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C. Grant Willson

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as of 06-Aug-2018

Agency Code:

Proposal Number: 54343CHPCS **Agreement Number: W911NF-09-1-0446**
INVESTIGATOR(S):

Name: Carlton Grant Willson
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Country: USA
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Final Report for Period Beginning 25-Aug-2009 and Ending 24-Aug-2016
Title: PECASE: Redox-Switchable Catalysis: Concepts and Applications in Polymer Chemistry
Begin Performance Period: 25-Aug-2009 **End Performance Period:** 24-Aug-2016
Report Term: 0-Other
Submitted By: Carlton Willson Email: willson@che.utexas.edu
Phone: (000) 000-0000
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STEM Degrees: **STEM Participants:**

Major Goals: The goal of this effort was to develop new methods for controlling the structures and properties of macromolecular materials. The general strategy is based on the study of materials that undergo changes in response to various stimuli. One focus of the effort was on demonstration of catalysts that change their activity in response to external stimuli. We also studied a class of polymers that respond to stimuli directly including structurally reversible polymers that respond to radiation by undergoing rapid and essentially complete depolymerization. Our goal was to exploit these "unzipping" polymers for design of new, very sensitive photoresist formulations that are useful for high resolution EUV and electron beam lithography. We also set out to establish a safe, living anionic polymerization methodology that allows the synthesis of new block copolymers. This methodology has been exploited to prepare block copolymers that spontaneously assemble into useful structure upon interaction with stimuli.

Accomplishments: Introduction: The theme of one aspect of this research work was the design, synthesis and demonstration of materials that change their catalytic activity in response to stimulation. We demonstrated methods and materials for modifying catalyst reactivity in response to oxidation and reduction and to exposure to light. The newest catalyst materials studied are photo-activated and pH dependent ruthenium compounds that catalyze ring opening metathesis polymerization. These materials are inert until exposed to light. In addition, new polymers have been designed and synthesized that undergo depolymerization in response to stimuli. In that regard, many polymers have been synthesnized that respond to exposure to radiation by undergoing rapid and essentially complete depolymerization. These polymers have enabled the design of a new, very sensitive photoresist formulation that is useful for high resolution EUV and electron beam lithography. The work has also enabled the establishment of a safe, anionic living polymerization methodology that enabled the synthesis of many new block copolymers. This methodology has been exploited to prepare block copolymers that self assemble in response to stimuli to produce sub 10nm patterns that are useful for the manufacture of advanced microelectronics.
Photosensitive catalysis studies: Introduction of an amine ligand on certain ruthenium complexes renders them catalytically unreactive, while treatment of these inert compounds with acid reactivates their catalytic function. An imine functionalized Grubbs type ruthenium catalyst was successfully synthesized and characterized (Figure 1). This complex does not catalyze ring-opening metathesis polymerization (ROMP), but it becomes very active upon addition of acid (Figure 2). Hence, the deactivated catalyst was added to COD (and cyclopentadiene dimer) together with a photoacid generator. Thus, exposure of the formulation to light generates acid which activates the catalyst. This formulation proved to be useful for generation of robust patterns by nanoimprint lithography as shown in Figure 3.
Photolabile polymer studies: The responsive catalysis efforts led to the discovery of polymers that are intrinsically photoresponsive. In this case, monomers are induced to polymerize by one mechanism, and the polymeric

products efficiently depolymerized by another. Several examples of metastable polymers were synthesized that upon reaction with the appropriate stimuli unzip rapidly back to monomer. Examples of such materials are known and poly(phthalaldehyde) is perhaps the most widely studied. We showed several years ago that o-phthalaldehyde can be polymerized if initiated with base at a temperature below 40 °C, the ceiling temperature (Tc) of the polymer. If the polymer is capped by acylation or alkylation while below Tc, the product is stable at room temperature. However, it is only metastable. If an ionic end group is generated by any means at a temperature above Tc, the equilibrium is reestablished and the polymer spontaneously "unzips". Polyphthalaldehyde is a fascinating material, but not sufficiently stable for considered use in an engineering applications. We have now found several new polymers that are sufficiently stable for use at room temperature and above. Many polymers were designed and auditioned but the best of these is based on the hydroxyester monomer shown in Figure 4. This monomer is a mixture of two isomers that can be separated. The cis-isomer efficiently forms a cyclic tetramer (Figure 5) but the trans isomer undergoes step growth polymerization as shown in Figure 6. The resulting polymer is stable under processing conditions but upon exposure to x-ray and electron beam radiation it undergoes rapid reversal tp produce toluene and CO2 (Figure 6). The unzipping reaction proceeds via a free radical pathway and is driven by the aromatization reaction that forms toluene.
Blending this unzipping polyester with a base soluble matrix resin such as the polynorbornene shown in Figure 7 provides a resist that requires at least 5 times less exposure dose than classical polymer resists such as PMMA and produces high resolution images (Figure 8) with several times less dose than a commercial acid catalyzed, chemically amplified resist. The formulation demonstrates among the highest sensitivity reported for EUV exposure as shown in Figure 8. The unzip resist is "chemically amplified". That is, many bonds are broken per photochemical event, but the gain in the system does not involve a catalyst, so there should be no diffusion blur of the sort that limits the resolution of the chemically amplified resists used in semiconductor device manufacturing today. If this formulation really does demonstrate high sensitivity through gain without blur, it will be of great interest to many. We will continue to characterize this very interesting material.
Comment: This project suffered a serious disruption in early 2015 when Professor Bielawski left the University of Texas to take a position abroad. Students were displaced, required to change advisors, moved to different laboratories, etc. The magnitude of the disruption is clear among other things from the low spending rate. The situation ultimately stabilized but it took a long time. I am proud to report that all of the students who stayed at UT have completed their theses and earned their PhDs. I have been delinquent in getting their work submitted for publication but I have the late drafts of 5 papers on my desk and am committed to getting them submitted before summer ends.

