Polymer Materials and Assay for Low Background Detectors

A Chemistry Perspective

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LRT 2015 Seattle WA

Radiopurity for Detector Materials

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- **Insulating materials**
  - plastics

    …*structural* plastics

- Radiopurity requirements are far more stringent than industrial chemical purity goals

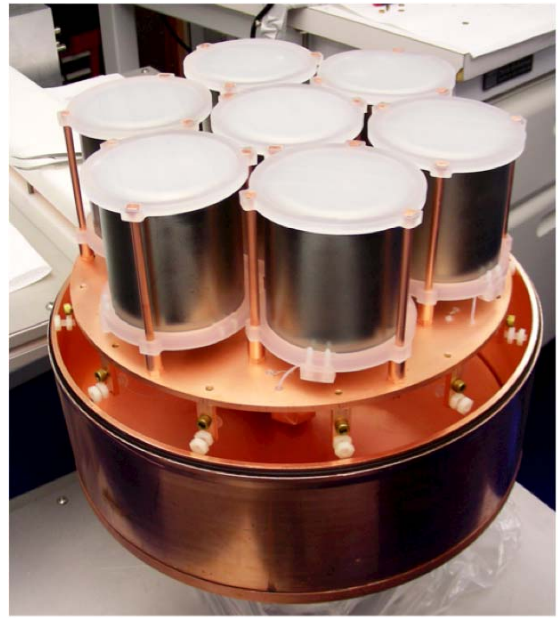
- PTFE and HDPE
  - available as pure materials, *only episodically*
  - don't have good structural properties

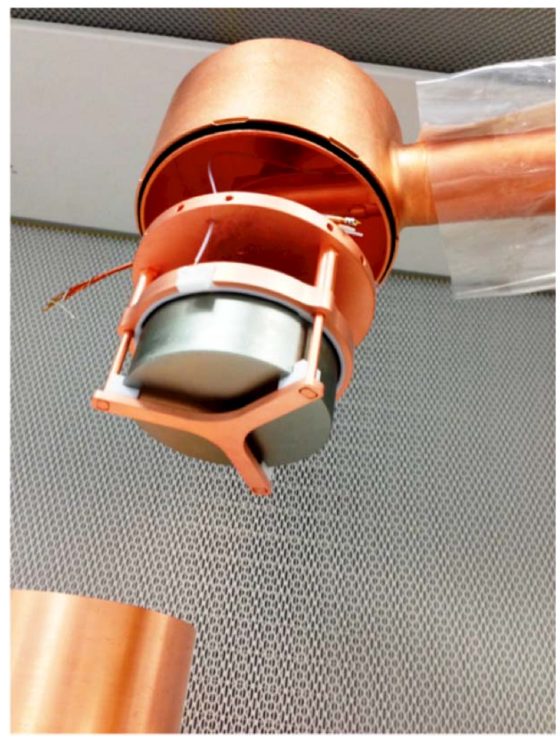
- U, Th, K

  Goals: Move from milliBq/kg to microBq/kg

  U: 1 part per trillion = 1 pg/g = 12 microBq/kg

  0.012 **milli**Bq/kg





Plastics are not Metals

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Metals	Plastics (polymers)
Refined from ore	Synthesized
Purity from refining processes	Purity as synthesized
Atomic basis	(Macro)Molecular basis Fillers may be added to obtain structural properties desired
Metals are similar	Each plastic is different
Dissolve in acid	Many don't dissolve, depending on the plastic
Analytical standards	No analytical standards for U,Th in plastic
Standard analysis methods	No standard method for metals in plastics at radiopurity levels, especially not for U, Th

Plastics are not Metals

Consequences	Plastics (polymers)
Synthesis may include inorganic potassium salts or metal catalyts	Synthesized
	Purity as synthesized
Useful to know the process chemistry Not generally purified, hard to purify	(Macro)Molecular basis Fillers may be added to obtain structural properties desired
Sourcing materials is crucial	Each plastic is different
Analysis methods must be developed, different for each plastic	Many don't dissolve, depending on the plastic
	No analytical standards for U,Th in plastic
Accuracy of analysis methods must be checked by using multiple techniques, and by understanding your analysis process	No standard method for metals in plastics at radiopurity levels, especially not for U, Th

Plastics Datasheets

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PES (Polyethersulfone)

High resistance to heat and combustibility, low smoke emission, and transparency are the combination of properties possessed by stock shapes extruded from PES. These, coupled with light weight, good impact resistance, dimensional stability, and chemical resistance, make stock shapes extruded from PES resin useful in the electrical/electronics, aerospace/aircraft, automotive, and mass transit industries. PES stock shapes are also applicable for heat and fire safety, food service, and hospital and health care items.

