Newsletter WINTER 2012 Edition

Polymer Technology Center

TEXAS A&M UNIVERSITY

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Polymer Technology Center
Texas A&M University
MS 3123
College Station, TX 77843-3123
Website: http://ptc.tamu.edu

Hung-Jue Sue
Director
(979) 845-5024
hjsue@tamu.edu

Isabel Cantu
(979) 458-0918
icantu@tamu.edu

MARK YOUR CALENDAR FOR PTC'S UPCOMING CONFERENCES!

- April 19th — SCRATCH @ Texas A&M University
- April 19th-20th — PTIC @ Texas A&M University

High-Resolution Pattering of Polymer Semiconductors for Advanced Organic Electronics

Dr. Xing Cheng, Dept. of Electrical and Computer Engineering

Semiconducting polymers, also known as conjugated polymers, have attracted wide-spread attentions in recent years for their exciting applications in organic light-emitting diodes (OLEDs), organic thin-film transistors (OTFTs), organic photovoltaic cells (OPVs), and organic sensors. By combining attractive electronic and optical properties with common features of plastic materials such as flexibility, low cost, easy processing and robustness, conjugated polymers have the potential to enable futuristic large-area and flexible electric and optoelectronic systems.

The first and foremost task of using conjugated polymers in electronic devices is to pattern them into specific sizes and shapes. For advanced applications, high-resolution patterning of conjugated polymers is required. Modern microelectronic fabrication techniques such as photolithography and electron-beam lithography cannot be directly employed to pattern polymer semiconductors because they degrade or even destroy the conjugated polymers by breaking the chemical bonds. In recent years, many alternative patterning techniques have been developed. However, those printing techniques, such as inkjet, laser thermal, micro-contact, and screen printing, can only pattern structures of tens of microns and larger due to various reasons.

Xing Cheng's research aims at addressing the patterning challenge for polymer semiconductors and fabricating high-performance organic electronic devices for integrated applications. In the last decade nanoimprint lithography emerged as a new patterning technique that received huge attention due to its characteristics such as sub-10 nm resolution, high throughput and low cost. Nanoimprint is basically a mechanical forming technique and it only uses heat and pressure to pattern polymers, thus it is fully compatible with conjugated polymers. With its high-resolution and low-cost, nanoimprint is the ideal lithography technique to address many patterning challenges in polymer semiconductors.

Xing Cheng's group has developed several nanoimprint-based patterning schemes to fabricate high-resolution structures in polymer semiconductors. By using transfer printing and solvent development, isolated polymer semiconductor patterns can be achieved (Fig.1). Patterning isolated semiconductor structures is an indispensable step towards large-scale integration of organic electronics. Currently deep sub-micron polymer semiconductor structures can be achieved by those techniques.

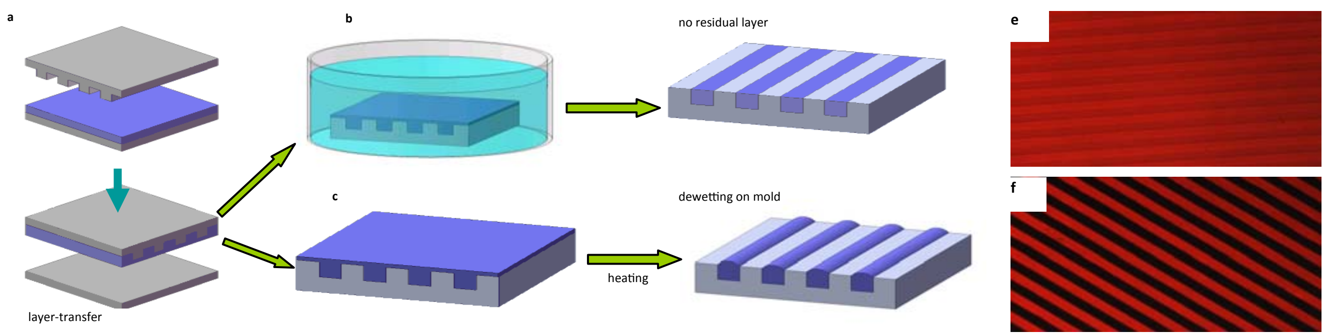


Fig. 1. Schematics of (a) layer-transfer method to place polymer film on a mold, (b) The solvent developing method and (c) the dewetting method to nondestructively remove residual layers. (e) and (f) are fluorescence microscope images of patterned MEH-PPV with (e) and without (f) residual layers. The line width is 5 µm.

