Design of Transparent Fluoropolymer Resists for Semiconductor Manufacture at 157 nm

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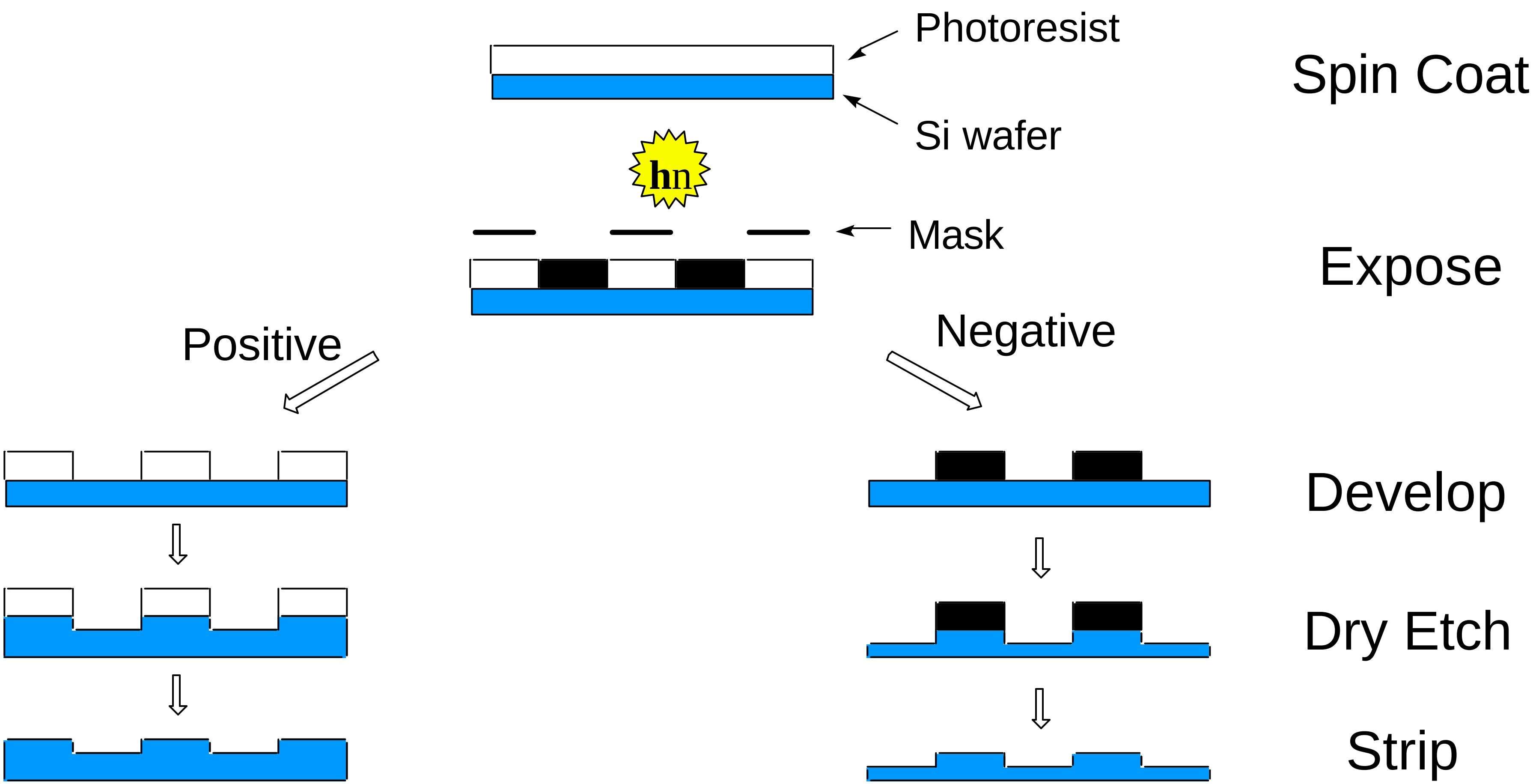
Outline

- Introduction to microlithography
  - Process technology
  - Materials needs
- Why *fluoro*polymer photoresists?
- Design of our fluoropolymer platform for 157 nm imaging
- Polymer synthesis issues
- Imaging results
- Extensions and future directions

Photoresists for Microlithography

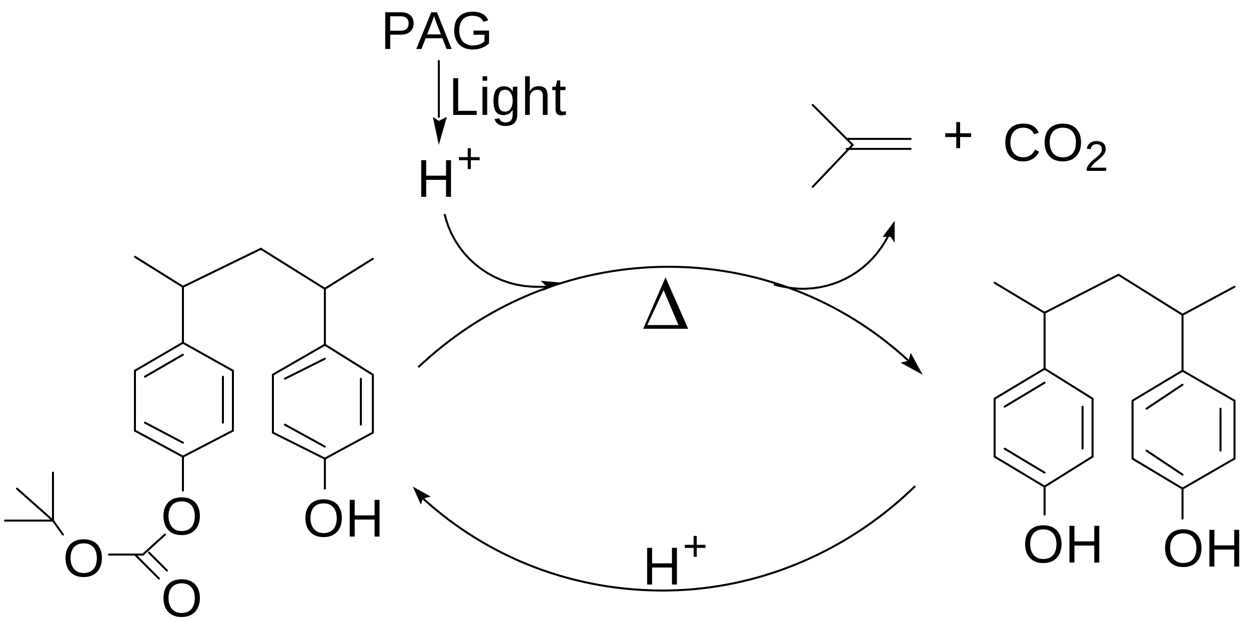
Materials Employed by the Semiconductor Industry to Create Patterns on the Silicon Wafers Which Will Become Computer Chips.



Photoresist Ingredients

- Polymeric Binder ⇦
- Photoacid Generator (PAG)
  - Captures Light to Generate Protons which Create Pattern
- Dissolution Inhibitor (DI)
  - Low MW Additive(s) to Increase Contrast
- Adhesion Promoters, Surfactants, Bases, Etc.

