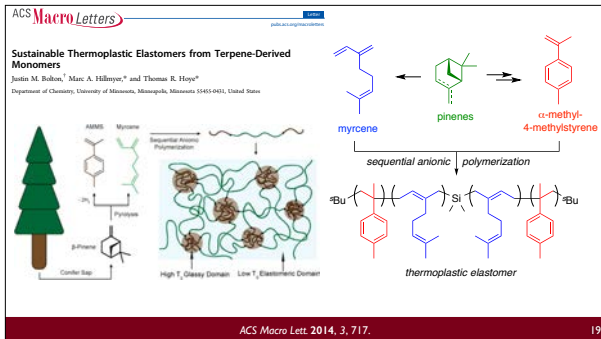


hillmyer@umn.edu

612-625-7834

15

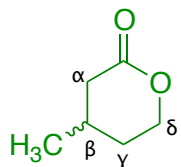




What is the approximate glass transition temperature of PLA?

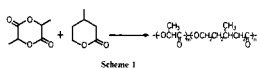
- (a) -60 °C
- (b) 0 °C
- (c) 60 °C
- (d) 160 °C

### $\beta$ -methyl- $\delta$ -valerolactone



valeric acid found in the valerian plant  
(*Valeriana officinalis*)

- Org. Syn. 1955, 35, 87
- Spicy-apple, sweet flavor in Turkish tobacco (Tobac. Sci. 1973, 18, 43)
- Cyclic ester susceptible to ROTEP
- ROTEP produces a low Tg polyester
- Early German & Japanese polymer patents (PUs)
- Extensive literature on use as synthon
- Very little in the literature on polymers



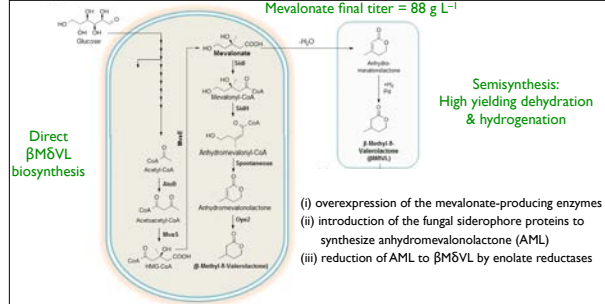
Scheme 1

Synthesis and degradability of a novel aliphatic polyester...

Nakayama et al. Polymer 1995, 6, 1295.

22

Mevalonate final titer = 88 g L<sup>-1</sup>

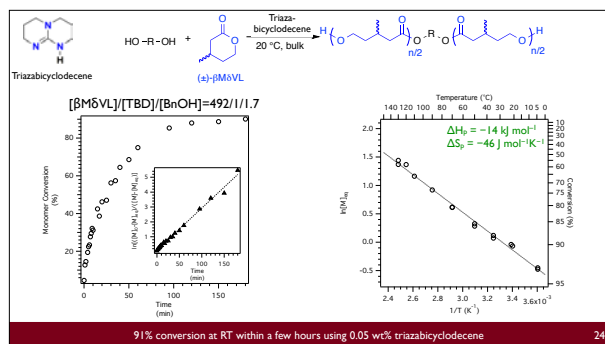


Direct  $\beta$ M $\delta$ VL biosynthesis

Semisynthesis:  
High yielding dehydration  
& hydrogenation

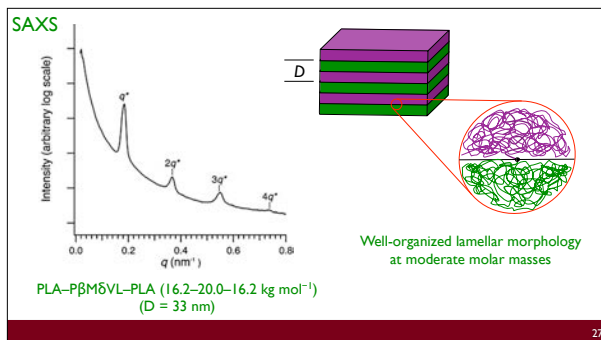
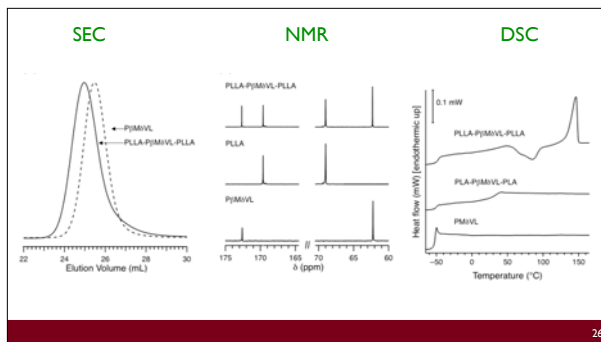
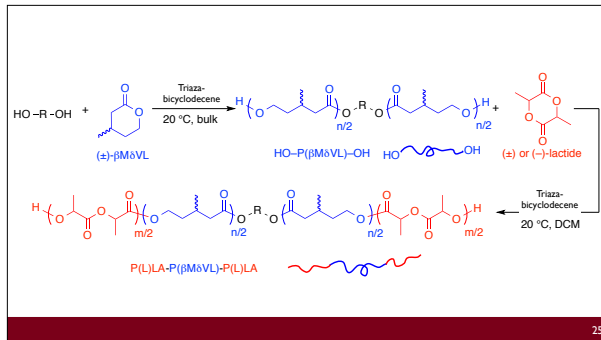
- overexpression of the mevalonate-producing enzymes
- introduction of the fungal siderophore proteins to synthesize anhydromevalonolactone (AML)
- reduction of AML to  $\beta$ M $\delta$ VL by enolate reductases

