Synthesis and Characterization of Fluoropropyl POSS

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AFRL/PRSP
**Title:** Synthesis and characterization of Fluoropropyl POSS

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**Performing Organization:** Air Force Research Laboratory (AFMC), AFRL/PRSM, 10 E. Saturn Blvd., Edwards AFB, CA, 93524-7680

**Distribution:** Approved for public release; distribution unlimited

**Subject Terms:**

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Outline

- POSS
- FluoroPOSS Synthesis
- Fluoropropyl POSS Synthesis
- Conclusion
Hybrid inorganic/organic polymers

Goal: Develop High Performance Polymers that REDEFINE material properties

- Hybrid plastics bridge the differences between ceramics and polymers

Distribution A: Approved for public release; distribution unlimited
Anatomy of a POSS nanostructure

Thermally and chemically robust hybrid (organic-inorganic) framework.

Precise three-dimensional structure for molecular level reinforcement of polymer segments and coils.

Nanoscopic in size with an Si-Si distance of 0.5 nm and a R-R distance of 1.5 nm.

May possess one or more functional groups suitable for polymerization or grafting.

Nonreactive organic (R) groups for solubilization and compatibilization.

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Importance of R groups: Affect compatibility with polymer matrix

50 Wt % POSS Blends in 2 Million MW PS

Domain Formation

Partial Compatibility

Complete Compatibility


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Integrated High Payoff Rocket Propulsion Technology (IHPRPT) Program
• National program focused by OSD/DDR&E/AT and coordinated with AF, NASA, Navy, Army, and industry.
• Goal-oriented technology development program for rocket propulsion.
  • Double the performance of rocket propulsion systems over current state of the art.
  • Decrease the cost of access to space for commercial and military sectors.

• Fluoropolymers are used in many seal applications in liquid rocket engines
  • Polychlorotrifluoroethylene (PCTFE)
  • Fluorinated Ethylene/Propylene (FEP)
• Fluoropolymer research is designed to:
  • Improve Isp
  • Improve Thrust to Weight ratio
  • Reduce Support Costs
  • Lengthen Mean Time Between Removal
Mechanical Problems

• During operation, wear ring seals preventing propellant flow from bypassing the impeller blades in the SSME turbopump warp, causing an estimated 1.5 sec loss of delivered $I_{sp}$.

\[ 1.5 \text{ sec } I_{sp} \times 3 \text{ SSMEs } \times 1000 \text{ lb payload/sec } I_{sp} \times 8,000/\text{lb payload} = \$36,000,000 \text{ per launch} \]

• Creep (cold flow of materials under load) causes the deformation of fluoropolymer seals in LREs, limiting their functional use time. (Mean Time Between Removal)

Surface Property Problems

• Fuel wetting of fluoropolymer seals allows fuel to leak past seals. A costly nitrogen purge is necessary to prevent fuel contact with oxidizer. (Reduce Support Costs and Thrust to Weight)
RSiX₃ acid or base hydrolysis

Blendables

Resin

Incompletely condensed cages

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Typical isomers produced

Most common compounds found in a cage mixture

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29Si NMR spectrum of cage mixture

Distribution A: Approved for public release; distribution unlimited
29Si NMR of Fluorohexyl cage mixture

Fluorohexyl Poss 02-08-05

--- CHANNEL f1 ---
NUC1 29Si
P1 10.00 ussec
P11 -3.00 dB
SF01 59.6214106 MHz

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NUC2 1H
PCFD2 100.00 ussec
P12 120.00 dB
P112 20.00 dB
SF02 300.1312005 MHz

F2 - Processing parameters
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WDW EM
SSB 0
LB 1.00 Hz
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300.0 K
D1 8.00000000 sec
d11 0.03000000 sec

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P11 -3.00 dB
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--- CHANNEL f2 ---
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F2 - Processing parameters
SI 32768
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WDW EM
SSB 0
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GB 0
PC 1.40
Redistribution reaction

Sublimation
Re-crystallization
KOH Extraction

Distribution A: Approved for public release; distribution unlimited
Crystal structures of FluoroPOSS$_8$T$_8$
FluoropropylₙTₙ

²⁹Si NMR

R = -CH₂CH₂CF₃

T₁₀ (~11%)

T₁₂ (~89%)

Distribution A: Approved for public release; distribution unlimited
Fluoropropyl₈T₈

F₃CH₂CH₂Si(OMe)₃ \xrightarrow{\text{NaOH} / \text{H}_2\text{O} / \text{solvent}} \text{Trisodium salt from trimethoxy silane}

F₃CH₂CH₂SiCl₃ \xrightarrow{F₃CH₂CH₂SiCl₃} T₈ from trisodium salt

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Trifluoropropyl $T_8$ POSS

$\text{CF}_3\text{CH}_2\text{CH}_2\text{Si(OCH}_3)_3 \xrightarrow{\text{NaOH/H}_2\text{O}} \text{THF} \xrightarrow{\text{R'SiCl}_3} \text{R} = -\text{CH}_2\text{CH}_2\text{CF}_3 \quad \text{R'} = -\text{CH}_2\text{CH}_2\text{CF}_3$