Training Opportunities: The students who worked on this project were trained to use an very wide range of tools including SEM, AFM, DSC, TGA, NMR, GPC, Ellipsometry, Electon Beam exposure, UV-Vis Spectroscopy, FTIR, reactive ion etching UV.lithography and a range of techniques used to produce and characterize thin films. This training was done in workshops at UT, and visits to The University of Minnesota, IMEC in Belgium, Argonne National Laboratory, Lawrence Berkeley National Laboratory where we had collaborations.

Results Dissemination: Nothing to Report

Honors and Awards: Dr. Willson is a Fellow of IBM, ACS, MRS, SPIE and PMSE and a member of the National Acvademy of Engineering. He has received a number of awards for his research, including the Arthur Doolittle Award, the Chemistry of Materials Award, the Carothers Award, The Cooperative Research in Polymer Science and Engineering Award, Applied Polymer Science Award, the Heroes in Chemistry Award and most recently, the Polymer Science award from the American Chemical Society. He was also presented with the Alexander von Humboldt Senior Scientists Award from the Federal Republic of Germany, the Technical Excellence Award and Aristotle Award from SRC, the Malcolm E. Pruitt Award from the CRC, the Monie A. Ferst Award from Sigma Xi and the Billy and Claude R. Hocott Distinguished Centennial Engineering Research Award from The Cockrell School of Engineering. He received the National Academy of Sciences Award for Chemistry in Service to Society and he was the recipient of the Dehon Little Award from the AIChE, the Zernike Award from the SPIE, the SEMI North America Award and the Gordon Moore Medal from the ECS. He was presented with the National Medal for Technology and Innovation by the President of the United States and he shared the Japan Prize

Protocol Activity Status:

Technology Transfer: Nothing to Report

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PARTICIPANTS:

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Participant: C. Grant Willson
Person Months Worked: **Funding Support:**
Project Contribution:
International Collaboration:
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National Academy Member:
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Andrew Dick
Person Months Worked: **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member:
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Participant Type: Graduate Student (research assistant)
Participant: Wontae Joo
Person Months Worked: **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member:
Other Collaborators:

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International Collaboration:
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Other Collaborators:

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Volume: 50 Issue: 44 First Page #: 10322
Date Submitted: Date Published:
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Article Title: Photoswitchable N-Heterocyclic Carbenes: Using Light to Modulate Electron-Donating Properties
Authors:
Keywords: carbenes, cyclization, nitrogen heterocycles, photochromism, photoswitch
Abstract: The first example of tuning the electronic character of an N-heterocyclic carbene (NHC) scaffold using light is described. Two novel photochromic 4,5-diarylimidazolone derivatives were synthesized and shown to undergo a photoinduced electrocyclic ring-closing reaction. Isolation, X-ray crystallography (which included the only hitherto example of a photocyclized diarylethene containing a heterocyclic linker), and extensive spectroscopic characterization was used to confirm and study the ring-closing reaction. Notably, the infrared spectroscopic data revealed a significant increase in ?CO (33 cm-1) upon photocyclization, indicating that nitrogen donation into the carbonyl bond, and thus the electron donating ability of the corresponding NHC, was diminished. Because the performance of NHC supported catalysts is largely dependent upon the donating ability of the NHC ligand, the ability to control their donicity using light is expected to guide the development of photo-switchable NHC suppor
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Volume: 134 Issue: 30 First Page #: 12693
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Article Title: Photoswitchable Organocatalysis: Using Light To Modulate the Catalytic Activities of N-Heterocyclic Carbenes
Authors:
Keywords: catalysis, photoswitchable, N-heterocyclic carbene, transesterification, amidation
Abstract: A 4,5-dithienylimidazolium salt was found to undergo electrocyclic isomerization upon exposure to UV radiation (?irr = 313 nm) under neutral and basic conditions; subsequent exposure to visible light reversed the reaction. Under ambient light and in the presence of base, the imidazolium species catalyzed transesterifications as well as amidations in a manner similar to those of previously reported N-heterocyclic carbene precatalysts. However, upon UV irradiation to effect the aforementioned photocyclization, the rate of the transesterification reaction between vinyl acetate and allyl alcohol was significantly attenuated (kvis/UV = 12.5), as was the rate of the condensation of ethyl acetate with aminoethanol (kvis/UV = 100). The rates of these reactions were successfully toggled between fast and slow states by alternating exposure to visible and UV light, respectively, thus demonstrating a rare example of a photoswitchable catalyst that operates via photomodulation of its electronic str
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Volume: 28 Issue: 23 First Page #: 6695
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Article Title: Redox-Active N-Heterocyclic Carbenes: Design, Synthesis, and Evaluation of Their Electronic Properties
Authors:
Keywords: redox-active, N-heterocyclic carbenes, catalysis, redox-switchable
Abstract: To investigate effects of redox-active functional groups on the coordination chemistry and electronic properties of N-heterocyclic carbenes (NHCs), we prepared a series of complexes comprising 1,3-diferrocenylimidazolylidene and -benzimidazolylidene (1 and 2, respectively), 1-ferrocenyl-3-methyl- and 1,3-diphenyl-5-ferrocenylbenzimidazolylidene (3 and 4, respectively), N,N0-diisobutyldiaminocarbene[3] ferrocenophane (FcDAC), and 1,3-dimesitylnaphthoquinoimidazolylidene (NqMes) ligands and coordinated [Ir (COD)Cl] (COD=1,5-cyclooctadiene), [Ir(CO)2Cl], and [M(CO)5] (M=Cr,Mo,W) units. The coordination chemistry of the aforementioned NHCs was investigated by X-ray crystallography, and their electronic properties were studied by NMR and IR spectroscopy, as well as electrochemistry.No significant variation in ?CO was observed among metal carbonyl complexes supported by 2-4 and FcDAC, indicating that the number (one vs two) of redoxactive groups, the location (N atom vs backbone) of the redox-
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Journal: Journal of Physical Organic Chemistry
Publication Identifier Type: DOI Publication Identifier: 10.1002/poc.1961
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Article Title: Advances in bis(N-heterocyclic carbene) chemistry: new classes of structurally dynamic materials
Authors:
Keywords: conjugated; dynamic; luminescence; N-heterocyclic carbene; polymers
Abstract: A major challenge in the pursuit of dynamic materials is the dichotomy between reversible structure and electronic conjugation. Guided by the precedence for N-heterocyclic carbenes (NHCs) to dimerize, couple with electrophiles and bind to transition metals, we proposed that linearly opposed bis(NHC)s could, in a similar manner, afford unsaturated homopolymers, alternating copolymers, and metallopolymers. To realize these goals, we developed synthetic methods for accessing ditopic NHCs and investigated their propensities to undergo homopolymerization via dimerization and copolymerization via coupling with ditopic electrophiles or divalent transition metals. The materials obtained from these reactions were of relatively high molecular weight, exhibited electronic properties that were consistent with extensively delocalized systems, and in many cases, were found to be thermally reversible. In addition to expanding the scope of carbene chemistry, these polymers represent significant advanc
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Journal: Organometallics
