IWetting properties of polysiloxane networks modified in situ with fluoroalkyl-substituted linear and POSS cage structures (Briefing Charts)

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Distribution A: Approved for Public Release; Distribution Unlimited.

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Briefing Charts

Unclassified

SAR

38
Wetting properties of polysiloxane networks modified in situ with fluoroalkyl-substituted linear and POSS cage structures

Raymond Campos, Sean M. Ramirez, and Joseph M. Mabry

August 17, 2015

ACS National Conference
Paradigms for low energy surfaces

**Crystalline surfaces**
- Immobilized chemical moieties with low polarizability (e.g. fluorine)
  \[ CF > CF_2 > CF_3 > SF_5 \]
- High crystallinity to prevent surface reorganization when in contact with liquids, biofouling sources, etc.

  Extreme liquid repellency when combined with surface roughness and re-entrant geometry

**“liquid-like” surfaces**
- Low energy barriers between metastable states
- Metal oxide surfaces and liquid-infused materials (e.g. SLIPS)

  Fluorine content not required to repel low surface tension liquids?

  Low CA hysteresis despite lower contact angle values
Surface modification of PDMS/siloxane networks

- Primarily oxide formation via O$_2$ plasma, UV/ozone, etc. and subsequent functionalization

- Functional PDMS (e.g. residual vinyl groups in network)

- Functional silsesquioxane networks
Properties of Fluorodecyl$_8$T$_8$ POSS

- Extremely low surface energy
- Surface migration in polymers
- Surface responsive behavior

Enabling....

Superomniphobic fabrics via dip-coating
Choi et al., Ang. Chem., 2009

Transparent Omniphobicity
Golovin et al., Ang. Chem., 2013

Extreme Omniphobicity
Pan et al., JACS., 2012

Oil/water emulsion gravity separation
Kota et al., JACS., 2012

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Surface Energy of Fluorodecyl₈T₈ POSS

fluorodecyl₈T₈ POSS  5.5 mN/m (Zisman analysis)*
8.8 – 10.2 mN/m (Girafalco-Good analysis)*

Zisman analysis
(only alkane probing liquids used)


Distribution A: Approved for public release; distribution is unlimited.
<table>
<thead>
<tr>
<th>Surface</th>
<th>Energy Range (mN/m)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>fluorodecyl₈T₈ POSS</td>
<td>5.5 (Zisman analysis)</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>8.8 - 10.2 (Girafalco-Good analysis)</td>
<td>*</td>
</tr>
<tr>
<td>Polytetrafluoroethylene</td>
<td>18 - 20 (Zisman analysis)</td>
<td>*</td>
</tr>
<tr>
<td>CF₃-(CF₂)ₙ-CF₃</td>
<td></td>
<td>*</td>
</tr>
<tr>
<td>CF₃ monolayer</td>
<td>6.7 (Zisman analysis)</td>
<td>*</td>
</tr>
</tbody>
</table>


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Fluorodecyl$_8$T$_8$ POSS

$R_f = -(\text{CH}_2)_2(\text{CF}_2)_8\text{F}$

Image displaying the helical conformation of fluorodecyl substituents in the solid state packing of fluorodecyl$_8$T$_8$ POSS

3 x 2 array of fluorodecyl8T8 POSS cages displaying a lamella-type packing

Distribution A: Approved for public release; distribution is unlimited.
a.)

+ 90° turn

-90° turn

b.)
c.)

Distribution A: Approved for public release; distribution is unlimited.
Helical crystal packing of fluoroalkyl-substituted urea
Helical crystal packing of fluoroalkyl-substituted urea
Functional Fluorodecyl POSS Compounds Enabled by Incompletely Condensed Intermediate

Scheme 1. Synthesis of Incompletely Condensed Fluoroalkyl Silsesquioxane$^a$

1 ($R_f = \text{CH}_2\text{CH}_2(\text{CF}_2)_7\text{CF}_3$) $\xleftrightarrow{b}$ 1a $\xrightarrow{c}$ 1b $\xrightarrow{d}$ 2 (53%)

$^a$ Conditions: All reactions were performed in C$_6$F$_6$ at 25 °C. $^b$CF$_3$SO$_2$H, 75 min; $^c$NBu$_4$HSO$_4$, 30 min; $^d$(CF$_3$)$_2$CH$_2$OH/H$_2$O (10:1), 12 h.


