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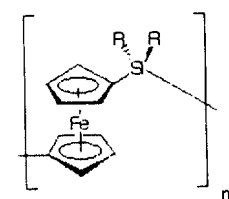
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**Article:** Chou SY, Zhuang L, Deshpande P. Lithographically induced self-assembly of periodic micro

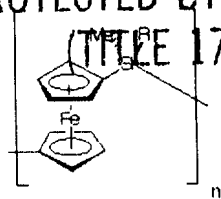
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1: R = OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>  
2: R = (OCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>OCH<sub>3</sub>



3: R = (OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OCH<sub>3</sub>  
4: R = OCH<sub>2</sub>CH<sub>2</sub>NMe<sub>3</sub><sup>+</sup>  
5: R = OCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>HCl

**327.**  
**SYNTHESIS AND SOLUTION PROPERTIES OF COMB-TYPE URETHANE-ASSOCIATIVE THICKENERS.** Peter T. Elliott and J. Edward Glass. *Polymers and Coatings Dept, North Dakota State University, Fargo, ND 58105, fax: 701-237-8439, pelliott@prairie.nodak.edu*

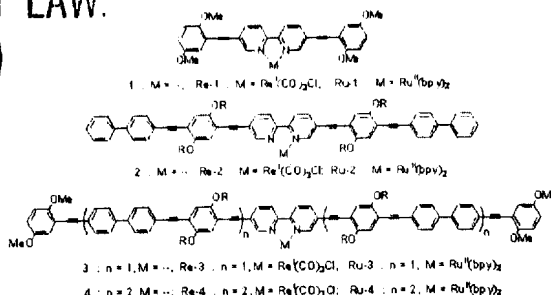
Comb-type urethane associative thickeners were synthesized by a step-growth method using a variety of mixtures of hydrophobes (1,2 hexadecanediol and 1,2 tetradecanediol), diisocyanate couplers (hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), 4,4' methylene bis(cyclohexyl isocyanate) (H12MDI)), and poly(ethylene glycol)s (8000 and 12000 molecular weight PEGs) to determine the structure-property relations for these types of polymers in relation to their aqueous solution thickening ability. These thickeners were also evaluated for surfactant sensitivity using both an anionic (sodium dodecyl sulfate) and nonionic surfactant (NP-10).

**328.**  
**LITHOGRAPHICALLY INDUCED SELF-ASSEMBLY OF PERIODIC MICROPILLAR ARRAYS IN A SINGLE HOMOPOLYMER FILM.** Stephen Y. Chou, Lei Zhuang, Paru Deshpande, Lei Chen, and Xiaoyun Sun. *NanoStructure Laboratory, Department of Electrical Engineering, Princeton University, Engineering Quad, Princeton, NJ 08544, fax: 609-258-1840, chou@ee.princeton.edu*

Lithographically-induced self-assembly (LISA) is a newly discovered pattern formation phenomenon occurring at micrometer or submicrometer length scale. In LISA, a plate (called mask), placed a distance above a thin single-homopolymer film heated about T<sub>g</sub>, causes the polymer film, initially flat on another plate, to self-assemble into periodic pillar arrays. The pillars, formed by rising against the gravitational force and the surface tension, bridge the two plates. The pillar height is equal to the plate-mask separation. If the mask surface has a protruding pattern or a surfactant pattern (with a shape of a triangle or rectangle, etc.), a LISA pillar array formed only under the pattern with its boundary aligned to the boundary of the mask pattern and with its lattice structure determined by the geometry of the mask pattern boundary. Direct observation of dynamic behavior of LISA showed that the pillars were formed one by one, first under the corners of a mask pattern, then the edges, and later the center. Our study also indicated that LISA is related to the interplay of electrostatics, fluid-hydrodynamics, and polymer-chemistry at nanometer scale.

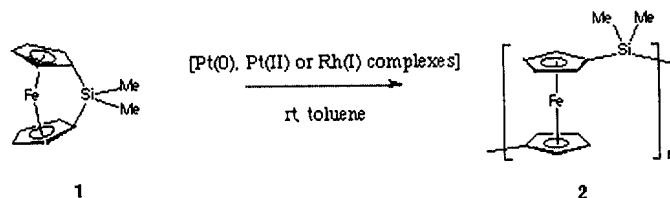
**329.**  
**OPTICAL SPECTROSCOPY OF TRANSITION-METAL-CONTAINING π-CONJUGATED OLIGOMERS AND POLYMERS.** Kirk S. Schanze, Keith A. Walters, Yiting Li, and Kevin D. Ley. *Department of Chemistry, University of Florida, PO Box 117200, Gainesville, FL 32611-7200, kschanze@chem.ufl.edu*

We are carrying out a detailed investigation that is exploring the photophysical and photochemical properties of polyphenylene ethynylene π-conjugated polymers and mono-disperse oligomers that contain d<sup>6</sup> transition metal complexes that strongly interact with the π-conjugated backbone. Recent work has focused on a series of polymers and oligomers and their corresponding (L)Re(CO)<sub>3</sub>Cl and (L)Ru(bpy)<sub>2</sub><sup>2+</sup> complexes (where L is the π-conjugated oligomer or polymer and the metal is complexed via a 5,5'-(2,2'-bipyridinedyl) unit). The focus of our studies has been to examine: (1) How does the metal-complex unit modify the properties of the <sup>1</sup>π,π\* and <sup>3</sup>π,π\* states of the π-conjugated system? (2) How does the delocalized π-conjugated system influence the properties of metal-to-ligand charge transfer (MLCT) excited states? Highlights from our recent work concerning the absorption, luminescence and fs/ps/ns time-resolved spectroscopy will be discussed.