Image Formation (248 nm)

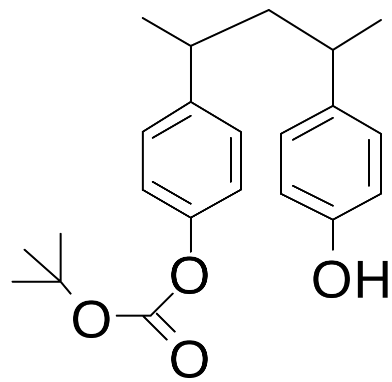


Insoluble in
Aqueous Base

Soluble in
Aqueous Base

- Chemical Amplification: Deprotection <u>Catalyzed</u> by Protons

Etch Resistance



PHOST

$$\text{Etch Rate} \propto \frac{\text{\# of Atoms in Monomer}}{\text{\# Carbon Atoms} - \text{\# Oxygen Atoms}}$$

$\Rightarrow$ Need high C/H ratio for good etch resistance

$\Rightarrow$ Aromatic or Polycyclic Groups

Photoresists for Microlithography

- Semiconductor Industry Driven by Miniaturization of Feature Size
  - Proportional to Wavelength of Light

λ (nm):	365 ⇨	248 ⇨	193 ⇨	157
Minimum Feature Size (nm):	180	130	100	70
Source:	Hg i-line	KrF Laser	ArF Laser	F_2 Laser

Photoresists for Microlithography

- New Wavelength Nodes Require New Binder Polymers
  - Light Should be Absorbed by PAG, Not Binder Polymer
    - Avoid Binder Decomposition and Outgassing
      - » 157 nm = 180 Kcal/Mole
    - Use Light Efficiently
    - Allow Light to Penetrate to Bottom of Film for Straight Sidewalls
      - » Absorbance < to << 2.0 μm^{-1}
- Transparency / Thickness Tradeoff
  - Thinner Films Can be More Absorbing but May Have More Defects and Less Etch Resistance

Polymer Binder Properties

- Functionality for image formation and subsequent dissolution in aqueous base
- Transparent at imaging wavelength
- Etch resistant
- High contrast
- Stable at processing temperatures (high Tg)
- Soluble in selected organic solvents for spin coating
- Right molecular weight for proper dissolution behavior
- Adhere to silicon or other substrates
- Suitable for commercial production
- Very pure (ppb metals)

Property conflicts, e.g. Transparency vs. Etch Resistance

Program Goal: Develop new polymer(s) with transparency at 157 nm, chemically amplified imaging, aqueous development <u>and</u> all other properties required for application as photoresist binder

Why Fluoropolymers?

Transparency at 157 nm!

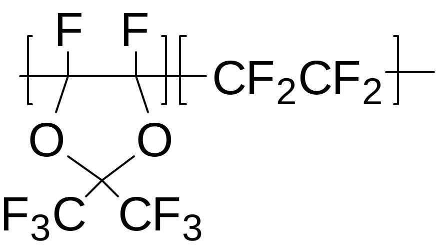
Polymer	Absorbance at 157 nm
Polyacrylic acid	11.00
Polynorbornene	6.80
Polyhydroxystyrene	6.25
Polymethyl methacrylate	5.69
Polyvinyl alcohol	4.16
Polydimethylsiloxane	1.61
Teflon®AF (amorphous perfluoropolymer)	0.70
Polyhydrosilsequioxane	0.06

Kunz et. al. J. Vac. Sci. Technol. 1999, 17, 3267

- All known photoresist platforms were too opaque for use as single layer resists at 157
- Only fluoropolymers and selected silicon polymers promise good transparency

Fluoropolymer Photoresist?

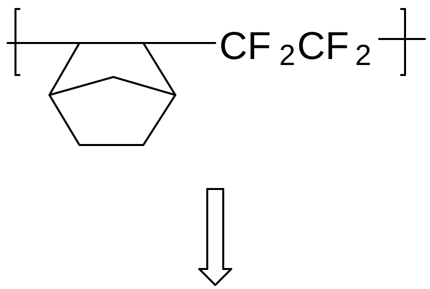
Teflon®AF



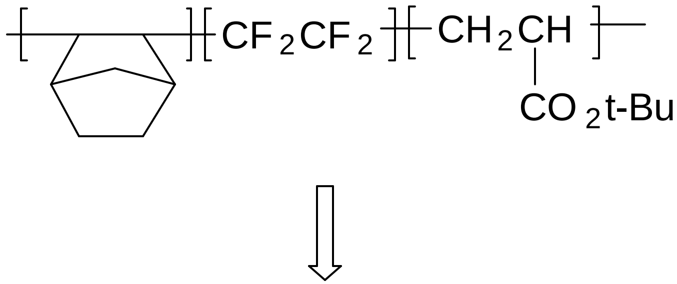
- High Tg (165 - 330 °C), Excellent Thermal Stability ☺
- Amorphous and Very Transparent ☺
- Very Hydrophobic ☹
- Soluble Only in Perfluorinated Solvents ☹
- No Functionality for Image Formation ☹
- Poor Etch Resistance ☹

⇒ Design Polymer which Retains First Two, Corrects Last Four

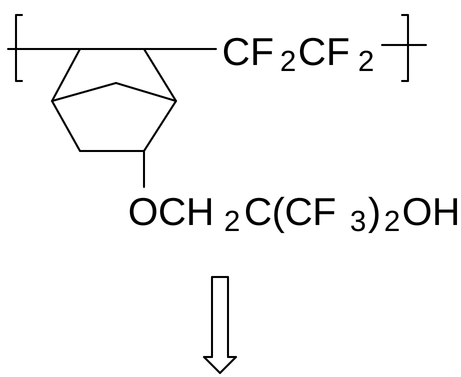
Evolution to a Fluorinated Photoresist



- Excellent transparency (A = 1.30 μm^{-1})
- Good etch resistance
- Tg = 150 °C
- Amorphous, soluble in organic solvents
- Need functionality for imaging

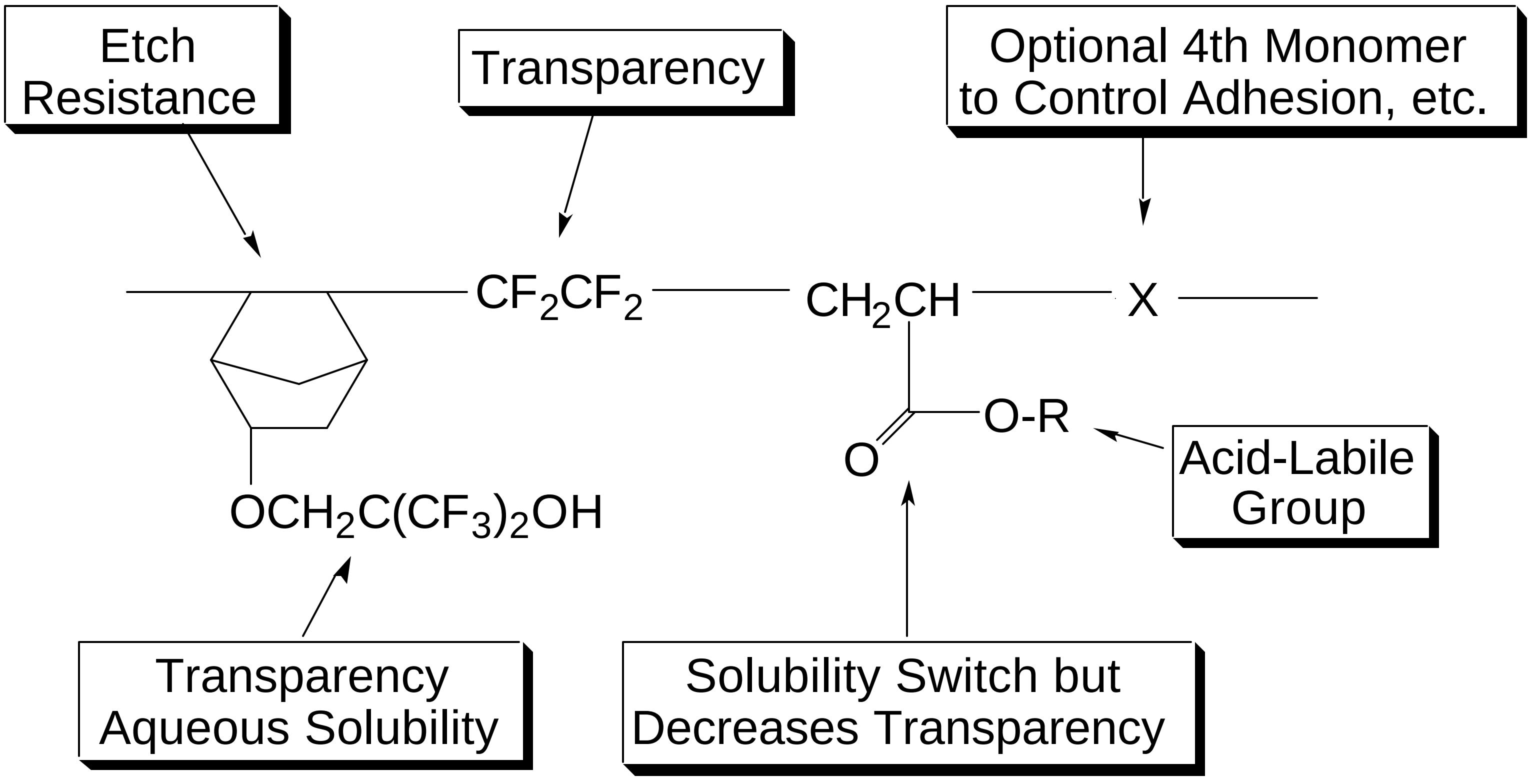


- Adding enough tert-alkyl ester for imaging and aqueous development pushes absorbance above 3.0 μm^{-1}