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29Si NMR Spectra of fluorodecyl POSS disilanol Intermediates and Product


Distribution A: Approved for public release; distribution is unlimited.
ORTEP representations of Fluorodecyl POSS Disilanol crystal structure


\( R_f = -(\text{CH}_2)_2(\text{CF}_2)_8\text{F} \)
F-POSS cage dimer side & top views

Side view

A view from the top

Clockwise (P)

Counter-clockwise (M)

Counter-clockwise (M)

Clockwise (P)

Distribution A: Approved for public release; distribution is unlimited.
F-POSS cage dimer (fluoroalkyl side chains shown as golden spheres): 2 intermolecular OH...O - bonds that hold dimer structure together.
F-POSS cage array: 3 dimers (6 cages) – top view
F-POSS cage “zigzag” array (16 cages) – top view

Distribution A: Approved for public release; distribution is unlimited.
Functional Fluorodecyl POSS Synthesis from Incompletely Condensed Fluorodecyl POSS


Distribution A: Approved for public release; distribution is unlimited.
Fluorodecyl₈T₈D₁(methyl, vinyl) POSS

Theoretical $[M \cdot Ag]^+$ = 4185.71 Da

Distribution A: Approved for public release; distribution is unlimited.
F-POSS Grafting to PDMS via Hydrosilylation

1, 5, 10, 20, 44 wt%
Vinyl: silane, 1:32, 1:8, 1:4, 1:2, 1:1

Distribution A: Approved for public release; distribution is unlimited.
Complete Conversion at 10 wt% F-POSS: 29Si NMR Spectra

Distribution A: Approved for public release; distribution is unlimited.
Incomplete Conversion at $\geq 20$ wt% F-POSS:

$^1$H NMR Spectra

44 wt% (1:1 vinyl:silane)

Distribution A: Approved for public release; distribution is unlimited.
F-POSS PDMS Amphiphile Aggregation

Chemical reaction:

\[
R\text{Si}(O\text{Si})_n\text{Si}H \xrightarrow{\text{Pt}(0)} \text{Si}(O\text{Si})_n\text{Si}R
\]

Crude rxn. mix. 4:1 C₆F₆:hexanes

44 wt% (2 mol eq.)

Distribution A: Approved for public release; distribution is unlimited.
Surface Wetting of Fluorodecyl POSS-PDMS Amphiphiles

Pure fluorodecyl₈T₈ POSS: Water $\theta_{\text{adv}} / \theta_{\text{rec}} = 124^° / 116^°$
Hexadecane $\theta_{\text{adv}} / \theta_{\text{rec}} = 80^° / 61^°$

Distribution A: Approved for public release; distribution is unlimited.
F-POSS PDMS Amphiphile Aggregation: Dynamic Light Scattering

PDMS (1000 cSt)
0.001 M, 25 C

CDCl3
0.001 M, 25 C

AK225
0.001 M, 25 C

57 ± 16 nm
63 ± 20 nm
197 ± 67 nm

7 ± 2 nm
18 ± 6 nm
251 ± 67 nm

Distribution A: Approved for public release; distribution is unlimited.
Thermal Stability of FPOSS-PDMS Micelles

In fluorinated matrix

PDMS

PDMS-TFP

5 wt% FPOSS-PDMS

Heat Flow (W/g)

Exo Up

Temperature (°C)

Heat Flow (W/g)

Diameter (nm)

PDMS

PDMS-TFP

Temp (°C)

25 35 45 55 65

0 20 40 60 80 100

Distribution A: Approved for public release; distribution is unlimited.
Surface Wetting of Fluorodecyl POSS-Enchained PDMS Elastomers

$R_f = -(CH_2)_2(CF_2)_8F$

Sylgard 184 (10:1 base:curative) + $70^\circ C/4$ hrs, $45^\circ C/17$ hrs $\rightarrow$ F-POSS enchained PDMS Elastomer (Black diamonds in figures)

Pure fluorodecyl$_8$T$_8$ POSS: Water $\theta_{adv}/\theta_{rec} = 124^\circ/116^\circ$
Hexadecane$\theta_{adv}/\theta_{rec} = 80^\circ/61^\circ$

Distribution A: Approved for public release; distribution is unlimited.
Surface modification of highly crosslinked siloxane networks

\[ \text{ethanol } \theta_{\text{stat}}/\theta_{\text{adv}}/\theta_{\text{rec}} = 8.9 \]
\[ 22.88 \pm 2.46 \]
\[ 0 \]

isopropanol completely wets and spreads

<table>
<thead>
<tr>
<th></th>
<th>( \theta_{\text{adv}}/ \theta_{\text{rec}} (^\circ) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>99.5 ± 0.6 / 93.2 ± 0.5</td>
</tr>
<tr>
<td>Hexadecane</td>
<td>33.6 ± 0.3 / 28.9 ± 0.3</td>
</tr>
<tr>
<td>Heptane</td>
<td>&lt;5 / 0</td>
</tr>
<tr>
<td>Methanol</td>
<td>29.3 ± 0.5 / 18.3 ± 2.4</td>
</tr>
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Surface modification of highly crosslinked siloxane networks

\[ \text{highly cross-linked siloxane network} \]