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Volume: 32 Issue: 10 First Page #: 0
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Article Title: Photoswitchable Metal-Mediated Catalysis: Remotely Tuned Alkene and Alkyne Hydroborations
Authors:
Keywords: photoswitchable, hydroborations, N-heterocyclic carbenes, catalysis
Abstract: A photochromic dithienylethene-annulated N-heterocyclic carbene (NHC)–Rh(I) complex was synthesized and found to undergo reversible electrocyclic ring closure upon alternate exposure to UV (?irr 313 nm) and visible (?irr >500 nm) radiation. Under ambient light, the Rh catalyst efficiently promoted the hydroboration of alkenes and alkynes with pinacolborane. However, upon UV irradiation to effect a photocyclization within the NHC ligand, the catalytic activity was reduced by up to an order of magnitude. The disparity in the rates was used to photoswitch the rates of a series of hydroboration reactions, thus demonstrating the first examples of photomodulating a transition-metal catalyst by tuning its electronic properties. The rate attenuation observed under UV irradiation was attributed to inhibition of the rate-determining reductive elimination step arising from a decrease in electron-donating ability of the photocyclized NHC ligated to the Rh center.
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Article Title: Photoswitchable NHC-promoted ring-opening polymerizations
Authors:
Keywords: photoswitchable, N-heterocyclic carbenes, catalysis, polymerizations
Abstract: The UV-induced photocyclization of a dithienylethene-annulated N-heterocyclic carbene precatalyst enabled photoswitchable ring-opening polymerizations of ?-caprolactone and ?-valerolactone. The polymerizations proceeded efficiently in ambient light, however UV irradiation attenuated the reaction rate (kamb/kUV = 59). Subsequent visible light exposure reversed the photocyclization and restored catalytic activity.
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Article Title: Redox-Switchable Ring-Closing Metathesis: Catalyst Design, Synthesis, and Study
Authors:
Keywords: errocene · homogene- ous catalysis, olefin metathesis, redox-switchable catalysis, ruthenium, spectroelectrochemistry
Abstract: High yielding syntheses of 1-(ferrocenylmethyl)-3-mesitylimidazolium iodide (1) and 1-(ferrocenylmethyl)-3-mesitylimidazol-2-ylidene (2) were developed. Complexation of 2 to [{Ir(cod)Cl}2] (cod=cis, cis-1,5-cyclooctadiene) or [Ru(PCy3)Cl2([DOUBLE BOND]CH-o-O-iPrC6H4)] (Cy=cyclohexyl) afforded 3 ([Ir(2)(cod)Cl]) and 5 ([Ru(2)Cl2([DOUBLE BOND]CH-o-O-iPrC6H4)]), respectively. Complex 4 ([Ir(2)(CO)2Cl]) was obtained by bubbling carbon monoxide through a solution of 3 in CH2Cl2. Spectroelectrochemical IR analysis of 4 revealed that the oxidation of the ferrocene moiety in 2 significantly reduced the electron-donating ability of the N-heterocyclic carbene ligand (?TEP=9?cm?1; TEP=Tolman electronic parameter). The oxidation of 5 with [Fe(?5-C5H4COMe)Cp][BF4] as well as the subsequent reduction of the corresponding product [5][BF4] with decamethylferrocene (Fc*) each proceeded in greater than 95?% yield. Mössbauer, UV/Vis and EPR spectroscopy analysis confirmed that [5][BF4] contained a ferroce
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Journal: Organometallics
Publication Identifier Type: DOI Publication Identifier: 10.1021/om4004829
Volume: 32 Issue: 15 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: Cationic Iridium Complexes Containing Anionic Iridium Counterions Supported by Redox-Active N-Heterocyclic Carbenes
Authors:
Keywords: redox, catalysis, iridium, ligands
Abstract: The first cationic iridium complex supported by two bulky, ferrocenylated N-heterocyclic carbenes, [(1)2Ir- (COD)]+[Cl]? ([2]+[Cl]?; 1 = 1-ferrocenylmethyl-3-mesityl- imidazol-2-ylidene, Fc-NHC; COD = cis,cis-1,5-cycloocta- diene), was synthesized and characterized. Treatment of the aforementioned complex with a mixture of [N(nBu)4]+[Cl]? and [Ir(COD)(Cl)]2 afforded [(1)2Ir(COD)]+[Ir(COD)- (Cl)2]? ([2]+[Ir(COD)Cl2]?), which featured cationic as well as anionic Ir centers. Electrochemical analysis of [2]+[Ir(COD)Cl2]? revealed that the complex displayed two reversible (iron- and iridium-centered) and two irreversible (iridium-centered) redox processes, which were assigned to the cationic and anionic components, respectively. Stirring [2]+[Ir(COD)Cl2]? under an atmosphere of carbon monoxide generated the corresponding Ir carbonyl complex [(1)2Ir(CO)2]+[Ir(CO)2(Cl)2]? ([3]+[Ir(CO)2Cl2]?). Cyclic voltammetry (CV) measurements of the aforementioned complexes containing [(1)2Ir (COD)]+ showed
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Journal: ACS Catalysis
Publication Identifier Type: DOI Publication Identifier: 10.1021/cs4003673
Volume: 3 Issue: 8 First Page #: 0
Date Submitted: Date Published:
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Article Title: Illuminating Photoswitchable Catalysis
Authors:
Keywords: catalyst; photoswitchable; photochromism; azobenzene; diarylethene
Abstract: Through the realization of conceptually new approaches aimed at controlling chemical reactions using light, the field of photoswitchable catalysis has seen rapid development over the past three decades. Although many photoswitchable catalysts are heterogeneous and utilize photosensitive surfaces, such as TiO2 and CdSe, significant attention has also been directed toward homogeneous analogues, primarily by capitalizing on the steric changes that accompany the E ? Z photoisomerizations of azobenzene or stilbene derivatives. More recently, photochromic diarylethene moieties have been used to switch the intrinsic catalytic activities and selectivities through alteration of the steric and electronic properties displayed by a supporting ligand. In addition to detailing the aforementioned advances, this perspective summarizes other important developments in photoswitchable catalysis and offers a viewpoint on the future outlook of the field.