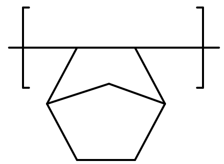


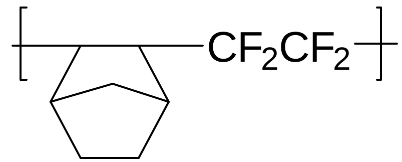
- Fluoroalcohols are acidic and transparent
- Readily protected as, e.g. methoxymethyl ether
- Outstanding transparency (A = 0.7 μm^{-1})
- Some loss in etch resistance
- Dissolves in aqueous base but dissolution rate too slow

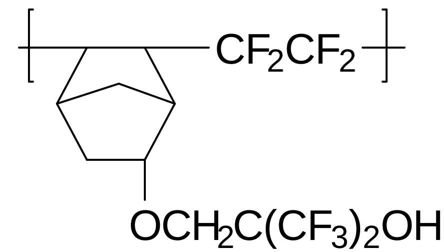
Fluorinated Photoresist
(Generation 1)



Fluorination and Transparency

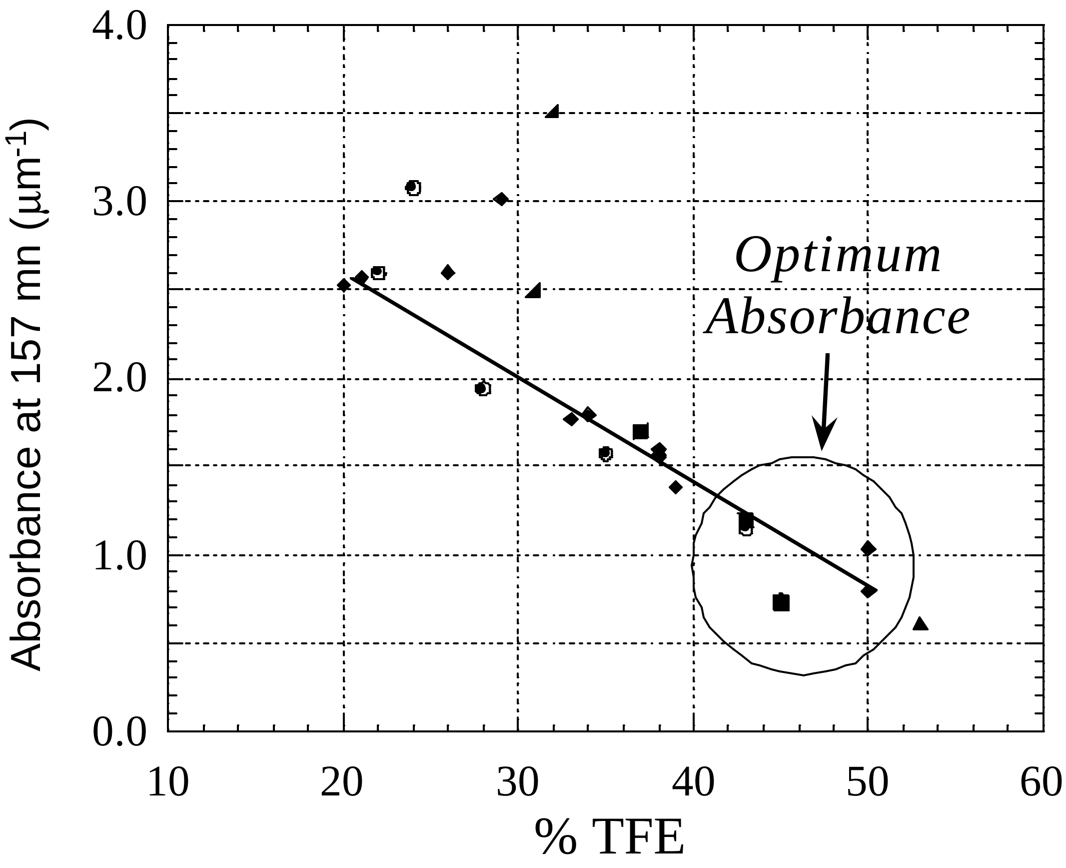






Absorbance at 157: **6.8** **1.3** **0.7**

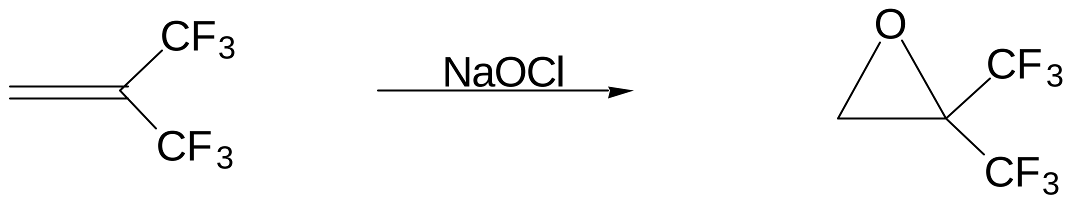
Absorbance Data
TFE / NB-F-OH / Acrylate Copolymers

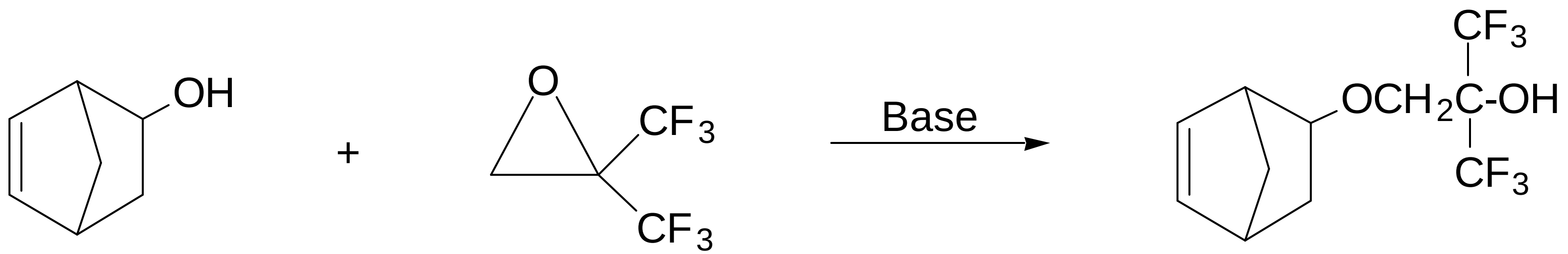


TFE Copolymer Properties

- TFE + norbornene-F-OH + acid-labile switch (alkyl acrylate)
  - 40 - 50 mole % norbornene fluoroalcohol
  - 15 - 40 mole % TFE
- Absorbance 0.7 - 2.7 μm^{-1}
  - Mostly controlled by ester content
- Etch rate 1.2 - 1.4 X Apex E
- Tg = 130 to 160 °C
- Mn = 3,000 - 15,000
  - Readily controlled by initiator concentration and/or use of chain transfer agent
- Soluble in standard organic solvents (e.g. acetone, THF)