Another key aspect in increasing OTFT's cutoff frequency is to reduce parasitic source/drain and gate overlap capacitance introduced by the fabrication process. The standard technique to eliminate this capacitance is to devise a self-aligned fabrication process to pattern the source/drain and gate electrodes. Cheng's group has recently developed a dual-layer nanoimprint scheme that enables the patterning of conjugated polymer and its gate dielectric in one step (Figs. 2 and 3). Subsequent uniform metal evaporation will easily produce the desired self-aligned OTFT device structure.

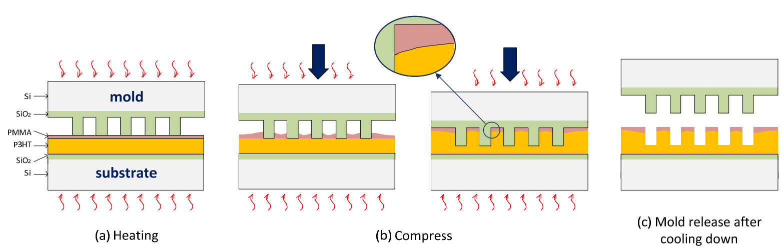


Fig.2 Schematics of dual-layer thermal nanoimprint lithography process for double-layer patterning.

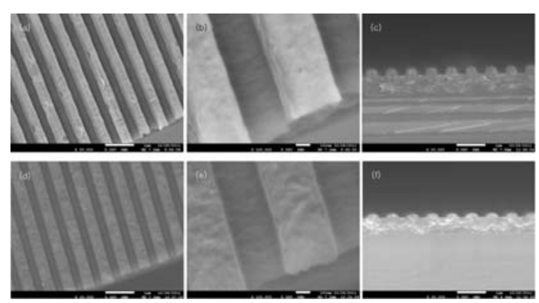


Fig.3 SEM images of double-layer patterning: PMMA and P3HT pattern (a, b: perspective view and c: cross-sectional view) and P3HT pattern after removing PMMA by dipping into solvent (d, e: perspective view and f: cross-section view)

Conjugated polymers are usually semicrystalline polymers with rigid polymer chain backbones. During nanoimprinting, polymer chains are stressed and stretched. Anisotropy of material properties, such as refractive index, optical absorption and carrier transport, appears in patterned polymer structures. Figure 2 schematically shows the chain orientation process and the resultant optical birefringence in polymer microstructures. Another impact of chain orientation after nanoimprint is the enhanced stability of polymer micro- and nanostructures due to increased inter-chain attraction. This characteristic is drastically different from amorphous polymers with flexible backbone in which stretched chains are thermodynamically instable. The stability of semicrystalline polymer micro- and nanostructures enables step-and-repeat thermal nanoimprint for patterning large-area substrate using a small template. Such patterning scheme also greatly improves the throughput of thermal nanoimprint process, which paves the way for future large-scale commercial manufacturing of organic devices with nanoimprint.

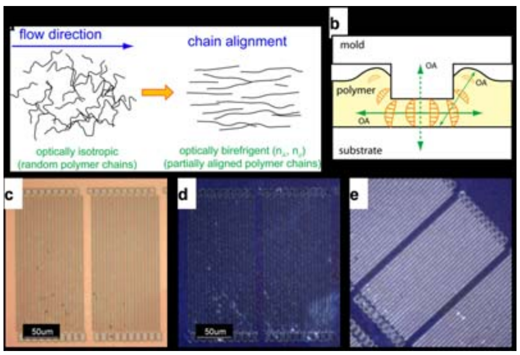


Fig.2. (a) A schematic of polymer chain extension and orientation caused by polymer flow during nanoimprint; (b) A schematic of polymer melt flow pattern during nanoimprint and the resultant optical axes of birefringence; (c) Optical microscope image of nanoimprinted PVDF; (d) Same PVDF structure viewed in polarizing microscope with crossed polarizers; (e) Sample is rotated by 45o with respect to (d).Optical birefringence is clearly seen in nanoimprinted areas.