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Publication Identifier Type: DOI Publication Identifier: 10.1039/c3dt51278a
Volume: 42 Issue: 36 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: Synthesis and study of olefin metathesis catalysts supported by redox-switchable diaminocarbene [3]ferrocenophanes
Authors:
Keywords: redox, olefin metathesis, switchable catalysis, catalysis, ligand design
Abstract: A redox-switchable ligand, N,N?-dimethyldiaminocarbene[3]ferrocenophane (5), was synthesized and incorporated into a series of Ir- and Ru-based complexes. Electrochemical and spectroscopic analyses of (5)Ir (CO)2Cl (15) revealed that 5 displayed a Tolman electronic parameter value of 2050 cm?1 in the neutral state and 2061 cm?1 upon oxidation. Moreover, inspection of X-ray crystallography data recorded for (5)Ir(cis,cis-1,5-cyclooctadiene)Cl (13) revealed that 5 was sterically less bulky (%VBur = 28.4) than other known diaminocarbene [3]ferrocenophanes, which facilitated the synthesis of (5)(PPh3)Cl2Ru(3-phenylindenylid-1-ene) (18). Complex 18 exhibited quasi-reversible electrochemical processes at 0.79 and 0.98 V relative to SCE, which were assigned to the Fe and Ru centers in the complex, respectively, based on UV-vis and electron pair resonance spectroscopic measurements. Adding 2,3-dichloro-5,6-dicyanoquinone over the course of a ring-opening metathesis polymerization of cis,cis-1,5-
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Publication Identifier Type: DOI Publication Identifier: 10.1016/j.jorganchem.2013.07.063
Volume: 0 Issue: 0 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: Metal-centered oxidations facilitate the removal of ruthenium-based olefin metathesis catalysts
Authors:
Keywords: Olefin metathesis; Catalysis; Recycling; Recovery; Redox; Phase tag
Abstract: Commercially available catalysts (SIMes)(PCy3)Cl2Ru(double bond; length as m-dashCHPh) (2) and (SIMes)Cl2Ru(double bond; length as m-dashCH-o-O-i-PrC6H4) (3) (SIMes = 1,3-dimesitylimidazolin-2-ylidene) were found to display reversible Ru oxidations via a series of electrochemical measurements. The redox processes enabled the catalysts to be switched between two different states of activity in ring opening metathesis polymerizations and ring closing metathesis reactions, primarily through changes in catalyst solubility. Moreover, treating a solution of 2 dissolved in C6H6/CH2Cl2/[1-butyl-3-methylimidazolium][PF6] (6:1:1.1 v/v/v) with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone was found to remove >99.9% of the catalyst, as determined by UV/vis spectroscopy. The methodology described herein establishes a new approach for controlling the activities displayed by commercially available olefin metathesis catalysts and for removing residual Ru species using redox-driven processes.
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Journal: European Journal of Organic Chemistry
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Article Title: 1,6-Enyne Cyclizations Catalyzed by N-Heterocyclic Carbene Supported Gold Complexes: Deconvoluting Sterics vs. Electronics
Authors:
Keywords: -heterocyclic carbenes;Gold;Isomerization;Enynes;Steric hindrance
Abstract: A series of N-heterocyclic carbene (NHC) supported gold(I) complexes were synthesized, characterized in solution as well as in the solid state, and examined as precatalysts for 1,6-enyne cycloisomerization reactions. The product mixtures obtained for a variety of 1,6-enyne isomerizations were governed primarily by the electronic properties of the aforementioned precatalysts. In particular, precatalysts containing electronic-rich NHC ligands showed increased selectivity for bicyclic products, whereas analogous precatalysts supported by electron-deficient NHCs preferentially afforded olefinic products.
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Journal: Macromolecular Rapid Communications
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Volume: 35 Issue: 2 First Page #: 210
Date Submitted: Date Published:
Publication Location:
Article Title: Electrochromic Poly(acetylene)s with Switchable Visible/Near-IR Absorption Characteristics
Authors:
Keywords: conjugated polymers; electrochromism; ferrocene; functionalization of polymers
Abstract: Ferrocene is incorporated into a poly(acetylene) derivative via the postpolymerization amidation of a polymer precursor bearing pentafluorophenyl ester-leaving groups with aminoferrocene. While the neutral polymer exhibits a strong absorbance at 553 nm due to its conjugated backbone, oxidation of the ferrocene moieties with silver tetrafluoroborate causes the material to absorb in the near-IR (?max ?1215 nm). Subsequent reduction of the oxidized polymer with decamethylferrocene restores the initial absorbance profile, demonstrating that the material features switchable visible/near-IR absorption characteristics.
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Date Received: 24-Nov-2016 Completion Date: 8/2/16 10:22PM
Title: Design and development of base-catalyzed materials for microelectronics applications
Authors: Andrew Dick
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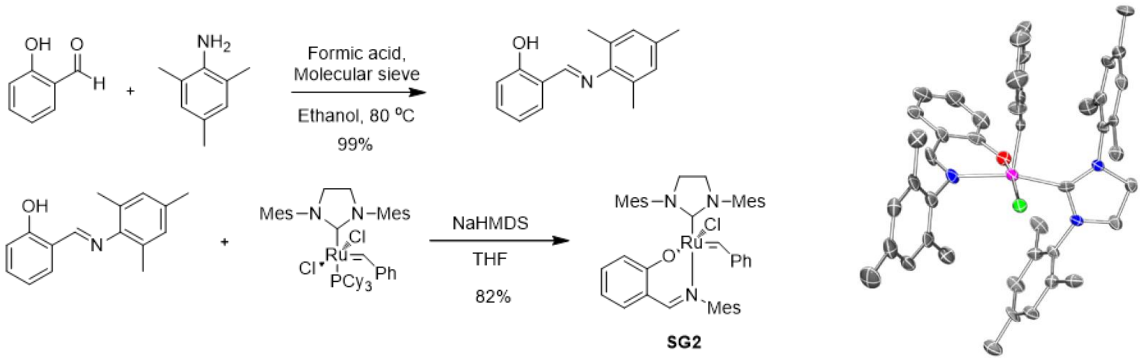