Monomer Synthesis





V. A. Petrov, Synthesis 2225 (2002)
V. A. Petrov, A. E. Feiring, J. Feldman WO 2000 66,575

Polymer Synthesis

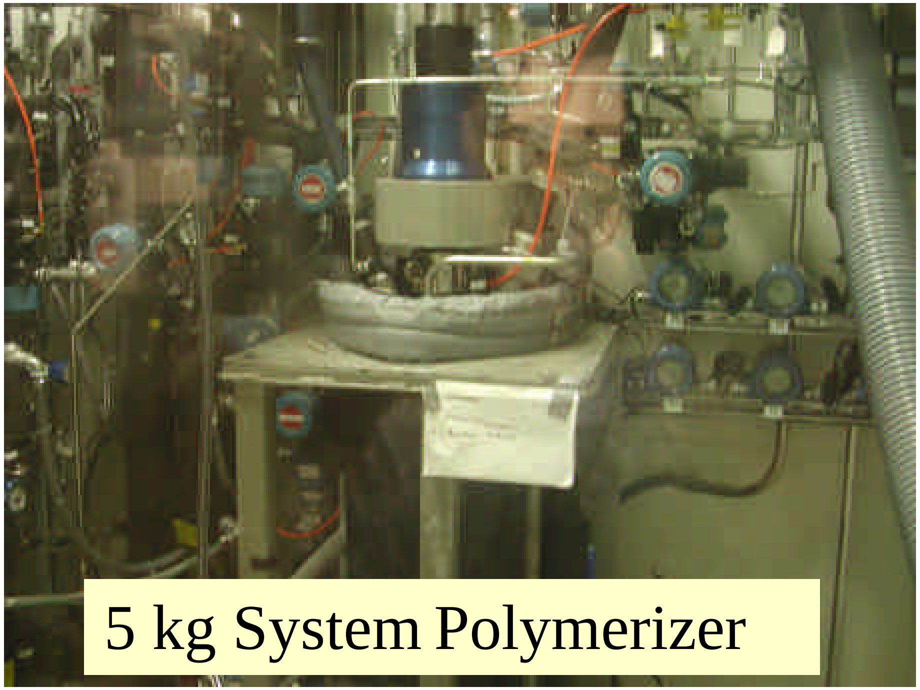
- Solution, free-radical polymerization
  - 40 - 60 °C and 200 - 400 psi
- TFE / norbornene dipolymer
  - Strong tendency for monomers to alternate
    - Typical for fluorocarbon / hydrocarbon olefin mixtures
  - Simple batch copolymerizations give 50 / 50 copolymer
- TFE / norbornene / acrylate terpolymers
  - Acrylate most reactive monomer
  - Carefully controlled semibatch process to obtain uniform polymers:
    - Precharge norbornene-rich mixture
    - Maintain constant TFE pressure
    - Feed intiator and acrylate-rich monomer mixture

TFE / Norbornene / t-Butyl Acrylate Copolymers

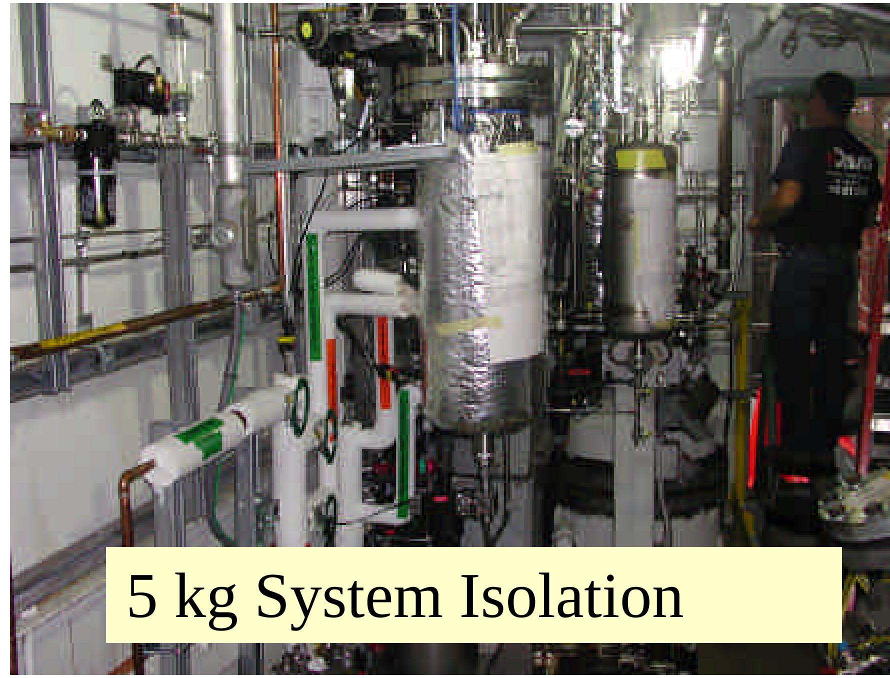
Monomer Comp.			Init.	Conv.	Mn	Polym. Comp.		
TFE	NBE	TBA	(mol %)	(%)		TFE	NBE	TBA
70	30		0.25	31	6700	52	48	
			1.0	89	4900	70	30	
68	30	2	0.25	26	5200	49	43	8
			1.0	91	4500	64	32	4
65	30	5	0.25	24	6200	37	44	19
			1.0	89	4300	56	40	5
60	30	10	0.25	27	6300	28	35	37
			1.0	87	5600	53	35	13
50	30	20	0.25	29	9900	16	28	56
			1.0	63	6400	42	40	18

Polymerization Issues

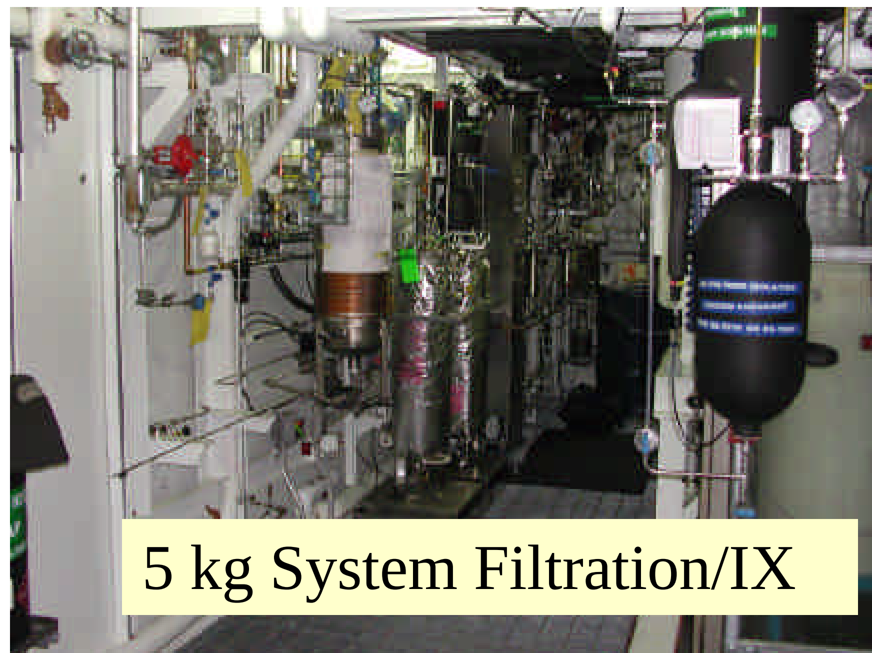
- TFE
  – Deflagrating Explosive & Cancer Suspect Agent
- Provisions for multiple monomer and initiator feeds throughout polymerization
  – Maintain product uniformity
- Meet customer needs for product quantity
  – Multiple reactors for production of 50 g to 5 Kg batches
- High purity
  – < 20 ppb each of multiple metals
    - Materials of construction
    - Monomer and solvent purity
    - Purification train