**330.**  
**TRANSITION-METAL-CATALYZED ROUTES TO TRANSITION-METAL-CONTAINING POLYMERS: MECHANISTIC INSIGHTS INTO THE RING-OPENING POLYMERIZATION OF [1]SILA-FERROCENOPHANES.** Karen Temple<sup>1</sup>, Frieder Jaekle<sup>1</sup>, Alan Lough<sup>1</sup>, John B. Sheridan<sup>2</sup>, and Ian Manners<sup>1</sup>. (1) *Department of Chemistry, University of Toronto, 80 St. George St, Toronto, ON M5S 3H6, Canada*, (2) *Department of Chemistry, Rutgers, State University of New Jersey, University Heights, NJ 07102*

Metal mediated ring-opening polymerization of [1]-silaferrocenophanes(1) by a variety of Pt(0), Pt(II) and Rh(I) complexes offers a very mild and convenient route for the formation of high molecular weight poly(ferrocenylsilanes) (2). The addition of Et<sub>3</sub>SiH permits excellent molecular weight control of 2 and moreover, this strategy has been extended to other Si-H functionalized molecules to yield novel block and graft copolymers. This talk will focus on mechanistic investigations including isolation of well-defined [2]-platiniferrocenophane precatalysts and their fate during the polymerization cycle.



**331.**  
**NEW STARBURST METALLODENDRIMERS BASED ON OCTA(DIPHENYLPHOSPHINO)-FUNCTIONALIZED SILSESQUIOXANE CORES.** Bo Hong and Hunter J. Murfee. *Department of Chemistry, U of CA, 516 Rowland Hall, Irvine, CA 92697-2025, bhong@uci.edu*

Surface-modified starburst dendrimers have been prepared by reaction of terpyridine-functionalized polyether monodendrons with an oligomeric polyhedral silsesquioxane (POSS) core. Subsequent reaction of these starburst dendrimers with ruthenium (II)-based precursors affords starburst metallogendrimers. These new dendrimers have been characterized using a combination of mass spectral (MALDI-TOF, ESI, and FAB/MS) and NMR (<sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P{<sup>1</sup>H}) analyses. Other characterization methods include photophysical (absorption, emission, excited-state lifetime, and quantum yield) and electrochemical (cyclic and square wave voltammetric) analyses. Photophysical data indicate that there is no intramolecular excited-state quenching even in the generation 3 metallogendri-mer, which possesses 32 ruthenium (II) centers. Electrochemical studies reveal the presence of charge trapping effects, as well as ligand-centered and metal-centered redox couples.

**332.**  
**POLYMERS, RINGS, AND OLIGOMERS CONTAINING GOLD(I) CENTERS.** Richard J. Puddephatt. *Department of Chemistry, University of Western Ontario, London, ON N6A 5B7 Canada, fax: 519-661-3022, pudd@uwo.ca*

Gold(I) forms linear 2-coordinate complexes so it is a good choice for incorporation into linear rigid-rod polymers. Conjugation effects are possible through pi-bonding. Neutral polymers may be synthesized with repeating groups (L-L-Au-X-Au)n or (L-X-Au)n, where L and X represent neutral or anionic donors within a bidentate ligand, L-L, L-X, or X-X. Cationic polymers result when only neutral bidentate ligands are used. If the bidentate ligands used are not strictly linear, there may be a competition between formation of polymers or large rings. Some of the factors affecting such equilibria have been elucidated. If

# LITHOGRAPHICALLY-INDUCED SELF-ASSEMBLY OF PERIODIC MICRO-PILLAR ARRAYS IN A SINGLE HOMOPOLYMER FILM

Stephen Y. Chou, Lei Zhuang, Paru Deshpande, Lei Chen, and Xiaoyun Sun

NanoStructure Laboratory  
Department of Electrical Engineering  
Princeton University, Princeton, NJ 08544, USA

Lithographically-induced self-assembly (LISA) is a newly discovered pattern formation phenomenon occurring at micrometer or submicrometer length scale.<sup>1</sup> In LISA, a plate (called mask), placed a distance above a thin single-homopolymer film heated about  $T_g$ , causes the polymer film, initially flat on another plate, to self-assemble into periodic pillar arrays (Figure 1). The pillars, formed by rising against the gravitational force and the surface tension, bridge the two plates. The pillar height is equal to the plate-mask separation. If the mask surface has a protruding pattern or a surfactant pattern (with a shape of a triangle or rectangle, etc.), a LISA pillar array formed only under the pattern with its boundary aligned to the boundary of the mask pattern and with its lattice structure determined by the geometry of the mask pattern boundary (Figure 2 and 3). Direct observation of dynamic behavior of LISA showed that the pillars were formed one by one, first under the corners of a mask pattern, then the edges, and later the center. Our study also indicated that LISA is triggered by an attractive force between the mask and the polymer, and it is related to the interplay of electrostatics, fluid-hydrodynamics, and polymer-chemistry at the nanometer scale. The exact origin of LISA is still under investigation. LISA has many applications in nanopatterning and fabrication of polymer electronic and optoelectronic devices.