The following physical property information is based on typical values of the base polyethersulfone resin (PES).

Applications Include:
- Printed circuits
- High intensity light bases
- Safety face shields
- Machine guards
- Connectors

Advantages of PES:
- Low smoke generation
- Excellent electrical properties at elevated temperatures
- Transparency
- Excellent chemical resistance
- Easily machined

Property	ASTM Test Method	Units	PES
Physical			
Specific Gravity			
Water Absorption @24 hours			
Mechanical			
Tensile Strength @yield			
Tensile Modulus			
Tensile Elongation @yield			
Tensile Elongation @break			
Flexural Strength @yield			
Flexural Modulus			
Compressive Strength @yield			
Compressive Modulus			
Izod Impact Strength Un-Notched Notched @73°F			
Hardness, Rockwell			
Thermal			
Heat Deflection Temperature @66 psi @264 psi			
Coefficient of Thermal Expansion			
Flammability Rating–UL94 @.031"	—	—	V-0
Thermal Conductivity	C177	$(BTU\cdot in)/(hr\cdot ft^2\cdot °F)$	1.13
Limiting Oxygen Index	D2863	%	39.3
Electrical			
Dielectric Strength	D149	V/mil	380
Dielectric Constant @1kHz	D150		3.50

Property	Units	Value
Radioactivity	Bq/g	?
K mass concn	pg/g	?
U mass concn	pg/g	?
Th mass concn	pg/g	?

R&D Capability in Radiopure Plastics

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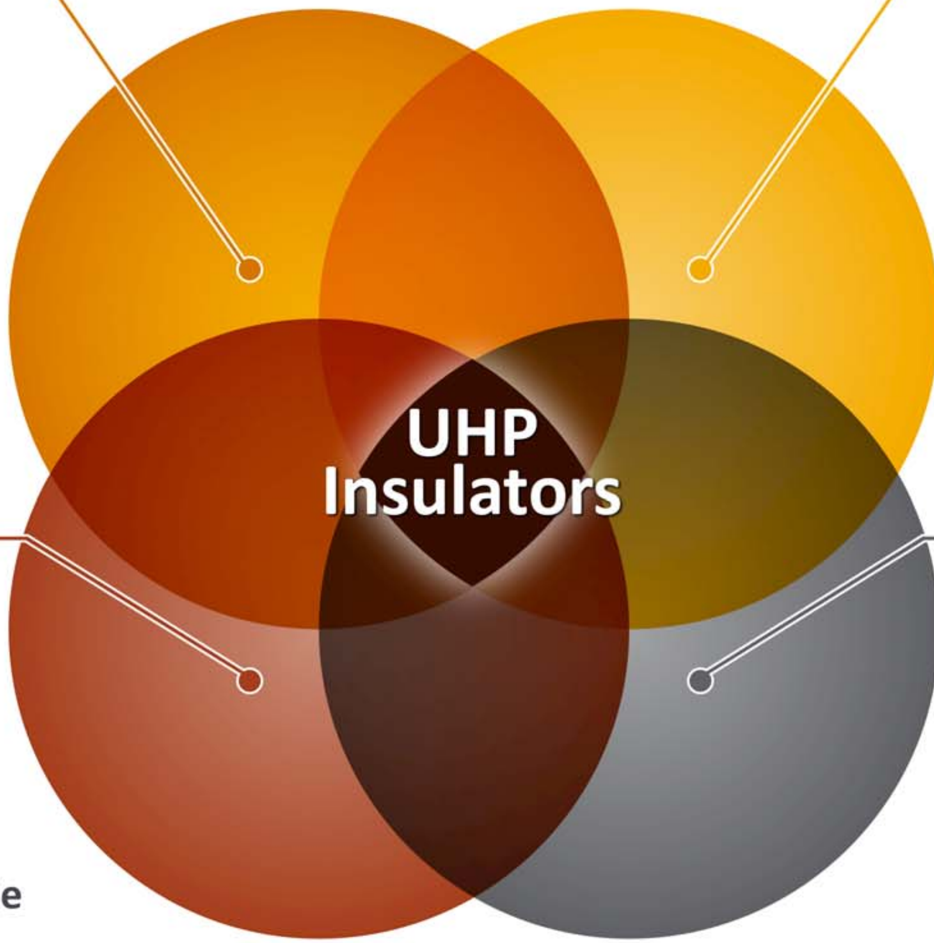
PURITY