5 kg System Polymerizer

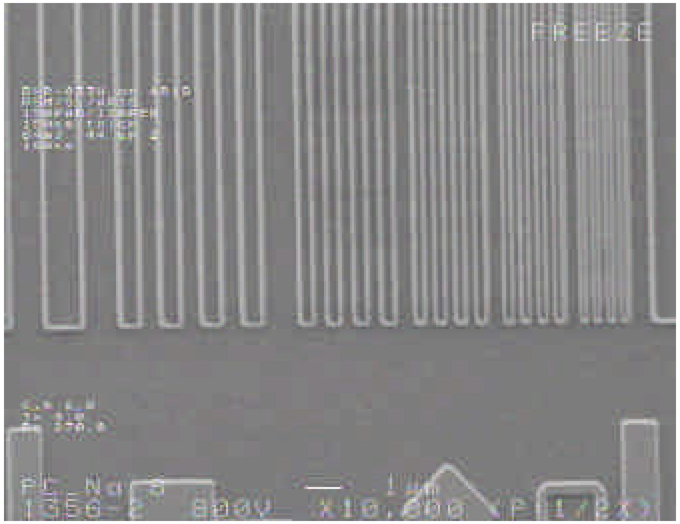


5 kg System Isolation



5 kg System Filtration/IX

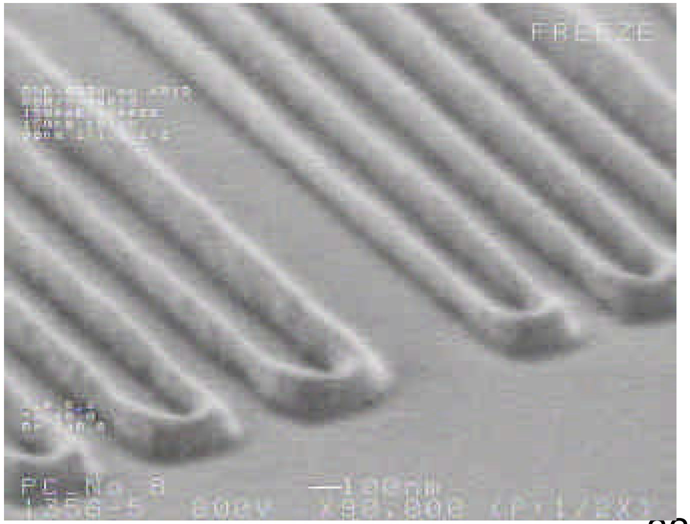
TFE Tetrapolymer Imaging



80 nm 1:1.5 Lines
150 nm film thickness

AR19 BARC

PEB = 120°C

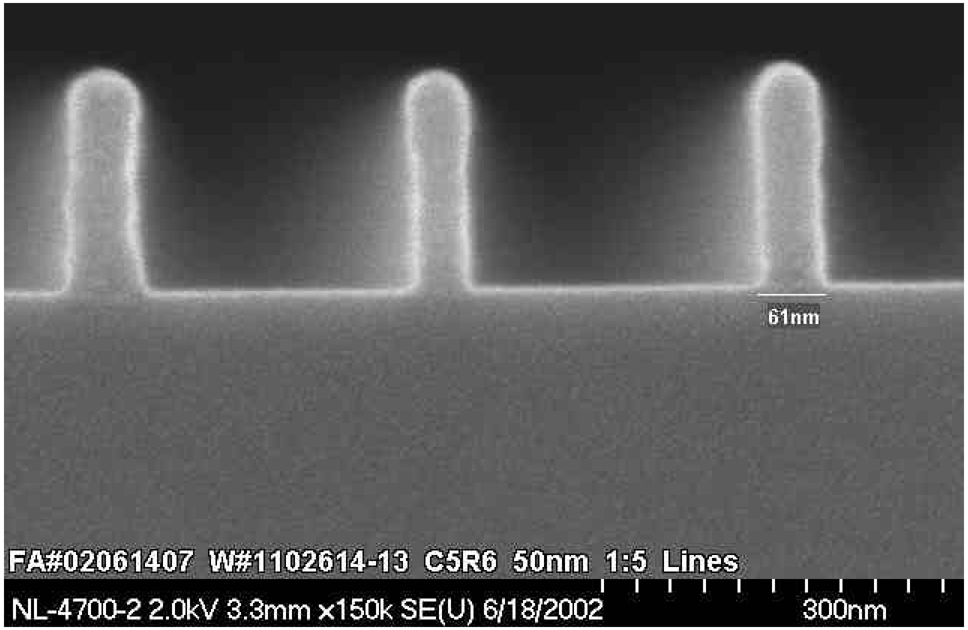


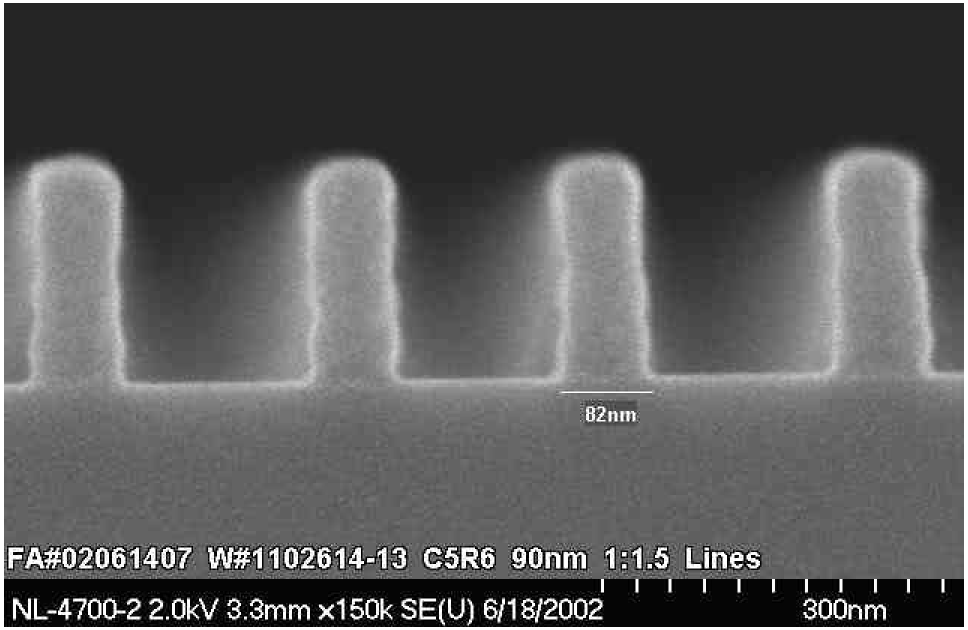