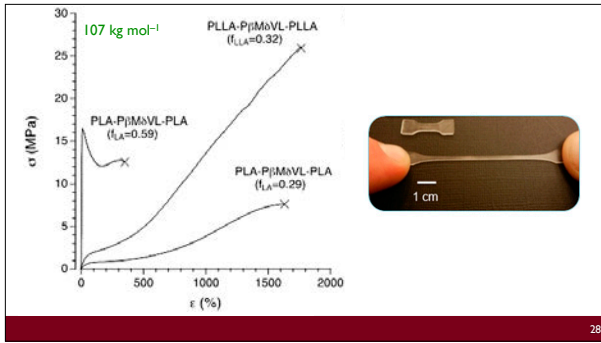
23



91% conversion at RT within a few hours using 0.05 wt% triaza-bicyclododecene

24





28



29

Discover efficient and precision conversions of renewable raw materials into innovative polymeric products that outperform the current suite of non-sustainable polymers from performance, environmental, and cost perspectives.

Next Generation Feedstocks thrust

Controlled Polymerization Processes thrust

Hybrid Polymer Structures thrust

d,l-lactide

C&E News June 2, 2014

Xiong et al. Proc. Natl. Acad. Sci. 2014, 111, 8357.

30

How much does Prof. Hillmyer love sustainable polymers?

- (a) not at all
- (b) somewhat
- (c) a lot
- (d) a little too much

31

**JACS**  
 JOURNAL OF THE AMERICAN CHEMICAL SOCIETY  
 COMMUNICATION

**Poly(propylene succinate): A New Polymer Stereocomplex**  
 Julie M. Longo, Angela M. DiCiccio, and Geoffrey W. Coates\*

Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853-1301, United States

**C&E News November 17, 2014**

"It is relevant to the world of industrial polymers because it addresses issues with biodegradation, renewable raw materials, and the demands placed on modern plastics. In this case, that is the ability to crystallize quickly from the melt and have a melting point above 100 °C. In principle, this discovery could be a keystone of a new line of thermoplastic polymers." - Eric P. Wasserman, Dow Chemical

**JACS spotlight**  
*J. Am. Chem. Soc.* 2014, 136, 15807–15808

*J. Am. Chem. Soc.* 2014, 136, 15897. (ACS Editors' Choice)

32

**ChemComm**  
 COMMUNICATION

**Olefins from biomass feedstocks: catalytic ester decarbonylation and tandem Heck-type coupling**

Alex John, Levi T. Hogan, Marc A. Hillmyer\* and William B. Tolman\*

View Article Online  
 DOI: 10.1039/C4CC00000A

*Chem. Commun.* 2015, 51, 2731

**carboxylic acids from biomass**

**useful olefins**

Previous dehydrative decarbonylation using arylhydrides:  
 $R-CO_2H + PhCO_2H \xrightarrow{PdCl_2, ML, ArH} R-CO + Ph-CO + 2 CO_2H$

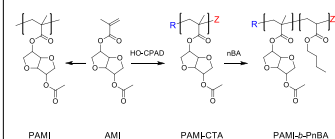
This report:  
 $R-CO_2H \xrightarrow{PdCl_2, ML, ArH} R-CO + CO + 2 CO_2H$  (decarbonylation)  
 $R-CO + ArH \xrightarrow{PdCl_2, ML} R-CH=CH-Ar + 2 CO_2H$  (coupled decarbonylation and Heck-type coupling)

33

## Poly(acetylated methacrylic isorbide) [PAMI]

ACS  
Sustainable  
Chemistry, Engineering

James J. Gallagher, Marc A. Hillmyer,\* and Theresa M. Reineke\*  
Department of Chemistry, University of Minnesota, 207 Pleasant Street SE,  
Minneapolis, MN 55455



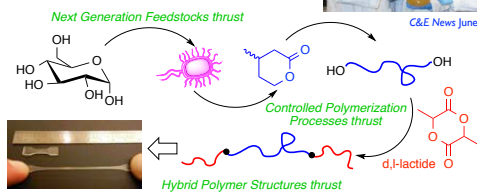
Thermally stable,  
high glass transition temperature  
polymethacrylate from sugar.

