Is an EUV Film Quantum Yield of 30 Possible?

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Resist TWG
San Jose, CA

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Z-Parameter

$$Z = D_0 \times LER^2 \times HP_{min}{}^3$$

$$\text{and } LER^2 \sim {}^1/_Q \text{, so } Z \sim {}^1/_Q$$

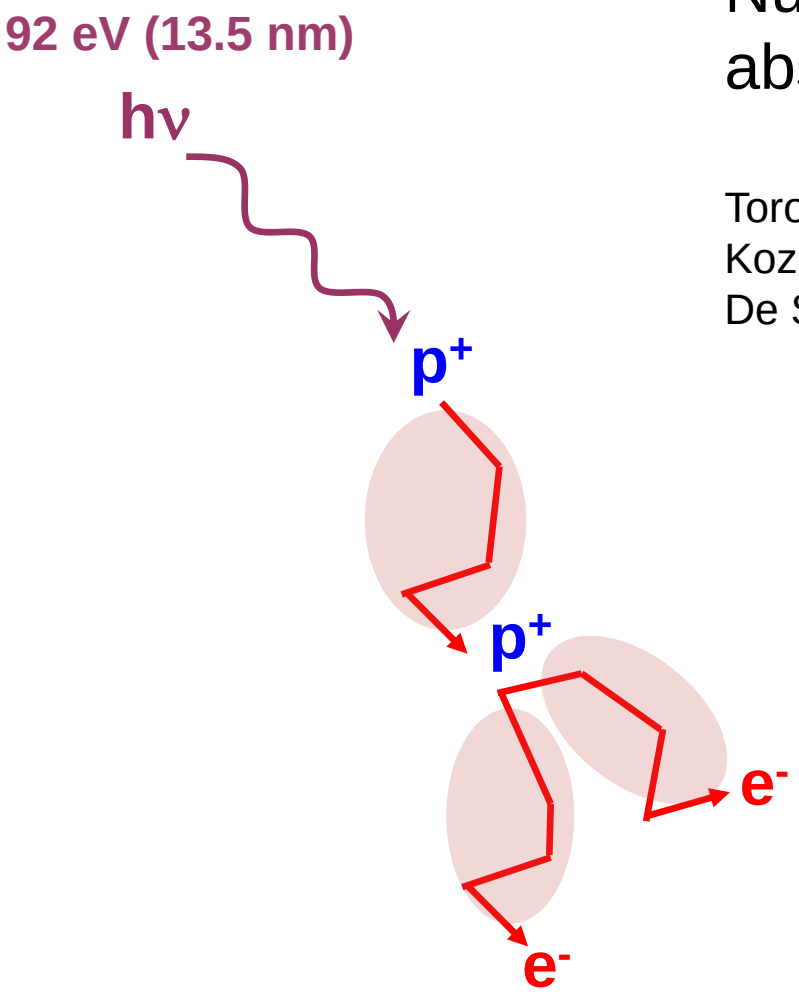
Gallatin et al., SPIE 2008
Gallatin, Naulleau, Brainard, SPIE 2007

For lower z parameter, increase quantum yield:

a) higher optical density (more photons absorbed)

b) better use of the energy from the photons that are absorbed

Electrons and Holes

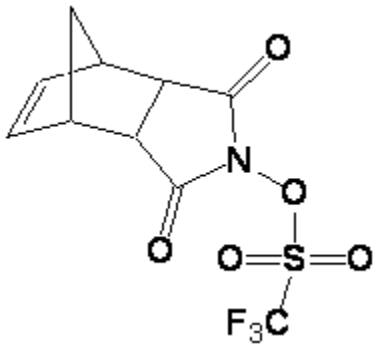


Number of electrons per absorbed photon is about **2-4**

Torok, Photopolymer S&T 2013
Kozawa SPIE 2008
De Schepper SPIE 2015

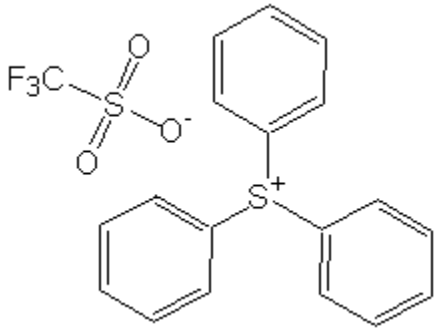
- Hole chemistry at most 4 reactions/photon
- Electron capture reaction at most 4 reactions/photon
- Use the rest of the energy loss events