TFE Terpolymer

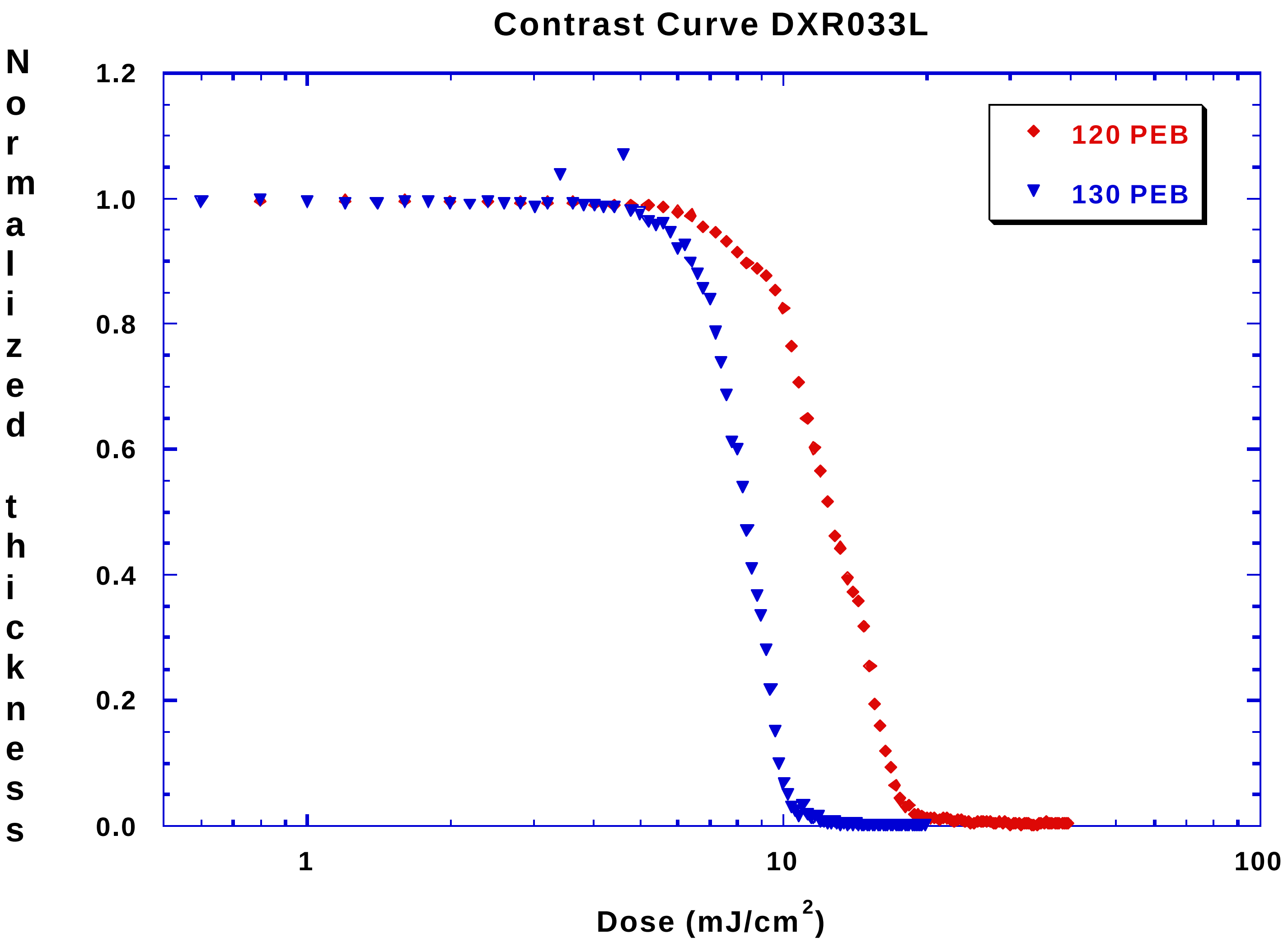
June 2002

Polymer absorption = 1.27 μm^{-1}

Absorption of formulated sample = 1.62 μm^{-1}







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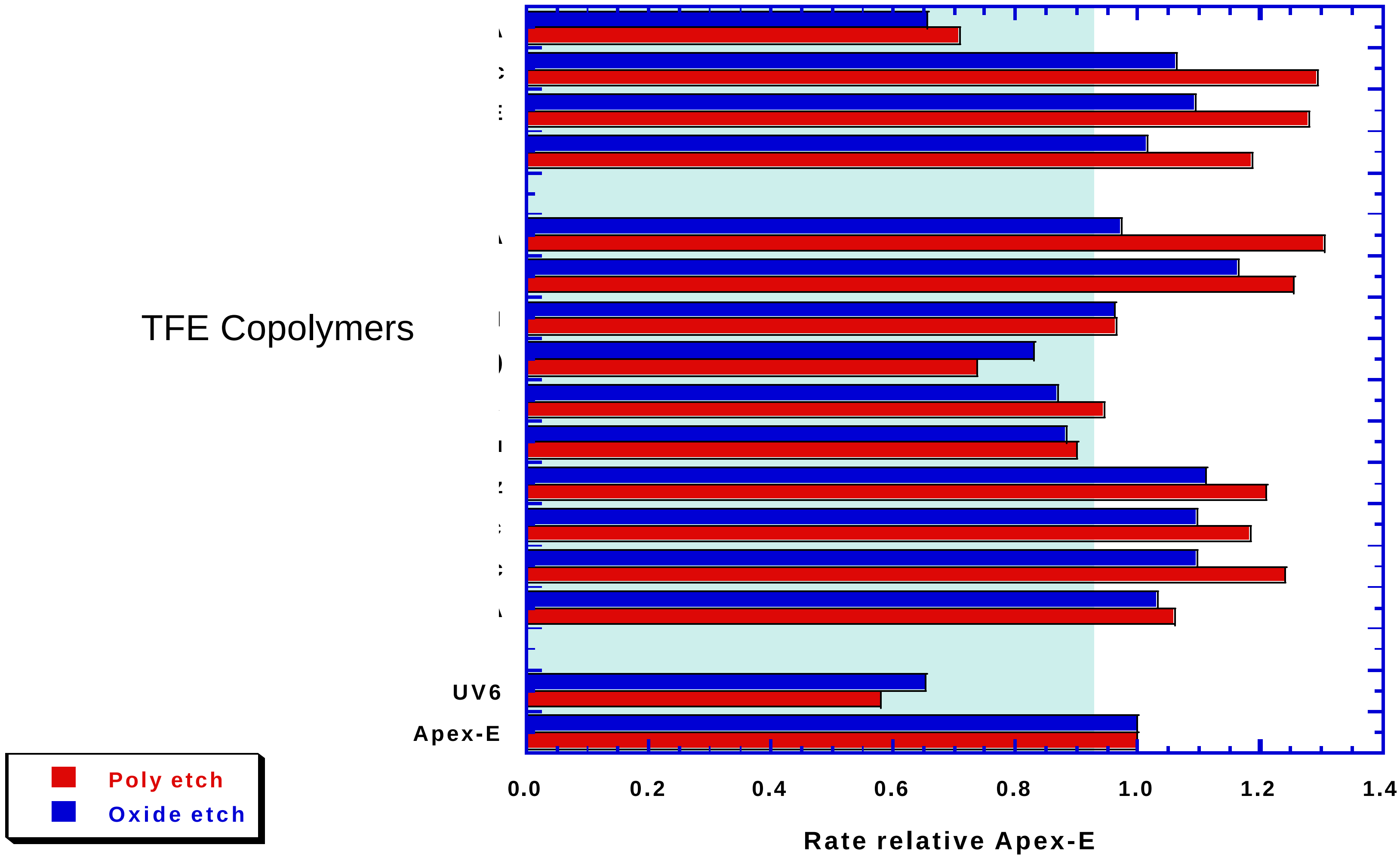
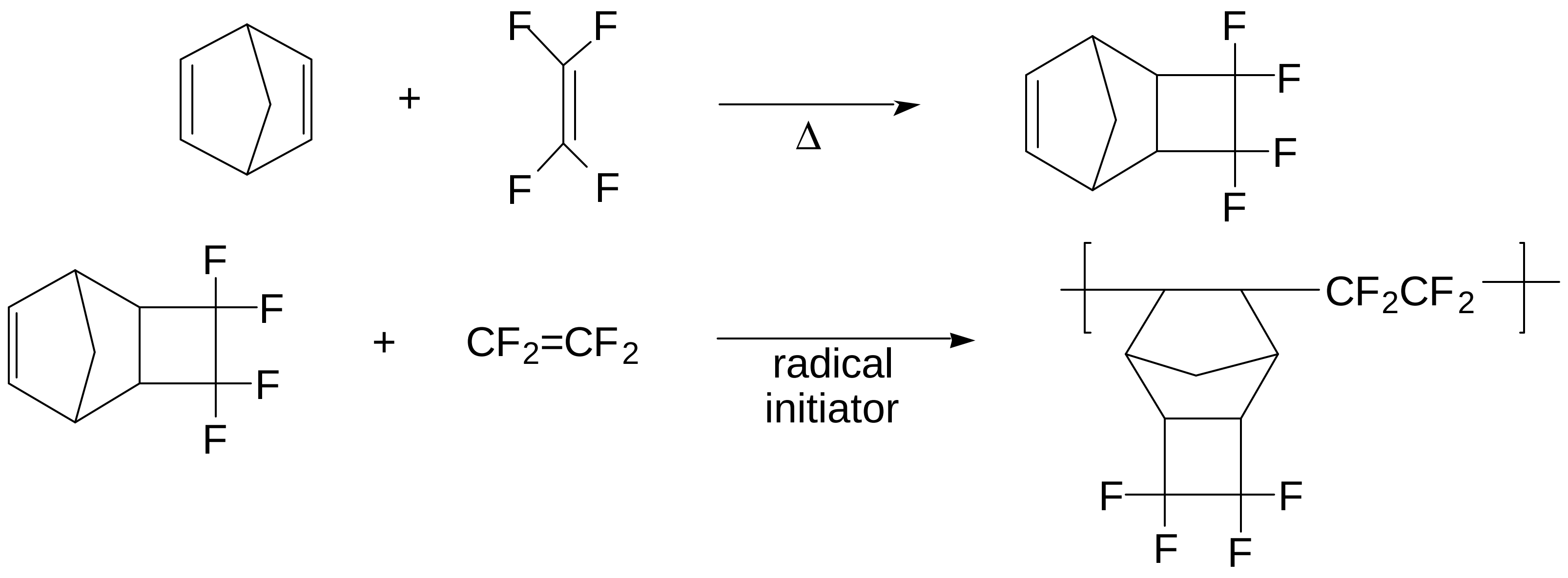
Etch Data