Nanoimprint-based patterning techniques are expected to enable nanoscale self-aligned polymer thin-film transistors with cut-off frequencies over hundreds of MHz. Those high-speed and high-frequency OTFTs are expected to achieve ubiquitous sensing and computing using plastic circuits. Nanoimprint is also considered an ideal technique for patterning high-resolution OLEDs for advanced flat-panel displays with very high pixel density. Due to its sub-10 nm resolution, nanoimprint has the capability to fabricate nanoscale-ordered bulk heterojunction structures for advanced OPVs. Moreover, the nanoimprint-based fabrication processes are low cost and compatible with step-and-repeat and roll-to-roll fabrication for large-scale and high-throughput production of organic electronic devices and integrated systems. For those reasons nanoimprint is expected to play a major role in future organic electronic devices and integrated systems.

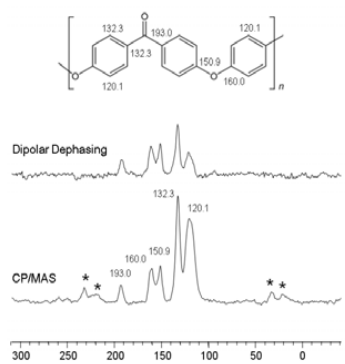
Characterization of PEEK (polyetheretherketone) Polymers by Solid-State NMR Spectroscopy

Dr. Janet Bluemel, Department of Chemistry

Poly(aryletherketone) or PAEK polymers are of great interest for extreme service environments in the oil and gas industry. These materials (PEEK, PEK, PEKEKK etc.) are often used in environments of high pressures and temperatures, while being exposed to steam, water-based drilling fluids or brines, or other corrosive chemical cocktails that are highly acidic, caustic, or oxidizing. The longevity of PAEK-based devices or components used in such environments is of paramount importance from both a cost/benefit perspective, as well as a safety perspective when such materials are used in critical service devices. An understanding of the mechanisms of degradation and deleterious interaction with the chemical environment that these materials are exposed to is critical in developing more robust and longer lived polymer structures. To enable such understanding, molecular level chemical reaction mechanisms must be understood.

Within the APPEAL (Advancing Performance Polymers for Energy AppLications) Consortium (Co-directors Dr. Tim Bremner, Hoerbiger, and Dr. Hung-Jue Sue, MEEN) my graduate student Johannes Guenther uses solid-state NMR spectroscopy as a powerful technique to study polymers on a molecular level.

The figure (below) shows a representative PEEK 13C CP/MAS spectrum. All signals can be assigned, for example, by using dipolar dephasing techniques that reduce the signal intensities of non-quaternary carbons.



Herewith, different PAEK brands can be distinguished, and the composition of blends can be determined.

Using 13C T1 relaxation time measurements, the ratio of mobile amorphous versus rigid (amorphous and crystalline) domains can be determined. These results were presented at the Smithers Conference in Houston in October 2011. Additionally, the miscibility of the components of polymer blends, such as PEKK-PBI (PBI: polybenzimidazole), can be investigated by using the 13C T1 relaxation times of strategically chosen signals.

Solid-state NMR also allows one to identify potential structural changes in pure polymers or blends after they have been exposed to the above-mentioned harsh conditions. For example, PEKK is not altered by exposition to water at ambient temperature, but after being treated with water steam at 148 °C, it shows major changes in the signal region corresponding to the carbons neighboring the keto groups. PBI shows minor changes when being treated with water at room temperature, but does not change any more upon steam treatment at 148 °C. Interestingly, the PEKK-PBI blend becomes more rigid upon exposure to water, and this effect is fully reversible when drying the material.

TAMU NEWS

TAMU Vs. Northwestern Wildcats in the Meineke Car Care Bowl 2011

TAMU went to Houston's Reliant Stadium to play against the Northwestern Wildcats on December 31st, 2011. This was TAMU's 33rd time in a bowl game. The final score was TAMU 33—Northwestern 22.

WHOOP!

Texas A&M is ranked No. 1 in Texas by business leaders worldwide, says The New York Times.