Figure 1. The synthesis and the x-ray structure of the inert form of the on/off catalyst.

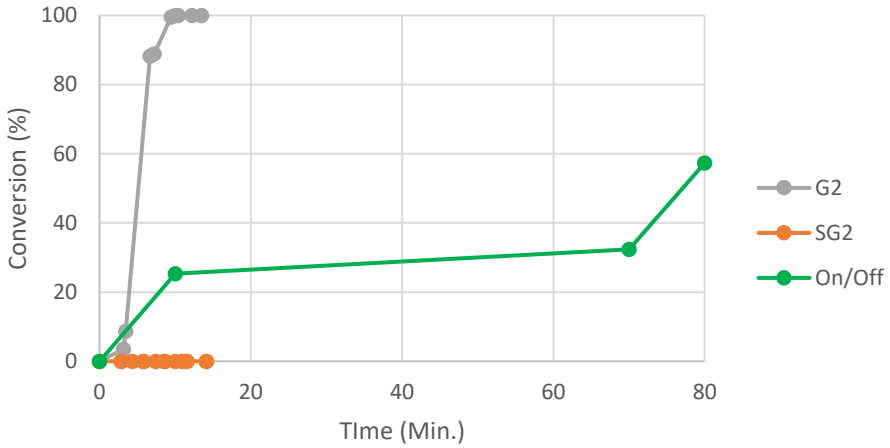

Figure 2. The conversion against time for reaction of cyclooctadiene with Grubbs catalyst (G2), with the new catalyst in the dark (SG2) and with 254nm exposure of the on/off formulation with light on for 10 minutes, off for 90 minutes and then back in for 10 minutes.

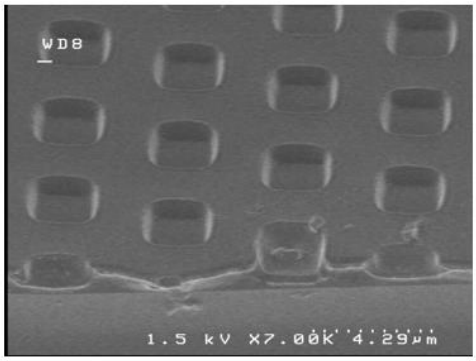

Figure 3. Micron scale patterns generated by imprint lithography using the on/off catalyst and cyclppendadiene dimer.