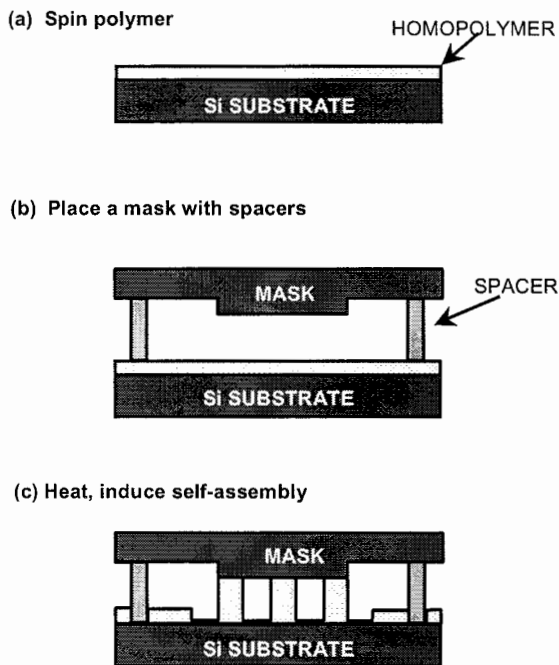


Figure 1. Schematic of lithographically-induced self-assembly (LISA): (a) A thin layer of PMMA spin-coated on a flat silicon wafer. (b) A mask of protruding patterns placed a distance above the PMMA film, but separated by a spacer. (c) During a heat-and-cool cycle, the PMMA film self-assembled into a periodic supramolecular pillar array, with the location and lattice structure of the array controlled by the patterns on the mask.

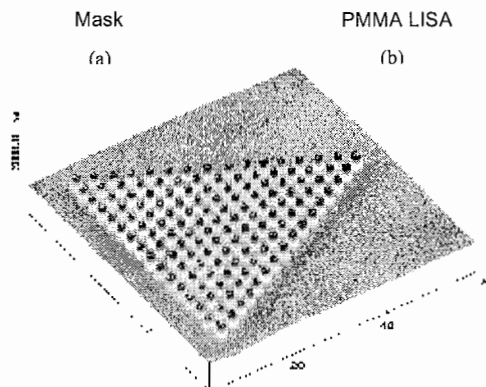
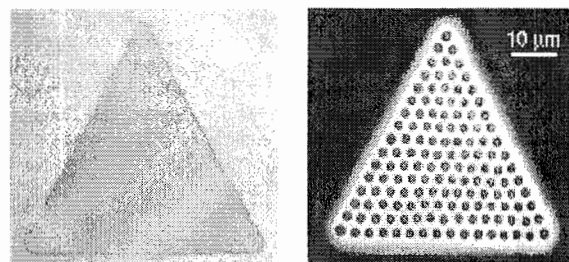
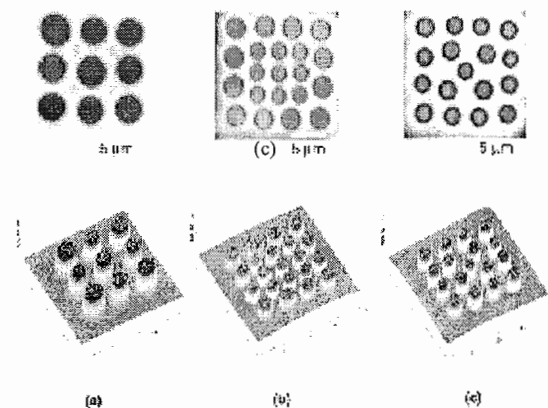


Figure 2. Optical micrographs of (a) a protruding triangle pattern on the mask and (b) the LISA of PMMA pillar array formed under the triangle pattern. (c) AFM of the pillar array. The size and shape of the pillar array is identical to the mask pattern, with the pillars at the edges of the array aligned to the edges of the mask pattern. The pillars have a close-packed hexagonal structure with a 3  $\mu\text{m}$  period, 1.6  $\mu\text{m}$  pillar diameter, and 530 nm height (equal to the initial



separation of the mask and substrate). The initial film thickness is 95 nm.

Figure 3. Optical and AFM images of the LISA of PMMA pillar arrays formed under protruding square patterns of a side of (a) 10  $\mu\text{m}$ , (b) 14  $\mu\text{m}$ , and (c) 14  $\mu\text{m}$ . The separation between the mask and the substrate in (a), (b), and (c) are 430 nm, 280 nm, and 360 nm, respectively

## References

- (1) S.Y. Chou and L. Zhuang, March Meeting of American Physical Society, March 1999, and J. Vac. Sci. and Technology, in press.