Read more about it at:
http://tamutimes.tamu.edu/2011/12/06/texas-am-fares-well-in-assessments-by-ceos-of-major-firms-2/

Kevin Sumlin Named Head Football Coach

Sumlin led the Houston Cougars to a school-record 12 wins in 2011 and the program's highest finish in the Bowl Championship Series rankings. He was recently named the 2011 Region 5 Coach of the Year by the American Football Coaches Association and is a finalist for the National Coach of the Year honors as well. The Cougars led the nation in total offense, passing offense and scoring offense this season, marking the second time in four years to accomplish that feat under Sumlin's direction.

"I am very excited about the opportunity to serve as the head football coach at Texas A&M University," Sumlin said. "Having coached there before, I understand the culture and embrace the commitment by the 12th Man regarding Aggie football. Aggieland is a special place and I look forward to working with the young men in the football program and recruiting the type of players we need to be successful in the SEC."

FORMER TEXAS A&M QUARTERBACK BUCKY RICHARDSON: "I am really excited that Kevin Sumlin is our next head coach. Kevin's energy and youth will give us a great lift as we enter a new era in the SEC. He already has great Texas ties, and once our Aggie fans get to know Kevin, they are really going to love him. He is a winner."

PTC NEWS

The PTIC Student Poster Session received 16 entrees for the competition. The recipients to the competition are listed below with their respective poster titles. PTC would like to congratulate these students and all the students that participated in this event. For those that did not place, there will be another opportunity in the Spring.

Polymer Technology Industrial Consortium (PTIC)
Student Poster Session October 27-28, 2011

Place	Name	Poster Title
1st	Kevin White	*"Characterization and differentiation of poly(aryl ether ketones)"*
2nd	Philip Imbesi	*"Next Generation Anti-biofouling Coatings: Improving processing and longevity through rapid, thiol-ene and thermally-reversible, Diels-Alder crosslinks"*
3rd	Melissa Hawkins	*"Amphiphilic PEG-Silanes: Enhancing Clot-Resistance of Silicones"*

The Polymer Technology Industrial Consortium PTIC held its semi-annual meeting on October 27th-28th, 2011 at College Station, TX with the following companies in attendance:

●Avery Dennison ●ExxonMobil ●Flint Hills Resources ●Hoerbiger Corporation of America, Inc. ●KANEKA ●KURARAY ●Greyhill Advisors ●Petroleum Geo-Services ●Quadrant Engineering Plastic Products ●The Research Valley Partnership, Inc. ●Total American Services, Inc. ●Toyo Ink America, LLC ● Washington Penn

The Advancing Performance Polymers in Energy AppLications (APPEAL) also met on November 3, 2011. Companies in attendance were:

●Baker Hughes ●Halliburton ●Hoerbiger

PTC Faculty

Name	E-mail Address	Office #
Perla Balbuena	Balbuena@tamu.edu	979-845-3375
Dave Bergbreiter	bergbreiter@tamu.edu	979-845-3437
Janet Bluemel	bluemel@tamu.edu	979-845-7749
Tahir Cagin	cagin@che.tamu.edu	979-862-1449
Elena Castell-Perez	ecastell@tamu.edu	979-862-7645
Xing Cheng	chengx@ece.tamu.edu	979-845-5130
Zheng D Cheng	zcheng@tamu.edu	979-845-3413
Abraham Clearfield	a-clearfield@tamu.edu	979-845-2936
Terry Creasy	tcreasy@tamu.edu	979-458-0118
Donald Darensbourg	d-darensbourg@tamu.edu	979-845-5417
Jaime Grunlan	jgrunlan@tamu.edu	979-845-3027
Melissa A. Grunlan	mgrunlan@tamu.edu	979-845-2406
Wayne Hung	hung@tamu.edu	979-845-4989
Helen Liang	hliang@tamu.edu	979-862-2623
Anastasia Muliana	amuliana@tamu.edu	979-458-3579
Ozden Ochoa	oochoa@tamu.edu	979-845-2022
K.R. Rajagopal	krajagopal@tamu.edu	979-862-4552
J.N. Reddy	jnreddy@tamu.edu	979-862-2417
Cris Schwartz	cschwartz@tamu.edu	979-845-9591
Dan Shantz	shantz@tamu.edu	979-845-3492
Hung-Jue Sue	hjsue@tamu.edu	979-845-5024
Steve Suh	ssuh@tamu.edu	979-845-1417
Jyhwen Wang	jwang@tamu.edu	979-845-4903
John Whitcomb	whit@aero.tamu.edu	979-845-4006
Karen L. Wooley	wooley@tamu.edu	979-845-4077
Nicole Zacharia	nzacharia@tamu.edu	979-845-2204