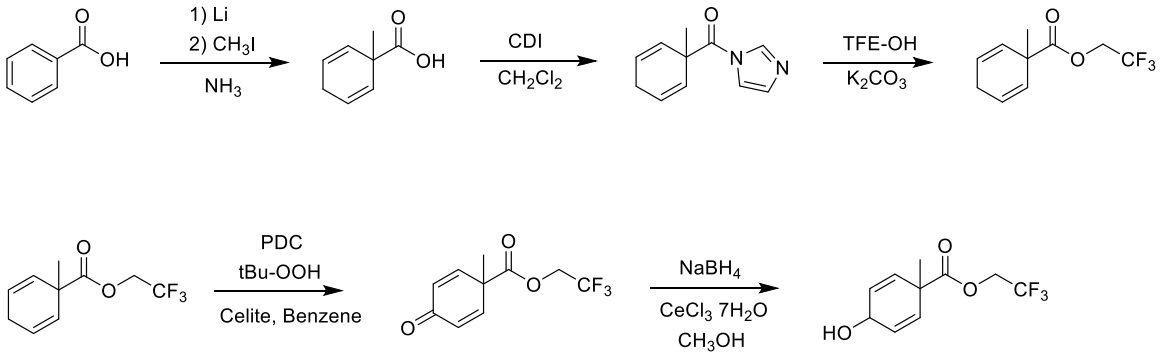

Figure 4. The synthetic pathway to the key hydroxyl ester monomer

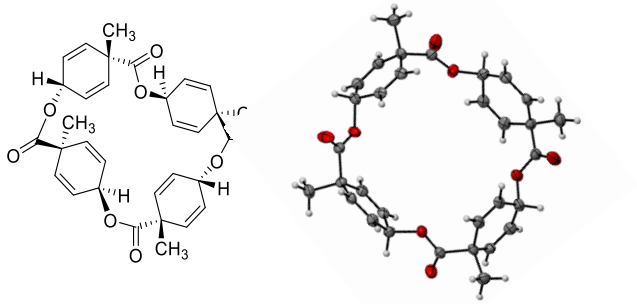

Figure 5. The structure of the cyclic tetramer that is generated from the cis-isomer of the diastereomeric monomer.

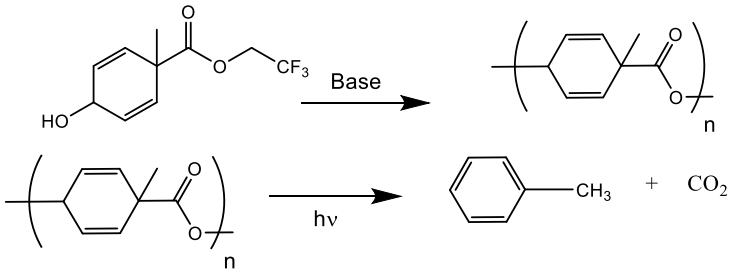

Figure 6. Base catalyzed polymerization and photo-depolymerization of the polyester