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\[ \theta_{\text{adv}} / \theta_{\text{rec}} (°) \]

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<th>Methanol</th>
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<tbody>
<tr>
<td></td>
<td>99.5 ± 0.6</td>
<td>33.6 ± 0.3</td>
<td>&lt;5</td>
<td>29.3 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>93.2 ± 0.5</td>
<td>28.9 ± 0.3</td>
<td>0</td>
<td>18.3 ± 2.4</td>
</tr>
</tbody>
</table>

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Surface modification of highly crosslinked siloxane networks

\[
\begin{align*}
\text{H-Si-O-Si-H} & + 4 \quad \text{Si-O-Si} & \rightarrow & \text{highly cross-linked siloxane network w/ covalently bound FPOSS surface} \\
\quad & (0.63 \text{ wt% fluorine}) & \quad & R_f = -(\text{CH}_2)_2(\text{CF}_2)_8\text{F}
\end{align*}
\]

\[
\begin{align*}
& \text{isopropanol } \Theta_{\text{stat}}/ \Theta_{\text{adv}}/ \Theta_{\text{rec}} = 54.35 \pm 4.41 \\
& \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \text{70.94} \pm 1.05 \\
& \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \text{40.5} \pm 0.86 \\
& \text{ethanol } \Theta_{\text{stat}}/ \Theta_{\text{adv}}/ \Theta_{\text{rec}} = 60.588 \pm 7.62 \\
& \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \text{73.97} \pm 1.0075 \\
& \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \text{41.4} \pm 1.2725 \\
\end{align*}
\]

\[
\begin{align*}
& \text{Water } \Theta_{\text{adv}}/ \Theta_{\text{rec}} (^\circ) = 116.5 \pm 0.3 / 102 \pm 1.1 \\
& \text{Hexadecane } 76.3 \pm 0.5 / 62 \pm 1.0 \\
& \text{Heptane } 56.1 \pm 0.9 / 39.2 \pm 1.2 \\
& \text{methanol } 75.2 \pm 0.9 / 49.9 \pm 1.5 \\
\end{align*}
\]
Surface modification of highly crosslinked siloxane networks

\[ \text{Si} - \text{O} - \text{Si} + 4 \ \text{Si} - \text{O} - \text{Si} \xrightarrow{\text{Pt}(0)} \text{Si} - \text{O} - \text{Si} \]

+ 1 wt% Rf = \( -(\text{CH}_2)_2(\text{CF}_2)_8\text{F} \)

\[ \theta_{\text{adv}} / \theta_{\text{rec}} (°) \]

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<tr>
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<th>Methanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>116.5 ± 0.3</td>
<td>76.3 ± 0.5</td>
<td>56.1 ± 0.9</td>
<td>75.2 ± 0.9</td>
</tr>
<tr>
<td>Error</td>
<td>102 ± 1.1</td>
<td>62 ± 1.0</td>
<td>39.2 ± 1.2</td>
<td>49.9 ± 1.5</td>
</tr>
</tbody>
</table>

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What about “liquid-like” surfaces and post-cure surface modification?
Post-cure surface modification of highly crosslinked siloxane networks with silane-term oligo(dimethylsiloxane)

\[
\begin{align*}
\text{Si} & \quad \text{O} & \quad \text{Si} & \quad \text{H} \\
\text{H} & \quad \text{Si} & \quad \text{O} & \quad \text{Si} & \quad \text{H} \\
\end{align*}
\]

+ 4 \[\begin{array}{c}
\text{Si} \\
\hline
\text{O} \\
\text{Si} \\
\hline
\text{Si} \\
\end{array}\] \[\begin{array}{c}
\text{Si} \\
\hline
\text{O} \\
\text{Si} \\
\hline
\text{Si} \\
\end{array}\]

\[\text{Pt}(0)\]

25-150°C

highly cross-linked siloxane network

“Pt(0)”

80-150°C

17 hrs.

Silane-terminated PDMS

50 Cst.

3000-5000 Da

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Post-cure surface modification of highly crosslinked siloxane networks with silane-term oligo(dimethylsiloxyane)