Some Photo Acid Generators (PAGs)



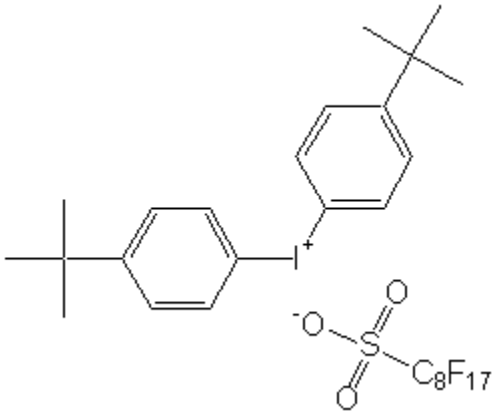
Norbornenedicarboximidyl triflate

NDT



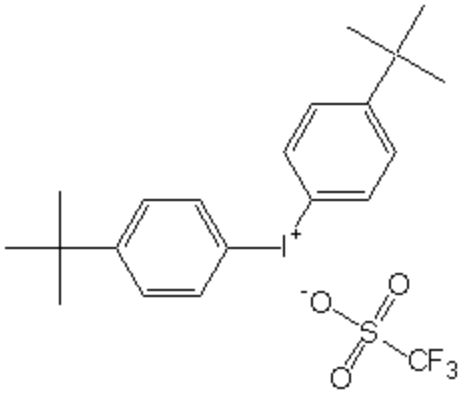
Triphenylsulfonium triflate

TPS-OTf



Bis-(4-tert-butyl-phenyl)-iodonium; PFOS

DTBI-PFOS



Bis-(4-tert-butyl-phenyl)-iodonium; triflate

DTBI-OTf

Find the Weakest Bond!

Look for Bonds to Heteroatoms

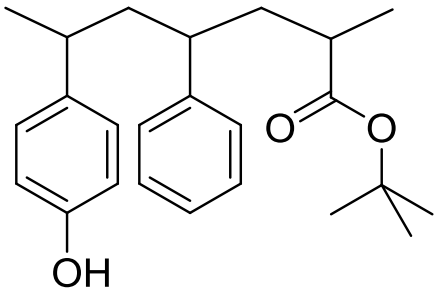
Typical is 2-3 eV

Then 92 eV sufficient for more than 30 reactions!

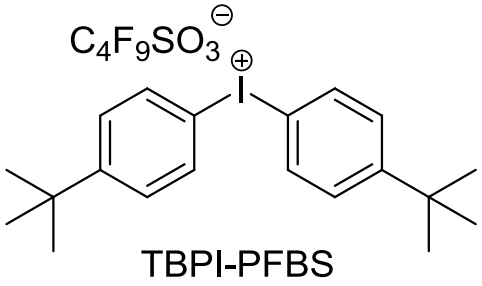
	Average ΔH_{bond} (eV)
C-H	4.3
C-C	3.6
O-O	2.0
C-S	2.8
C-I	2.2
N-O	2.4

Open-Source Photoresist: OS2

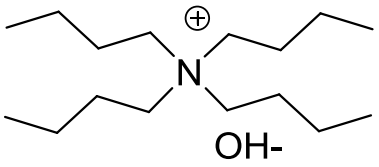
Our baseline material for most of this analyis is an Open Source Chemically Amplified Resist, Called OS2.*



PHS/Sty/TBA
65/20/15 mol %



15 wt.%



1.5 wt% TBAL

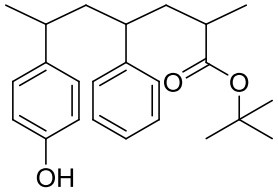
This material was previously measured to have a quantum yield of 3 (3 acids produced per absorbed EUV photon)

*Higgins, Brainard et al. JJAP *50*, 036504, **2011**

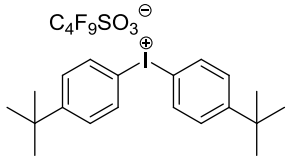
Where does the energy go? look at ionization events