TFE Copolymers

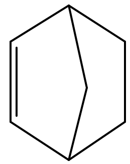
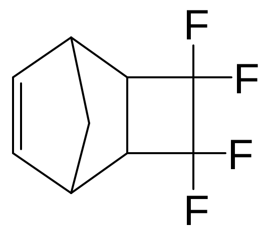
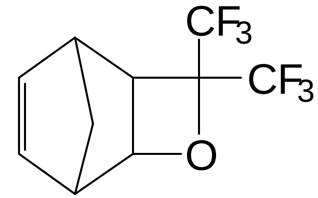
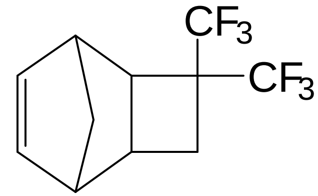


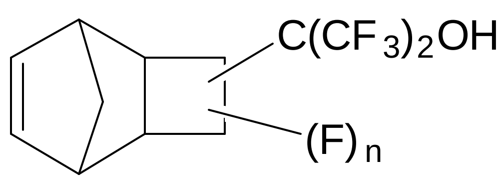
Extensions and Future Directions

- Improved properties by incorporating more fluorine in polycyclic segment?
  - Needs to be remote from double bond for good polymerizability
- Bicyclo[2.2.1]heptene (NB) ➡ Tricyclo[4.2.1.0[2,5]]nonene (TCN)



TFE / TCN Copolymers

TFE Copolymer Properties				
Tg	150 °C	228 °C	213 °C	203 °C
Absorbance at 157 nm	1.30	0.69	0.55	0.61

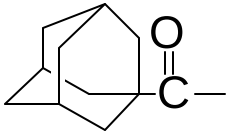
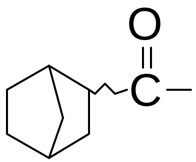
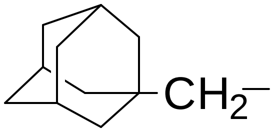
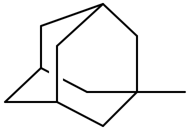
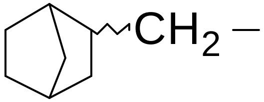


TFE / Vinyl Ether Copolymers

- TFE Copolymerizes Readily with Vinyl Esters and Vinyl Ethers to Give Amorphous Copolymers:
  - TFE / Vinyl Acetate   Tg = 48 °C
  - TFE / Butyl Vinyl Ether   Tg = 20 °C
- Tg Too Low; Poor Etch Resistance for Resists
- Incorporate Pendant Groups
  - Bulky for High Tg
  - Carbon Rich (Polycyclic) for Etch Resistance
  - Saturated for Transparency

TFE Copolymers

$$CF_2{=}CF_2 + CH_2{=}CH(OR) \longrightarrow -CF_2CF_2CH_2CH(OR)-$$

R	Tg	Mn	Etch Rate	Absorbance at 157 nm
	149 °C	33500		6.5
	86 °C	42800		5.0
	121 °C	37300	0.9	6.1
	140 °C	27500		
	66 °C	57400	1.0	3.3

TFE/Vinyl Ester and Vinyl Ether Copolymers

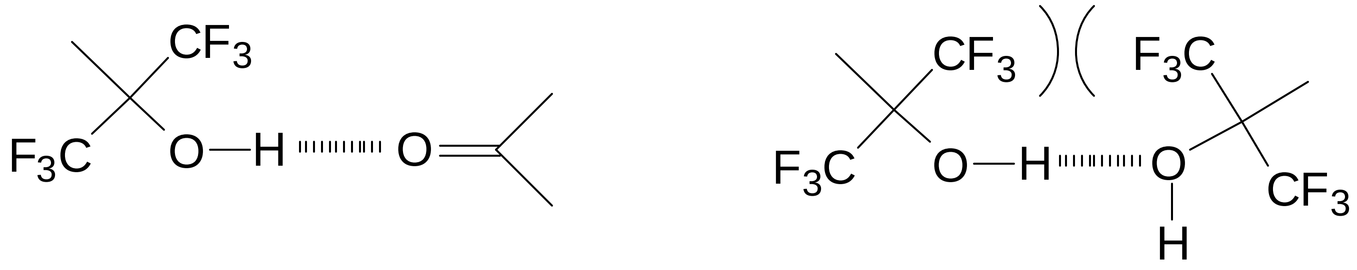
- Readily prepared in moderate to good conversion
- Significant Tg increase from adding bulky side chains
- Good etch resistance
- High absorbance at 157 nm

→ Saturation and Fluorination does not guarantee transparency at 157 nm

A. E. Feiring, E. R. Wonchoba, B. E. Fischel, T. V. Thieu, M. Reza Nassirpour
J. Fluorine Chem. 2002, 118, 95.

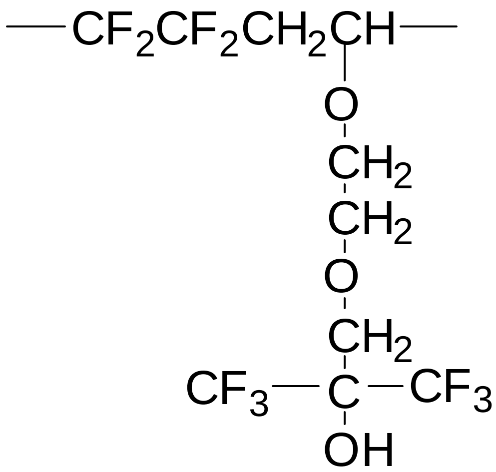
Hexafluoroisopropanol Groups in Polymers

- Excellent Hydrogen Bond Donor
- Less Tendency towards Self-Association than Phenols, Carboxylic Acids, Aliphatic Hydroxyls



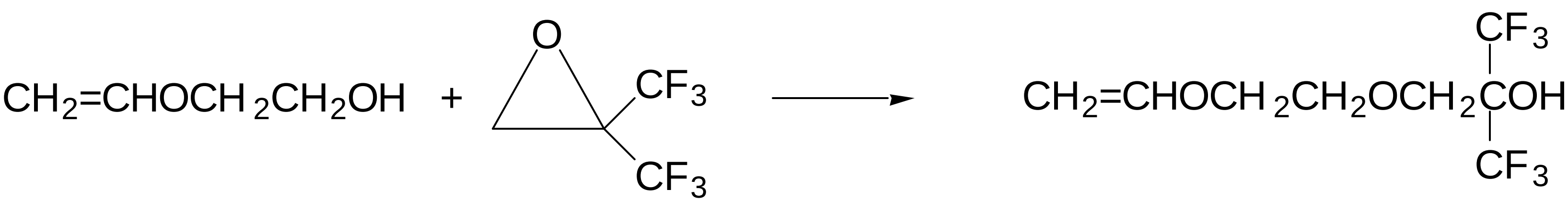
⇒ Useful Substituent for Enhancing Polymer Miscibility