- Polymer synthesis leads to purity
- Source business requires purity
- May be improved locally

APPLICABILITY

- Structural properties
- Temperature/ vacuum compatibility
- Cleaning procedure compatibilty
- Iterate properties vs. detector functions

electrical



SOURCING

- Understand the supply chain
- Supply chain access
- Source will stay in business
- Sustainable partnerships possible

QUALITY

- Source controls their purity
- Ease of analysis to required levels
- Purity known to very low levels
- Understand sources of contamination

Sustainable

Structural Polymer Examples

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Data from GOPHER (SOUDAN) courtesy SuperCDMS team

	Unit	450G903	Nylon 101 NC010	SUMIKAEXCEL 3600G	SZ6505HF	E6807T
Material Details						
Polymer Family	-	PEEK	Polyamide	PES	Mica-Filled LCP	Talc Filled LCP
U-238	mBq/kg	20.53 +/- 0.763*	< 1.34	1.208 +/- 0.360	380.7 +/- 15.66	2788 +/- 20.53
Th-232	mBq/kg	11.85 +/-0.78*	1.644+/- 0.473	1.141 +/- 0.447	73.79 +/- 0.8634	29.38 +/- 7.323
K-40	mBq/kg	10.90 +/- 1.49*	1.513 +/- 1.377	1000 +/- 30.43	99150 +/- 2950	13.17 +/- 3.680
Co-60	mBq/kg	< 0.11*	< 0.1974	< 0.42	Undetermined	0.532 +/- 0.289
Cs-137	mBq/kg	< 0.13*	< 0.2528	<0.45	Undetermined	Undetermined

PEEK (black)
U: 20
Th: 12
K: 11
milliBq/kg

Nylon
U: <1.34
Th: 1.6
K: 1.5
milliBq/kg

PES
K: 1000
milliBq/kg

LCP:Mica
K: 99150
milliBq/kg

LCP: Talc
U: 2788
milliBq/kg

More Polymer Examples

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	PE	PE
	HDPE	UHMWPE
PNNL	ICPMS	ICPMS
	milliBq/kg	**milli**Bq/kg
U	0.354	19

	PTFE
	NXT-75
EXO	NAA
	milliBq/kg
U	< 0.023
Th	< 0.006
K	0.099

Hoppe et al. LRT2013

PE and PTFE are
***not* good structural plastics**

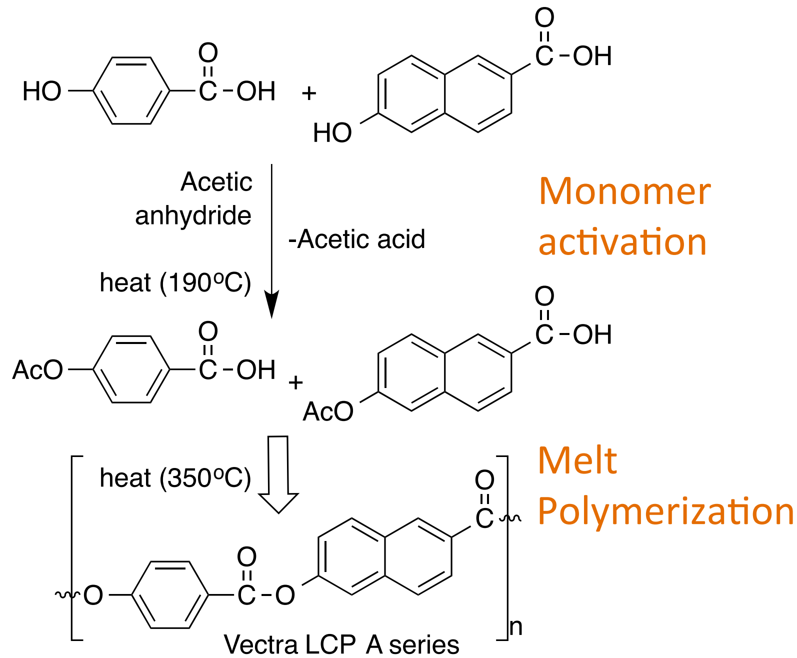
	PCTFE
	Neoflon
EXO	Ge
	milliBq/kg
U	5.560
Th	< 2.310
K	< 30.400