(isorbide comes from the  
hydrogenation &  
dehydration of glucose)

Discover efficient and precision conversions of renewable raw materials into innovative polymeric products that outperform the current suite of non-sustainable polymers from performance, environmental, and cost perspectives.



C&E News June 2, 2014





## *“Making Plastic Greener Through Next Generation Polymers”*



**Dr. Marc Hillmyer**  
Director  
Center for Sustainable Polymers,  
University of Minnesota



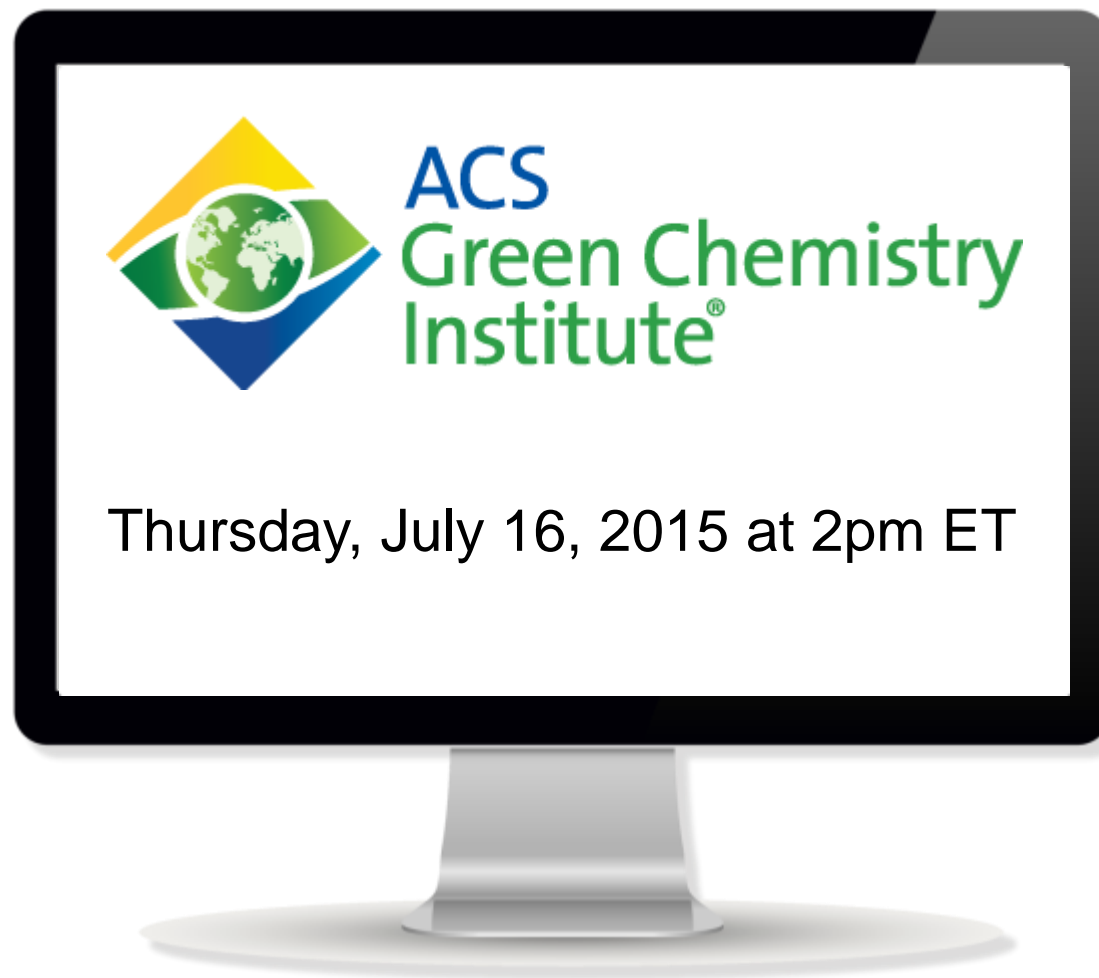
**Dr. Joseph Fortunak**  
Professor of Chemistry,  
Howard University

*Slides available now! Recordings will be available to ACS members after one week.*

[www.acswebinars.org](http://www.acswebinars.org)

This ACS Webinar is co-produced with the ACS Green Chemistry Institute

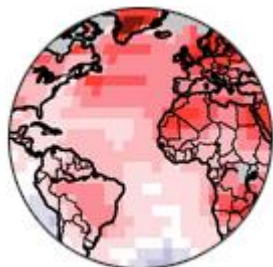
Join us for the next GCI ACS Webinar  
July 16<sup>th</sup> live from the Conference!



