Phenylsilanes to Polymers

Leslie E. Smith
1966 - 70

Eisch Organometallic Symposium
SUNY - Binghamton
Radical Anions of Phenylsilanes

- Radical anions were known to be intermediates in important synthetic reactions; their electron density distributions determine probable products.

- The electronic structure of a number of hydrocarbon anion radicals had been measured but those of organometallics were just being explored.

- Of particular interest was the effect of bridging silyl groups where electron delocalization would depend on $\pi$-$\pi$ overlap.
Results and Conclusions

<table>
<thead>
<tr>
<th>Organosilane</th>
<th>$a_H$ (nH), (G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhSiMe$_3$ (I)</td>
<td>$a_p$ 8.10 (H)</td>
</tr>
<tr>
<td>Ph$_2$SiMe$_2$ (II)$^a$</td>
<td>$a_p$ 4.21 (2H)</td>
</tr>
<tr>
<td>Ph$_3$SiMe (III)$^a$</td>
<td>$a_p$ 2.80 (3H)</td>
</tr>
<tr>
<td>Ph$_3$SiSiPh$_3$ (V)</td>
<td>$a_p$ 4.20 (2H)</td>
</tr>
<tr>
<td>Ph$_3$SiCl (VI)</td>
<td>Spectrum of I, then of III</td>
</tr>
<tr>
<td>Ph$_3$Si-c-C$_3$H$_5$ (VII)</td>
<td>$a_p$ 2.80 (3H)</td>
</tr>
<tr>
<td>Ph$_3$SiCH=CH$_2$ (IX)$^a$</td>
<td>$a_H$ 5.02 (2H)</td>
</tr>
<tr>
<td>Ph$_3$SiCH=CHMe (X)$^a$</td>
<td>$a_H$ 5.0 (H)</td>
</tr>
<tr>
<td>Ph$_2$Si(CH=CH$_2$)$_2$ (XI)$^b$</td>
<td>$a_p$ 7.10 (H)</td>
</tr>
<tr>
<td>Ph$_3$SiC=CMe (XII)</td>
<td>$a_H$ 9.52 (3H)</td>
</tr>
</tbody>
</table>

$^a$ In DME containing 2% of HMPT. $^b$ Only in highly dilute (10$^{-5}$ M) DME. $^c$ Not observed.
Results and Conclusions

Splittings in accord with Hückel spin densities; Significant spin density is on silicon

Phenyl rings not equivalent in DME; HMPT restores equivalency
NIST mission:
To promote U.S. innovation and industrial competitiveness by advancing measurement science, standards, and technology

NIST assets include:

~ 2,800 employees
~ 2600 associates and facilities users
~ 1,600 field staff in partner organizations

Laboratories - Gaithersburg, MD & Boulder, CO
Baldrige National Quality Program
Manufacturing Extension Partnership
Technology Innovation Program
New Framers of the Declaration of Independence Act to Save It in Parchment

By WARREN E. LEARY

WASHINGTON, Feb. 6 — The framers of the Declaration of Independence, in keeping with the practice of the day, wrote the formal document on parchment rather than paper so that it would last longer. But surely few thought that the text they wrote would survive for more than two centuries.

Today, another group of framers confronts the precious documents. They are scientists, engineers, designers and archivists, and they will soon begin constructing new encasements and frames to protect the texts on which the nation is based.

This week, the National Archives and Records Administration is expected to unveil the design of the new enclosures, airtight cells of titanium and aluminum that will hold the documents behind tempered glass in an atmosphere of inert argon gas. The encasements, resembling large, deep picture frames, will replace similar enclosures that were made almost 50 years ago and appear to be prematurely deteriorating.

The integrity of the protective cases is significant because they hold the foundation documents of the country, known as the Charters of Freedom. These are the original parchment sheets on which are written the Declaration of Independence, the United States Constitution and its first 10 amendments, the Bill of Rights.

The Charters, as they are called, have made the National Archives

Leslie Smith, materials designer

Dick Rhorer, constructor

IN DETAIL

Preserving the Nation’s Heritage

The National Institute of Standards and Technology has commissioned a new design for the cases that display the nation’s most revered documents.

more closely matches conditions outside the cases if they have to be opened, he said. This helps prevent shock to the document under these circumstances.

The institute’s engineers, led by Richard Rhorer and Christopher Evans, have built a manufacturing model of the casement for testing in the spring before making a prototype.

Engineers are also sending samples of titanium, which has a gray finish, to metal-coating companies to see if the tough metal can be given the bronze color desired for the frame. Mr. Rhorer said it was unclear whether anodization, an electrolytic process that can put a colored, oxide film on metal, will be able to produce the color and tone that is desired. “This shows how involved this is,” he said. “We normally be concerned if the metal is ‘warm’ enough

NY Times, Sunday, February 7, 1999
Films and Coatings
- Wetting
- Optical properties
- Dielectric properties
- Crystallization
- Mechanical Properties

Membranes & Barrier Films
- Adsorption and time release
- Selective permeation

Lubricants and Adhesives
- Adhesion and Tribology

Polymer Blends
- Thermodynamics and kinetics
- Phase separation morphology
- Composition, temperature, processing
- Additives (fillers, CO₂, process aids)

Block Copolymers
- Surface ordering
- Quantization effects
- Surface energy
- Temperature
- Microstructure

Millifluidics
- Mixing and Stability
- Interfacial Tension
- Complex Rheology

Biofunctional Materials
- Biocompatibility
- Inflammatory response
- Surface topography
- Protein adsorption
- Cell adhesion
- Patterned cell growth
Measurement of polymer libraries

Library Preparation
Thickess ($h$) Gradient Via Flow Coating

Polymer Solution + Temperature ($T$) Gradient Heating Stage

Automated Data Acquisition
Digitized Output

Robotic Translation Stage

Informatics
- Divide Sample into Virtual Array
- Optimize Cell Size
- Process and Analyze Images
- Map Phase Behavior

Time
Polystyrene Film Dewetting Thickness-Temperature Library
Symmetric block copolymers form lamellae parallel to the substrate

For certain thicknesses, complete lamellae form and the surface is smooth

Otherwise incomplete lamellae form with holes or islands
Thickness Gradient Morphology

- Optical micrograph of 25k PS-b-PMMA annealed 6 h

Surface Energy

- Substrate energy controls which block goes to surface

Silane self-assembled monolayer on Si surface exposed to UV gradient to produce surface energy gradient
Thickness vs. Surface Energy Map

Smith, Sehgal, Douglas, Karim, Amis
Macromol. Rapid Comm. 2003, 24, 131

- Substrate surface energy gradient:
  - $\approx 52 \text{ mJ/m}^2$
  - $\approx 32 \text{ mJ/m}^2$

- Surface patterns:
  - $h \sim 2.0 L_0$
  - $h \sim 2.5 L_0$

- Surface patterns:
  - $\approx 60 \text{ nm}$
  - $\approx 80 \text{ nm}$
Acknowledgements

Carson Meredith, Georgia Tech

Alamgir Karim, University of Akron

Eric Amis, United Technologies Res Center

Michael Fasolka, NIST

Chris Stafford, NIST

Naval Air Systems Command
Office of Naval Research
National Heart, Lung, and Blood Institute, NIH
Bureau of Foods, FDA
National Archives and Records Administration

Prof. John Eisch, SUNY Binghamton