Leonard et al, 2008
EXO paper

Vectra LCP (Liquid Crystal Polymer)

- LCPs:
  - structural polymers
  - unique injection molding characteristics
    - fine-pitch connectors

- Vectra:
  - Batch polymerization in 10,000 pound batches in North Carolina on two staggered reactor lines
  - Precursor batch held under nitrogen!



Vectra LCP (Liquid Crystal Polymer)

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FOR TICONA INTERNAL USE ONLY – CONFI

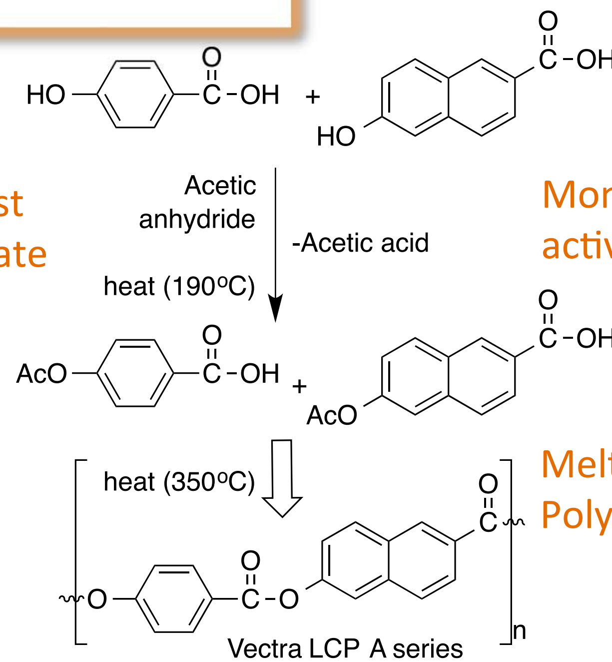
First Stage - Acetylation

- Monomers charged to acetylator with catalyst (30-60 ppm potassium acetate

- unique injection molding characteristics
  - fine-pitch connectors

- Vectra:
  - Batch polymerization in 10,000 pound batches in North Carolina on two staggered reactor lines
  - Precursor batch held under nitrogen!

Catalyst
K acetate



Monomer
activation

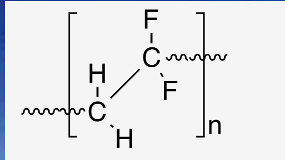
Melt
Polymerization

39 ppm: 1200 milliBq/kg

Other routes exist to make the same or similar LCPs using tin or antimony based catalysts
Journal of Polymer Science Part A: Polymer Chemistry. Vol.38, 19, 3586–3595, 2000.