Here's Whats Happening at the TAMU SPE Student Chapter

Howdy! The Texas A&M University Society of Plastics Engineers (TAMU SPE) is a student organization dedicated to promoting awareness of polymer science and engineering with monthly technical meetings, interaction with industry professionals through consortia and plant visits, and participation in national conferences. The monthly seminar series is our initiative to provide SPE members and the student body with technical and practical knowledge related to the polymer industry. The experience has enabled students to gain an understanding on industrial processes and concerns, to be aware of opportunities regarding polymer-related careers for scientists and engineers, and to create networking opportunities between students, industry leaders, and faculty.

For our September seminar, we were fortunate enough to have Dr. James Stevens of the Core Research and Development Department of the Dow Chemical Company present his research on high throughput experimentation in polyolefins research. In October, Dr. Tim Bremner, the Vice-President of Advanced Engineering and Materials Technology for Hoerbiger Corporation of America, presented a talk on challenges in the design and utilization of poly(aryl ether ketones) in oil-field applications. Our November speaker was Dr. Kishori Deshpande of Dow Chemical Company, and she shared with the group her research on sustainability efforts at Dow through process intensification. Thanks in no small part to the exceptional group of speakers, we have had excellent participation from undergraduate and graduate students, and even a few faculty members, drawn from a variety of disciplines.

In addition to the great set of speakers for our monthly seminar, we have taken part in a number of smaller events throughout the semester. On October 10, we toured the BASF polyurethanes plant in Houston, TX along with the SPE South Texas Chapter. It was great getting to meet and talk with members of the industry and we are extremely indebted for the experience. Everyone in the Texas A&M group was excited about not only gaining a new appreciation of polyurethane technology (and learning about the differences in MDI and TDI!), but also getting to interact a chance to interact with industry members at the BBQ dinner afterward. We are very grateful to the SPE South Texas chapter for including us with their tour, and particularly to Suzanne Diecks for organizing the event.

The student chapter also participated in the Chemistry Open House, an annual free events sponsored by the American Chemical Society and various departments at Texas A&M. We engaged in activities throughout the day and taught kids to make bouncing balls using only glue, borax, and corn starch. We also took part in the bi-annual PTIC Student Poster Session at the end of October.

We look forward to continuing the recruitment effort next semester and constantly improving our organization. Next semester we will have several members give oral presentations, poster presentations, and volunteer at the 2012 International Polyolefins Conference in Houston, TX. We will also have a plant visit to the Huntsman Advanced Technology Center in the Woodlands, TX. Please contact us if YOU are interested in participating in our monthly seminar series or hosting a plant visit. If you have any questions or suggestions, contact us at spe@plastics.tamu.edu. Be sure and visit our newly updated website http://plastics.tamu.edu for chapter news, seminar information, events, member information, research highlights, and chapter photos.

Thanks and gig'em

Kevin L. White

SPE President, Texas A&M Student Chapter


BASF Plant Tour in May 2011 (Freeport, TX)


Blackwell Plastics Tour in May 2011 (Houston, TX)


Chemistry Open House in October 2011 (College Station, TX)

BASF Polyurethanes Plant Tour in October 2011 (Houston, TX)

Halloween Party with SPE members and family


PTIC Meeting in October 2011

Polymer Specialty Certificate Updates	
Students that have applied for Certificate	25
Students that have received the Polymer Specialty Certificate	16
For more information: http://ptc.tamu.edu/certificate.html	

TAMU/SPE Student Chapter

To find out more about the TAMU/SPE Student Chapter please contact Kevin White at: whitek@tamu.edu

Kevin White, SPE Student Chapter President

Visit the SPE Student Chapter website at: http://plastics.tamu.edu/

PTC Newsletter prepared by: Isabel Cantu
Edited by: Garrett Nowak & Kevin White