Hexafluoroisopropanol Groups in Polymers



TFE-*alt*-HFIPVE

- Alternating 1:1 Copolymer
- Mn = 173000, Mw = 329000
- Tg = 12 °C



Polymer Blends with TFE-*alt*-HFIPVE

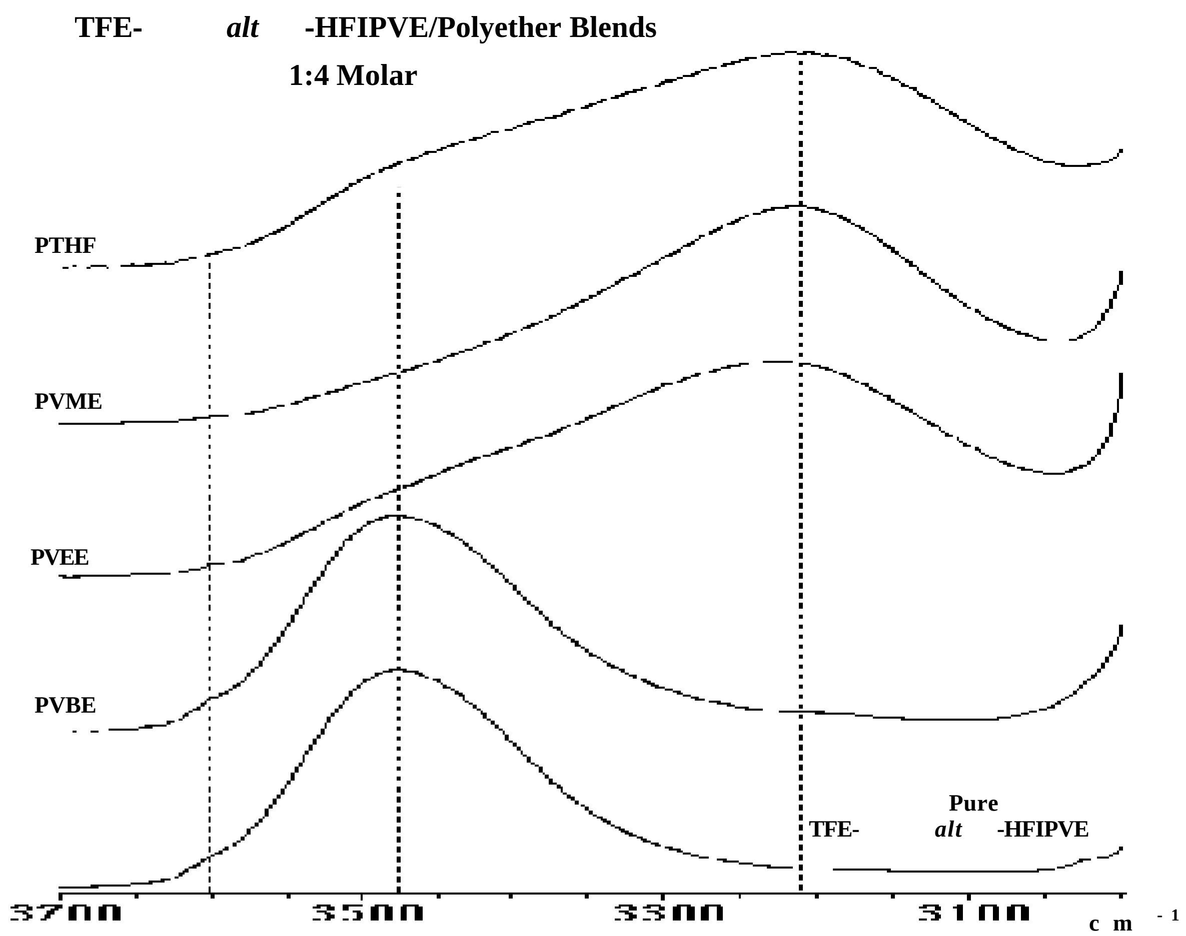
- Polymer Miscibility Evaluated by Infrared and DSC

– Polymethyl Methacrylate	Miscible
– Polyethyl Methacrylate	Miscible
– Polybutyl Methacrylate	Miscible
– Ethylene-co-Vinyl acetate (70 %)	Miscible
– Polymethylvinyl Ether	Miscible
– Polyethylvinyl Ether	Miscible
– Polypropylvinyl ether	Phase Separated
– Polybutylvinyl Ether	Phase Separated

- HFIP Group is powerful blending agent but very sensitive to steric effects

K. S. Guigley, A. E. Feiring, P. C. Painter, M. M. Coleman, J. Macromol. Sci. Physics 2002, B41, 207

Infrared Studies of Blends with Polyethers



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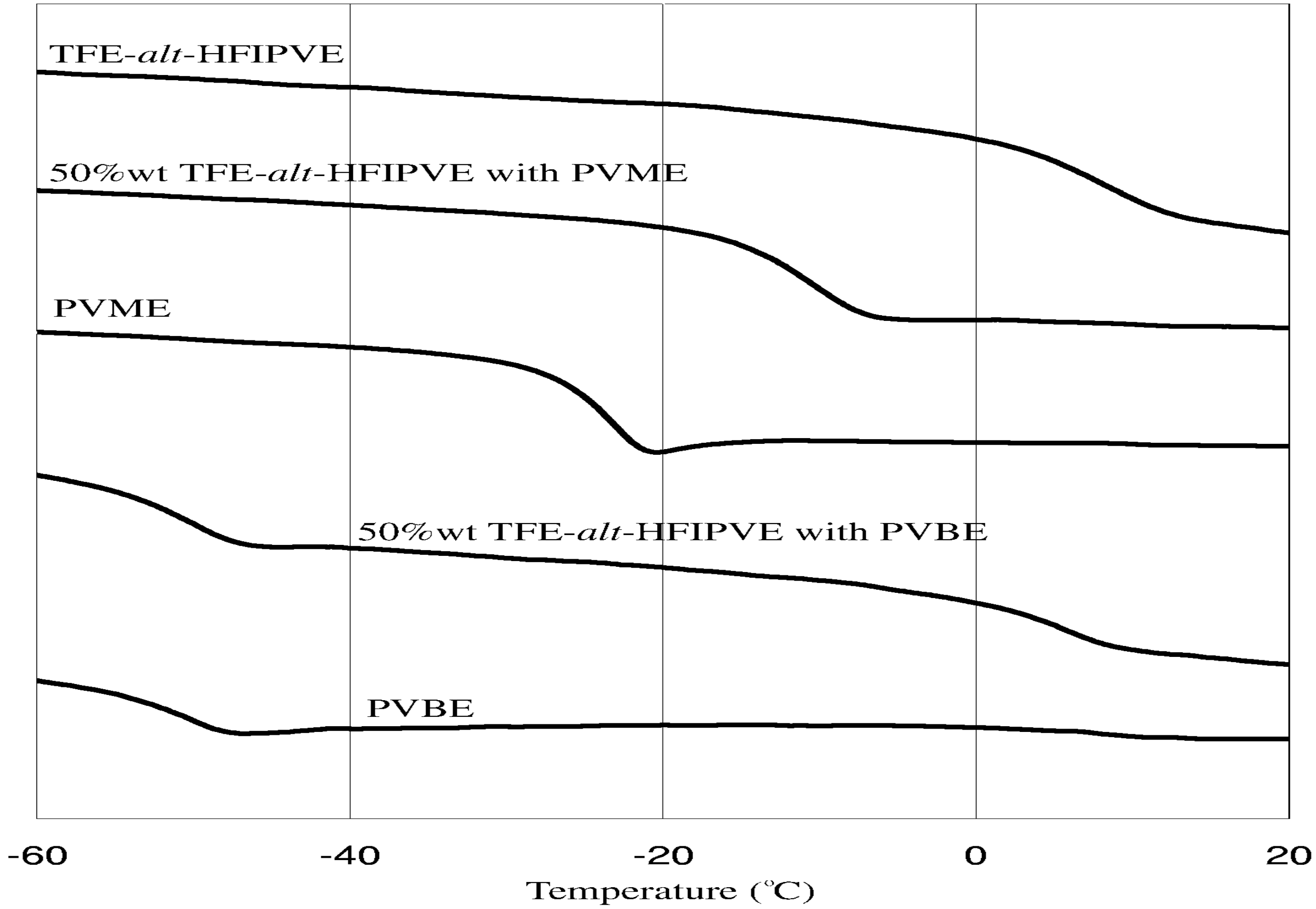
DSC Data on Blends



Summary

- Fluorinated groups critical for transparency and development in next generation photoresists
- Demonstrated:
  - Fluoropolymers with good transparency, etch resistance, thermal stability and aqueous developability
  - 60 nm isolated line imaging of ~160 nm thick resists
  - Manufacture on multikilogram scale
- Families of novel amorphous, high Tg TFE copolymers
  - TFE / TCN Copolymers
  - TFE / Bulky vinyl esters and vinyl ethers
- Utility of hexafluoroisopropanol groups in polymers
- Continuing challenge for resists: Optimize properties in a single polymer

The Resist Teams

Andy Feiring, Brian Fischel, Ed Wonchoba, Ying He, Tho Thieu, Reza Nassirpour

Jerry Feldman, Mary Blasko

Slava Petrov, Bob Smith

Bob Wheland, Gregg McCauley

Frank Schadt, Mark Ramsdell

Mike Crawford, Bob Smalley

Roger French, Dave Jones

Rick Zumsteg, Bill Wheeler, Vince Neal

Ken Leffew, Kevin Crather

Bill Farnham, Hugh Craig

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Pressure Research Laboratory
Synthesis Service
Corporate Center for Analytical Science

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Business Manager: John Schmieg