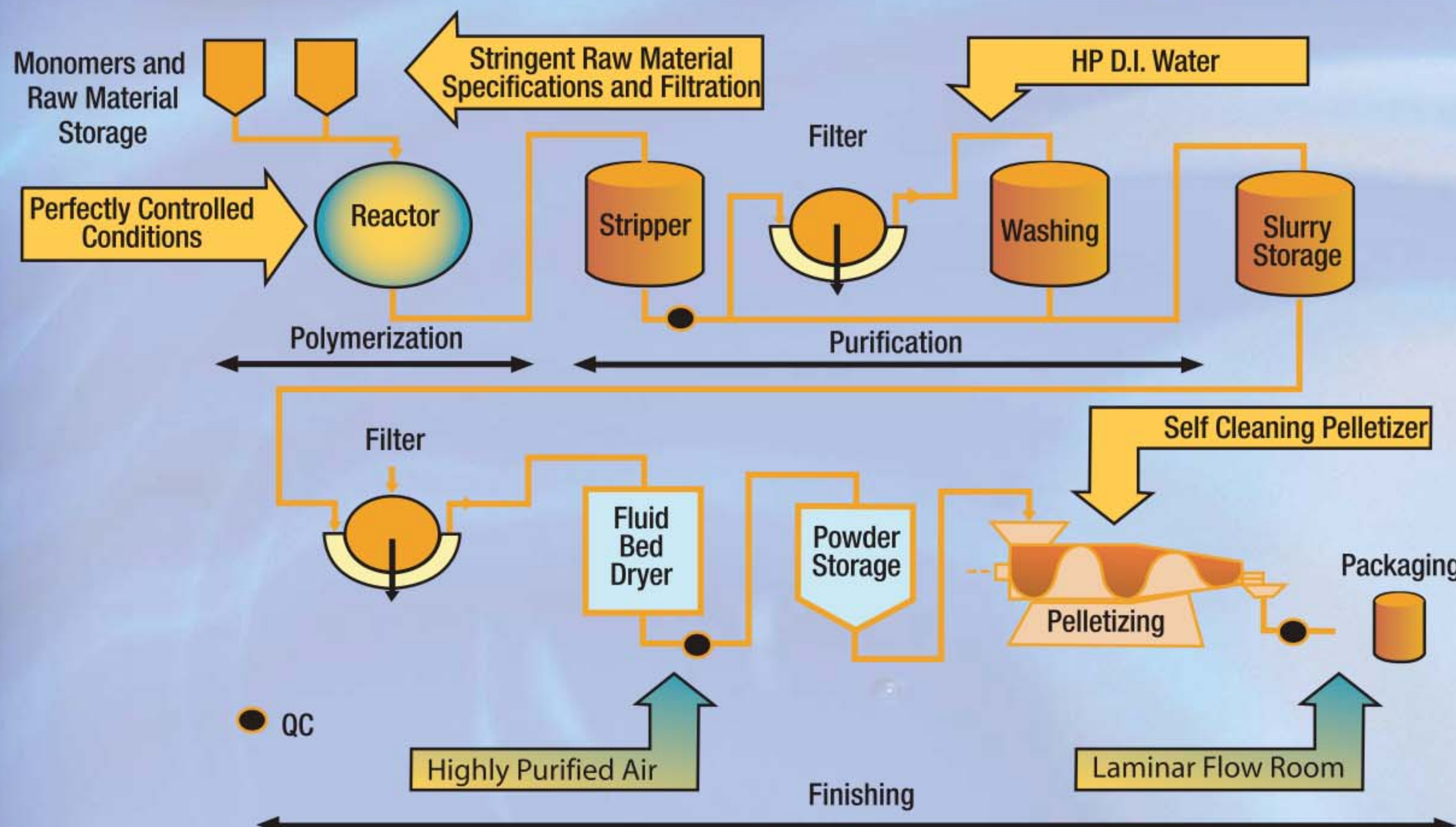
Solef® HP PVDF

Semiconductor industry



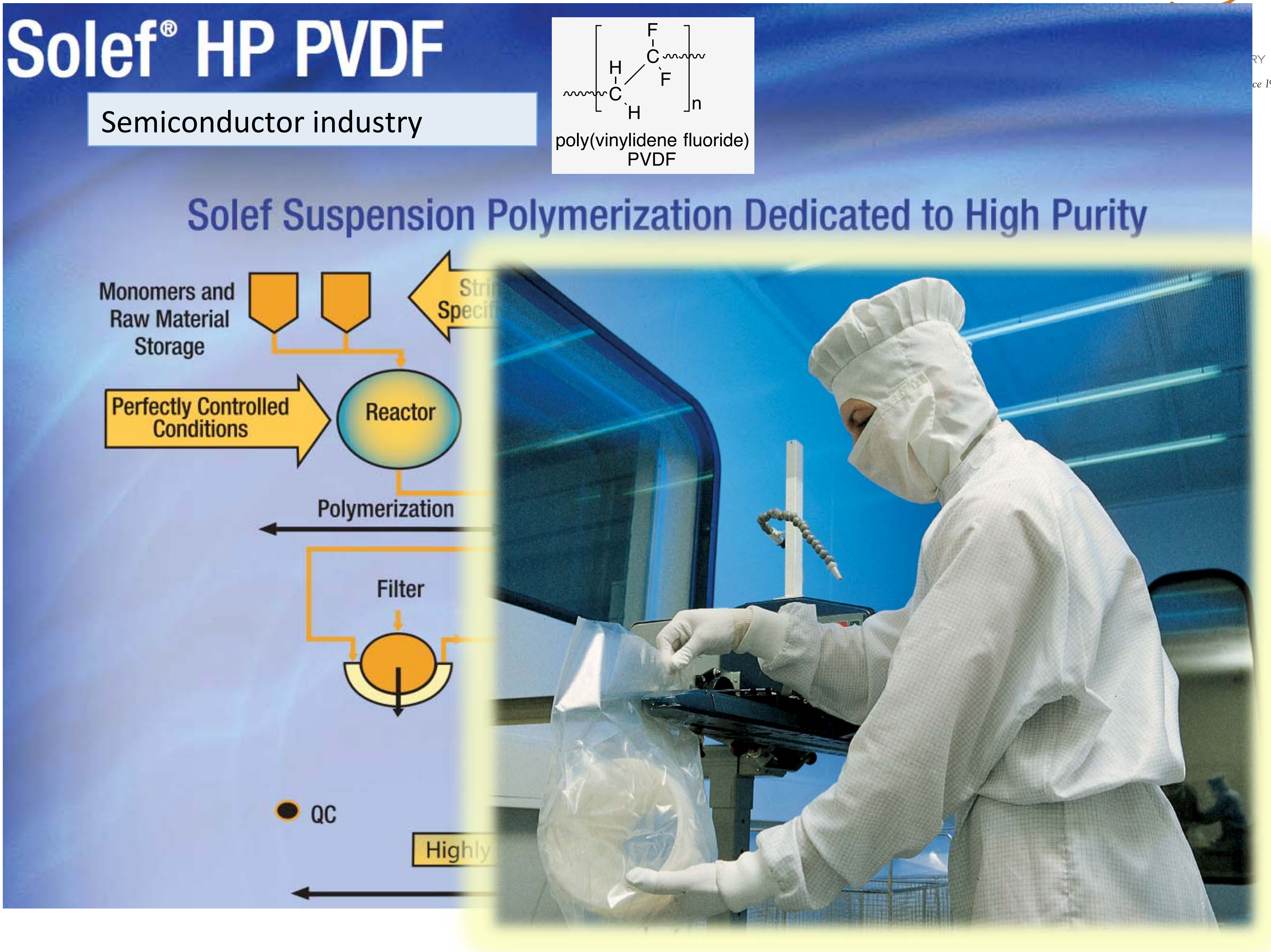
poly(vinylidene fluoride)
PVDF

Solef Suspension Polymerization Dedicated to High Purity



Semiconductor industry

poly(vinylidene fluoride)
PVDF



Sourced: PVDF Powder, Pellets, Parts

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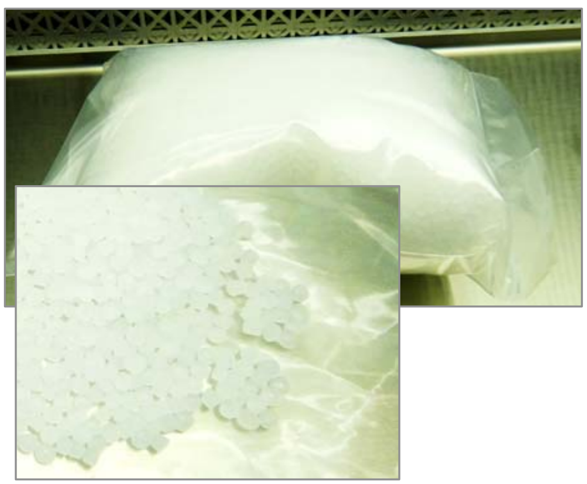
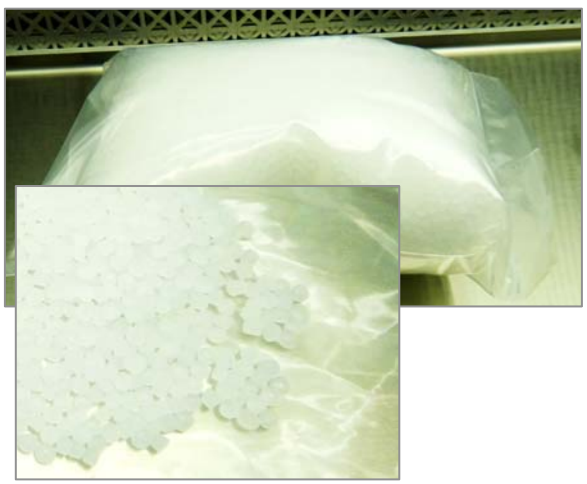
Powder sampled from Solef HP production line