<http://www.acs.org/content/acs/en/greenchemistry.html>

# Upcoming ACS Webinars

[www.acs.org/acswwebinars](http://www.acs.org/acswwebinars)



Thursday, March 12, 2015 at 2pm ET

## “Bringing CO<sub>2</sub> Monitoring to You: Communicating Atmospheric Chemistry”

**Alexis Shusterman**, PhD candidate, UC Berkeley  
2014 ACS Chemistry Champions Competition Runner-Up

**Dr. Darcy Gentleman**, Manager, Engagement and Science Communications,  
The American Chemical Society



Wednesday, March 18, 2015 at 11am CST

## “Panorama Energético en la Era de la Sustentabilidad: Energías Renovables y Dispositivos Emergentes”

**Dr. Luis Echegoyen**, Profesor de Química, Universidad de Texas, El Paso

**Dr. Héctor D. Abruña**, Profesor de Química, Universidad de Cornell

**Dr. Ingrid Montes**, ACS Junta de Directores y Profesora de Química Orgánica, Universidad de Puerto Rico, Recinto de Río

Contact ACS Webinars ® at [acswwebinars@acs.org](mailto:acswwebinars@acs.org)

## *“Making Plastic Greener Through Next Generation Polymers”*



**Dr. Marc Hillmyer**  
Director  
Center for Sustainable Polymers,  
University of Minnesota



**Dr. Joseph Fortunak**  
Professor of Chemistry,  
Howard University

*Slides available now! Recordings will be available to ACS members after one week.*

[www.acswebinars.org](http://www.acswebinars.org)

This ACS Webinar is co-produced with the ACS Green Chemistry Institute

# How has ACS Webinars<sup>®</sup> benefited you?



“Today's webinar on transitioning from organic solvents was the best Webinar in which I participated both from the ACS and other organizations. It also gave me a genuine familiarity with the scope and benefits of green chemistry, which until now was something out there but to which I paid only modest attention.”

*Fan of the Week*

Steve Hirsch, Ph.D.



Be a featured fan on an upcoming webinar! Write to us @ [acswebinars@acs.org](mailto:acswebinars@acs.org)



## Benefits of ACS Membership



**Chemical & Engineering News (C&EN)**  
The preeminent weekly news source.



**NEW! Free Access to ACS Presentations on Demand<sup>®</sup>**  
ACS Member only access to over 1,000 presentation recordings from recent ACS meetings and select events.



**NEW! ACS Career Navigator**  
Your source for leadership development, professional education, career services, and much more.

[www.acs.org/2joinACS](http://www.acs.org/2joinACS)

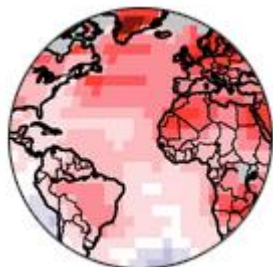
ACS Webinars<sup>®</sup> does not endorse any products or services. The views expressed in this presentation are those of the presenter and do not necessarily reflect the views or policies of the American Chemical Society.





# Upcoming ACS Webinars

[www.acs.org/acswebinars](http://www.acs.org/acswebinars)



Thursday, March 12, 2015 at 2pm ET

## “Bringing CO<sub>2</sub> Monitoring to You: Communicating Atmospheric Chemistry”

**Alexis Shusterman**, PhD candidate, UC Berkeley  
2014 ACS Chemistry Champions Competition Runner-Up

**Dr. Darcy Gentleman**, Manager, Engagement and Science Communications,  
The American Chemical Society



Wednesday, March 18, 2015 at 11am CST

## “Panorama Energético en la Era de la Sustentabilidad: Energías Renovables y Dispositivos Emergentes”

**Dr. Luis Echegoyen**, Profesor de Química, Universidad de Texas, El Paso

**Dr. Héctor D. Abruña**, Profesor de Química, Universidad de Cornell

**Dr. Ingrid Montes**, ACS Junta de Directores y Profesora de Química Orgánica, Universidad de Puerto Rico, Recinto de Río

Contact ACS Webinars ® at [acswebinars@acs.org](mailto:acswebinars@acs.org)