Distribution A: Approved for public release; distribution unlimited
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PULPROG           zgig30
TD                65536
SOLVENT           CDCl3
NS                993
DS                4
SWH           23809.523 Hz
FIDRES          0.363304 Hz
AQ                1.3763061 sec
RG                32768
DW               21.000 usec
DE                6.00 usec
TE                300.0 K
D1                8.00000000 sec
d11             0.03000000 sec

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PL1              -3.00 dB
SF01            59.6214106 MHz

-------- CHANNEL f2 --------
CPDPRG2          waltz16
NUC2              1H
PCPD2            100.00 usec
PL2              120.00 dB
PL12              20.00 dB
SF02            300.1312005 MHz

F2 - Processing parameters
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Single peak in T₈ region

Corner capped Trifluoropropyl POSS
**Trifluoropropyl POSS**

**1H NMR Trifluoropropyl POSS**

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**Proton ratio 1:1**

**Distribution A: Approved for public release; distribution unlimited**
**13C NMR Trifluoropropyl POSS**

Corner Capped TFP-POSS

![NMR Spectra](image)

**Current Data Parameters**
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- **EXPN**: 2
- **PROCNO**: 1

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- **Time**: 9.35
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- **PROBHD**: 5 mm QNP 1H/15F
- **TD**: 65536
- **SOLVENT**: CDCl3
- **NS**: 2982
- **SN**: 17985.611 Hz
- **AQ**: 0.274439 Hz
- **RG**: 1.8219508 sec
- **DW**: 32768
- **DE**: 27.800 usec
- **TE**: 300.0 K
- **d11**: 0.03000000 sec
- **d12**: 0.00002000 sec

--- CHANNEL f1 ---
- NUC1: 13C
- P1: 6.25 usec
- PL1: 0.00 dB
- SFO1: 75.4752653 MHz

--- CHANNEL f2 ---
- CPDPRG2: waltz16
- NUC2: 1H
- PCPD2: 80.00 usec
- PL2: 0.00 dB
- PL12: 20.00 dB
- PL13: 20.00 dB
- SFO2: 300.1312005 MHz

**F2 - Processing parameters**
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- **WDW**: EM
- **SSB**: 0
- **LB**: 1.00 Hz
- **PC**: 1.40

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**Distribution A**: Approved for public release; distribution unlimited
Me corner-capped Fluoropropyl T₈ POSS

\[
\text{CF}_3\text{CH}_2\text{CH}_2\text{Si(OCH}_3)_3 \xrightarrow{\text{NaOH/H}_2\text{O}} \xrightarrow{\text{THF}} \xrightarrow{R'\text{SiCl}_3} \text{CF}_3\text{CH}_2\text{CH}_2\text{Si} - \xrightarrow{7} \text{CF}_3\text{CH}_2\text{H}_2\text{Si} - \xrightarrow{7} \text{CH}_3\text{Si} - \xrightarrow{1}
\]

Proton ratio 14 : 14 : 3

Distribution A: Approved for public release; distribution unlimited
Conclusions

• Conventional base catalyzed synthesis yields cage mixtures of fluoro-POSS
  – Redistribution method converts cage mixtures to pure T₈ POSS
• Fluoropropyl POSS does not readily convert to pure T₈ POSS as longer chained fluoro-POSS do
  – New synthetic corner-capping method produces pure T₈
• NMR and x-ray data determined that the new method was a success
The Polymer Working Group at Edwards Air Force Base is:

Dr. Steve Svejda
Lt. Amy Palecek
Mr. Pat Ruth
Dr. Sandra Tomczak
Mrs. Tini Vij
Dr. Darrell Marchant
Lt. Scott Iacono

Dr. Joe Mabry
Mrs. Sherly Largo
Dr. Tim Haddad
Lt. Will Cooper
Dr. Rusty Blanski
Lt. Laura Moody
Mrs. Sarah

AFOSR, PRS

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POSS polymer incorporation

Cross-linker  Pendant Polymer  Bead Copolymer

POSS Blending

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Redistribution reaction

Sublimation
Re-crystallization
KOH Extraction
Abstract

Fluorinated polyhedral oligomeric silsesquioxanes (POSS) are under investigation for potential lubricant applications. POSS compounds are characterized by a rigid, inorganic core consisting of silicon and oxygen, offering properties similar to those of ceramics; in addition to organic functional groups protruding from the inorganic core, offering organic functionality. Synthesis of POSS generally yields cage mixtures giving varying confirmations of the POSS (Si-O) core denoted by the number of silicon atoms present with T8 being the most abundant conformation. Synthesis of trifluoropropyl-POSS is an exception to this generalization which adopts a preferred T10 conformation, with a minor amount of T8 and T12 isomers. Herein, we describe an alternate synthetic route for the preparation of pure T8 trifluoropropyl-POSS not possible by conventional methods. The POSS cages are characterized by multinuclear NMR as well as low-temperature, single crystal x-ray diffraction studies.