92 eV (13.5 nm)

hν



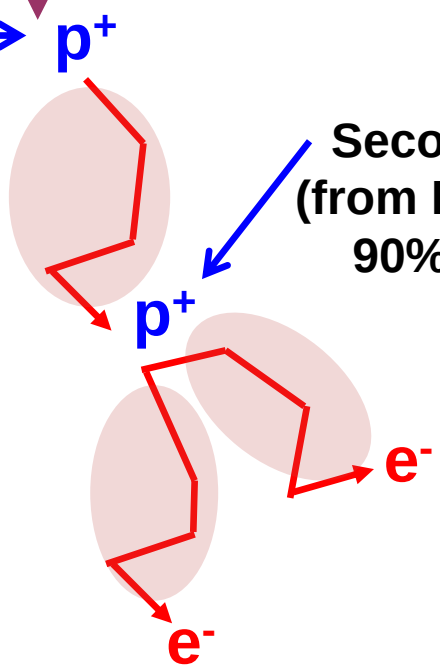
HOStyr/Styr/TBA



TBPI-PFBS

15 wt.%

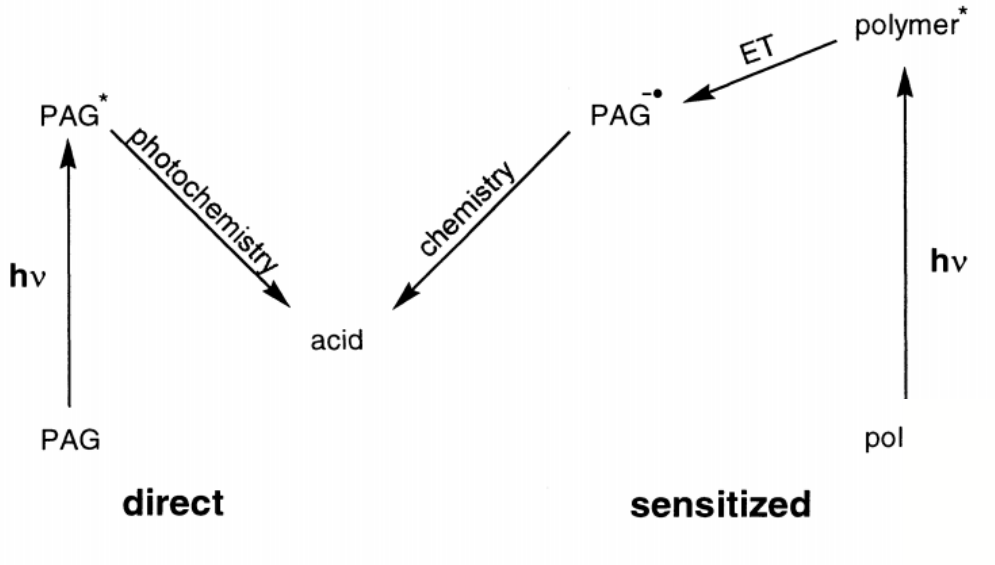
Primary photon absorption
(from CXRO website)
75% in polymer, 25% in PAG



Secondary electron ionization
(from LESiS simulation software)
90% in polymer, 10% in PAG

For this material with 15% PAG, a little over 15% of ionization events in PAG
Is the other energy lost?

Polymer sensitization

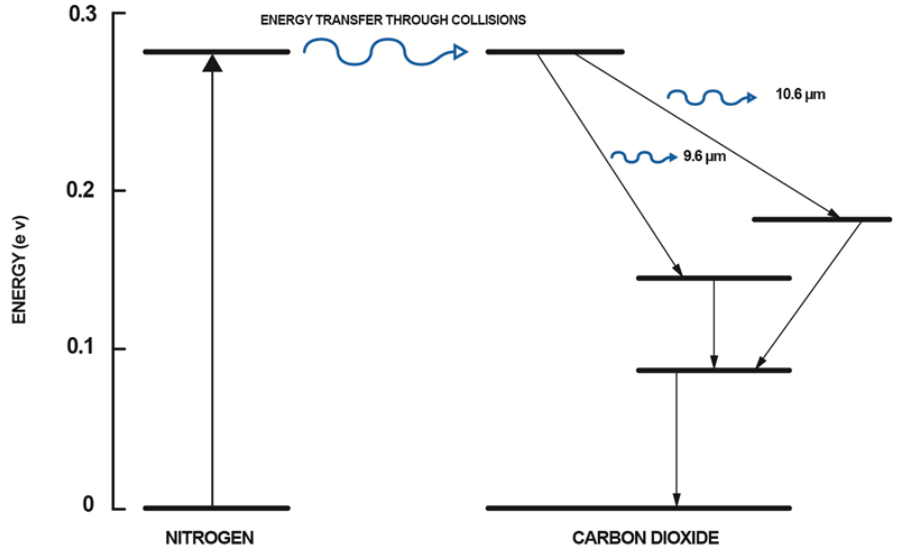


For 193 nm exposures, polymer sensitiz can increase quantum yield by 10x!