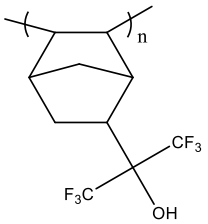

Figure 7. Poly(norbornene Hexafluoroallcohol) PNBHFA from Promerus Company

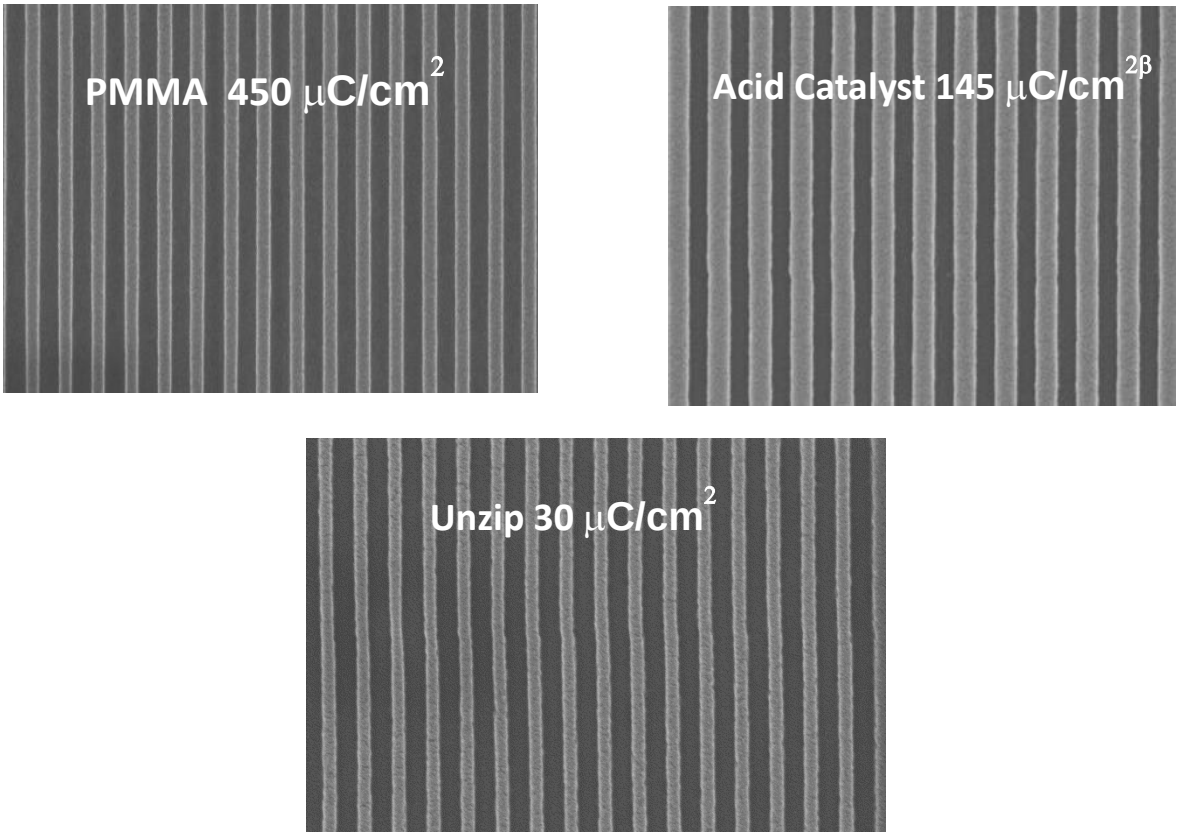

Figure 8. Electron beam exposure of the PNBHFA g/ unzip blend at 100 Kev. The patterns are 100nm lines and spaces. The experiments were carried out at The University of Minnesota. Note that the patterning dose required to print the new resist is more than 1 order of magnitude less than that required to pattern PMMA and over a factor of 3 less than that required to pattern an acid catalyzed commercial electron beam resist.

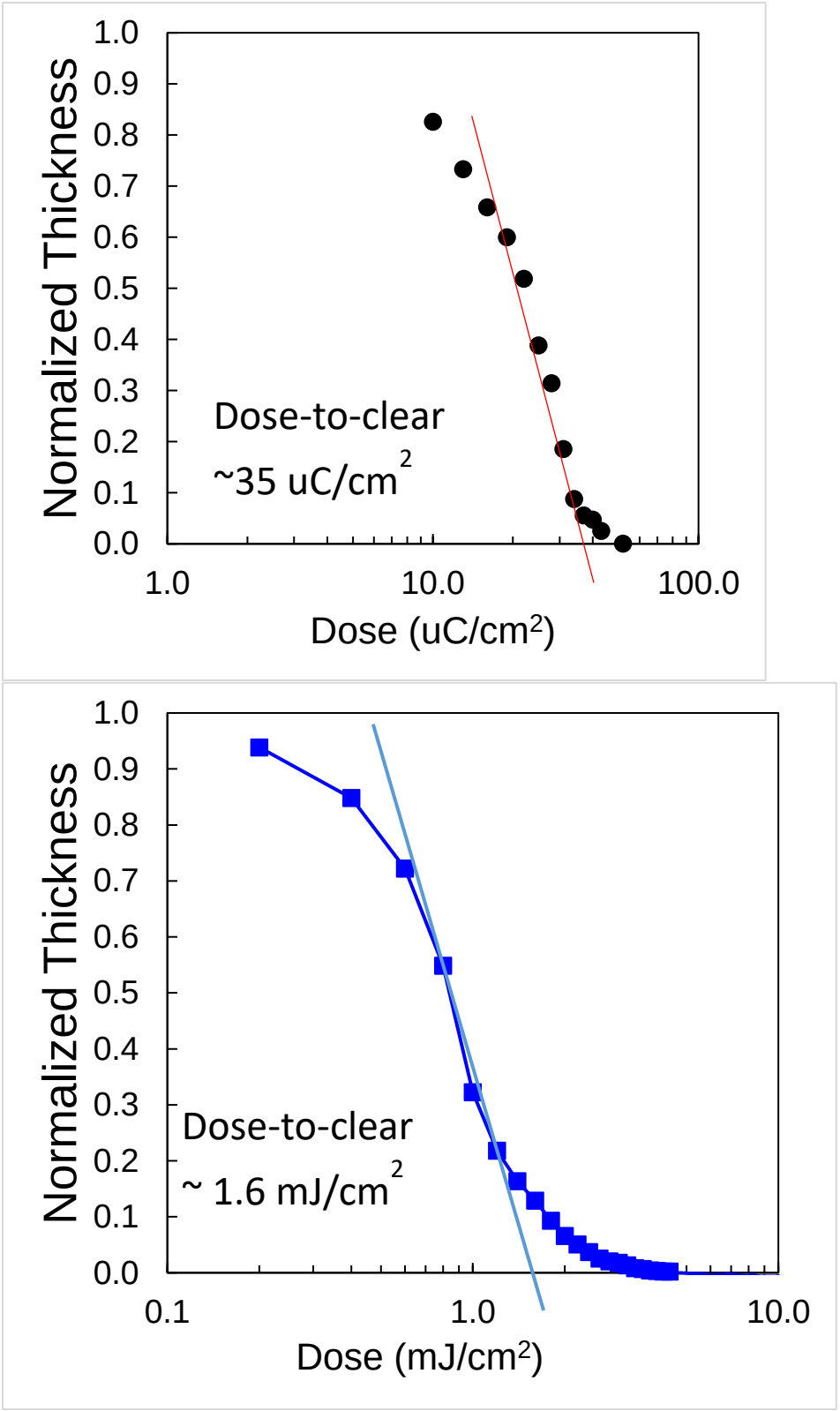

Figure 9 Electron beam (upper) and EUV (lower) Contrast curves for the new Resist