Pellets from self-cleaning pelletizer in laminar flow room

Injection molded parts double bagged in clean room

Assay on PVDF Pellets



Pellets from self-cleaning
pelletizer in laminar flow room

<u>Mass Spectrometry by ICP-MS</u>
assays under development at PNNL

PVDF
insoluble
fluoropolymer)

Dry ash/ UHP copper foil

~~U: ~< 1 milliBq/kg~~
~~Possibly as low as < 65 uBq/kg~~
~~Th: nd~~

U: ~ 0.010 milliBq/kg
Th: ~0.003 milliBq/kg

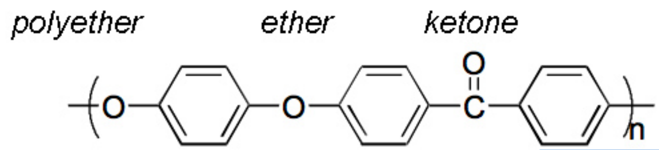
<u>Counting</u>

Sample counting at SOUDAN
slow to get statistics

Poly aromatic ether ketone polymers

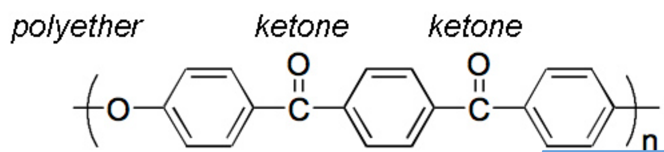
very good **structural polymers** even without fillers

PEEK



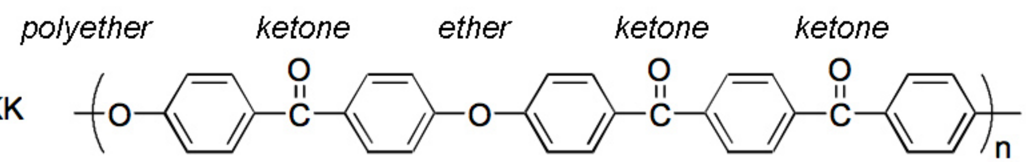
Biomedical

PEKK



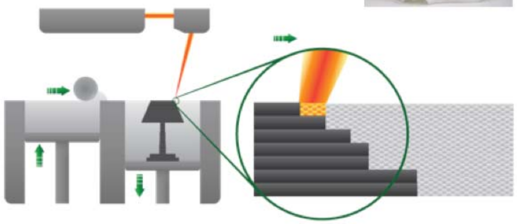
Biomedical

PEKEKK



Sourced: PEKK and PEEK

PEKK



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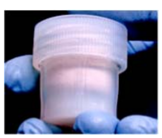
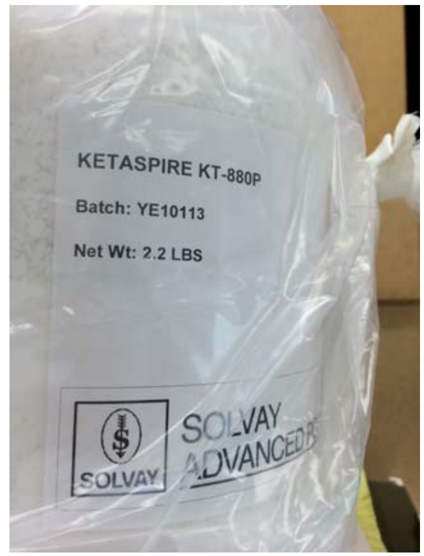
Disk 2



Powder

Pucks

PEEK



PEEK flake

Synthesis → **Flake**

Grinding → Powder

Extrusion → Pellets

Soluble in sulfuric acid for analysis by ICP-MS

Sourced: PEKK and PEEK

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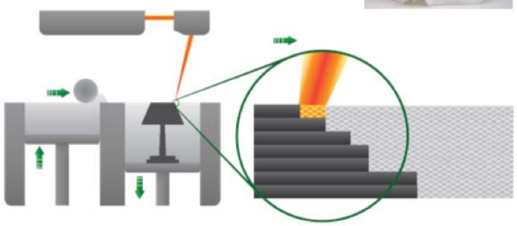
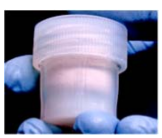
PEKK



Disk 1
Disk 2

Pucks

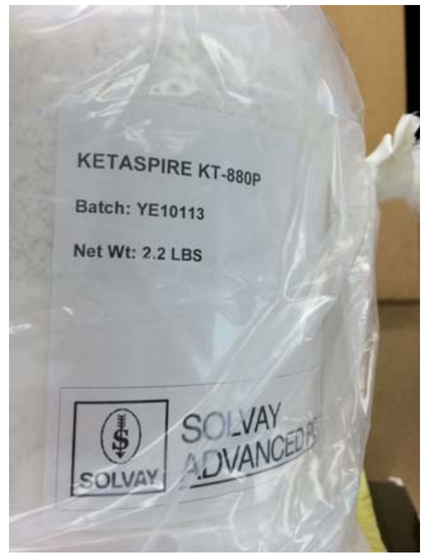


Powder

PEKK dissolve in tracered acid		
	pg/g	**milliBq/kg**
U	270	3.335
Th	900	3.654
nat K		

Phase I SBIR proposed

PEEK



PEEK flake

Synthesis → **Flake**

Grindin

Extrusi

PEEK flake dissolve in tracered acid		
	pg/g	**milliBq/kg**
U	250	3.088
Th	55	0.223
nat K		

VICTREX PEEK GOPHER results)		
	pg/g	milliBq/kg
U		20.530
Th		11.850
K-40		10.900

Sample waiting at SOUDAN

LA – ICP-MS

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- Direct solid sampling by laser ablation (LA)
  - \+ no sample preparation, fast
  - \- no matrix matched standards, not quantitative

- PNNL developments
  - Pb and U have similar total atom efficiencies from LA-sampling to detection in at least some plastics
  - Screening: is sample less than 1 milliBq/kg, yes or no
  - Working toward more quantitative approaches
  - Potential to drive detection limits down 100x with better laser and MS

To be described at the MARC conference in April

Summary

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Chemistry Perspective

- Looking at polymer synthesis, reagents, catalysts
- Sourcing materials
  - semiconductor and biomedical industries
  - Materials before contamination by handling and processing
- Assay
  - Dissolution ICP-MS
  - LA ICPMS
- Purification

Highlights

structural plastics

PTFE NXT-75	milliBq/kg
U	< 0.023
Th	< 0.006
K	0.099

- PVDF pellets
  - U: 0.010 **milli**Bq/kg
  - Th: 0.003 **milli**Bq/kg
  - Counting at SOUDAN

VICTREX PEEK	GOPHER milliBq/kg
U	20.530
Th	11.850
K-40	10.900

- PEEK flake
  - U: 3 **milli**Bq/kg
  - Th: 0.2 **milli**Bq/kg

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- Miguel Daal
- David Nelson
- Erik Kramer

SOUDAN

- Mark Pepin

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