Cameron et al., SPIE 2001
Fedynyshyn et al., SPIE 2003
Fedynyshyn et al., SPIE 2008
Barclay, G. G. et al., Polymeric Material Sci Eng, 1994
And many others

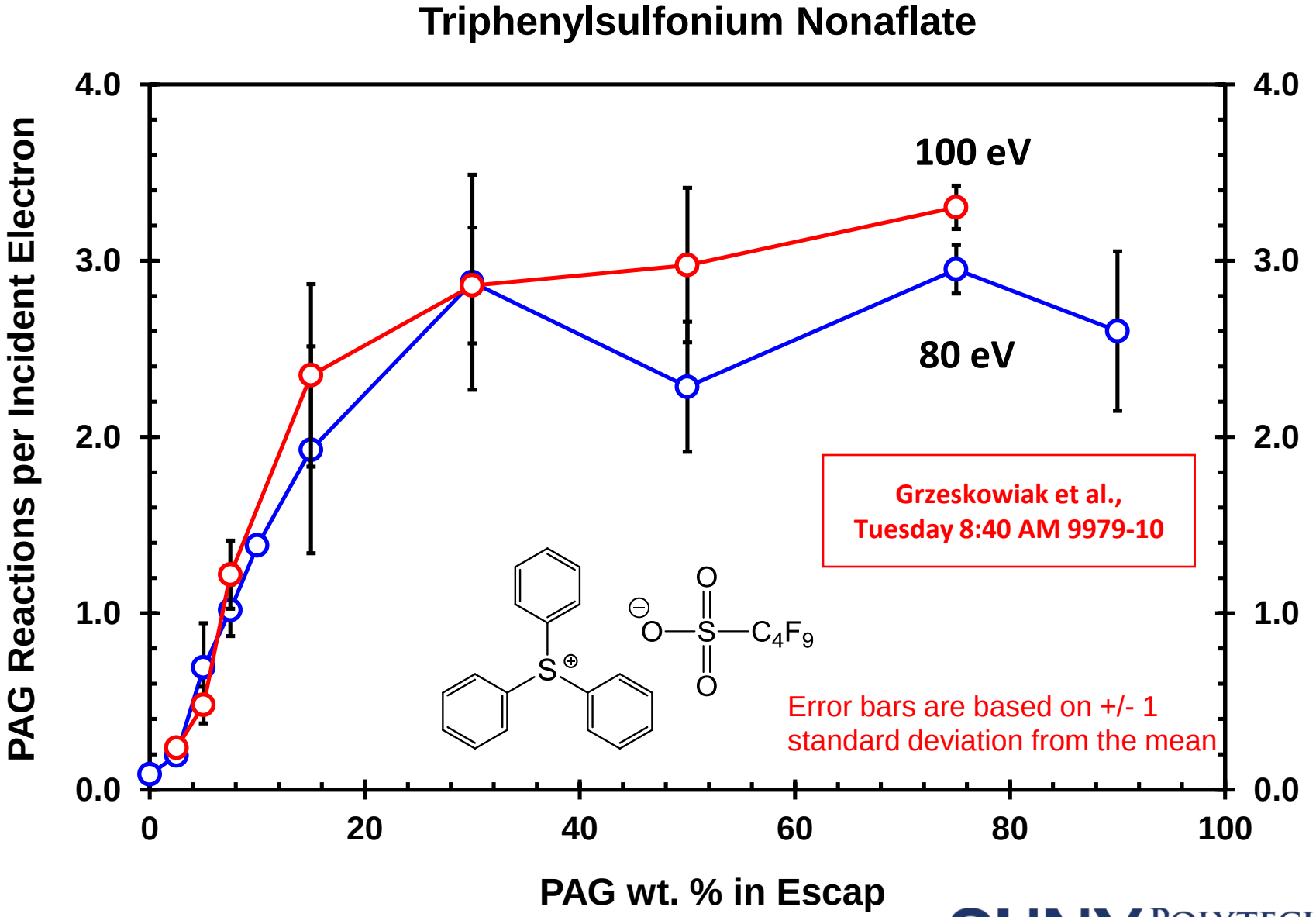
Similar principle as energy transfer in the light source

CO_2 LASER



http://chemwiki.ucdavis.edu/Core/Analytical_Chemistry/Instrumental_Analysis/Lasers

No clear indication of Polymer sensitization of PAG



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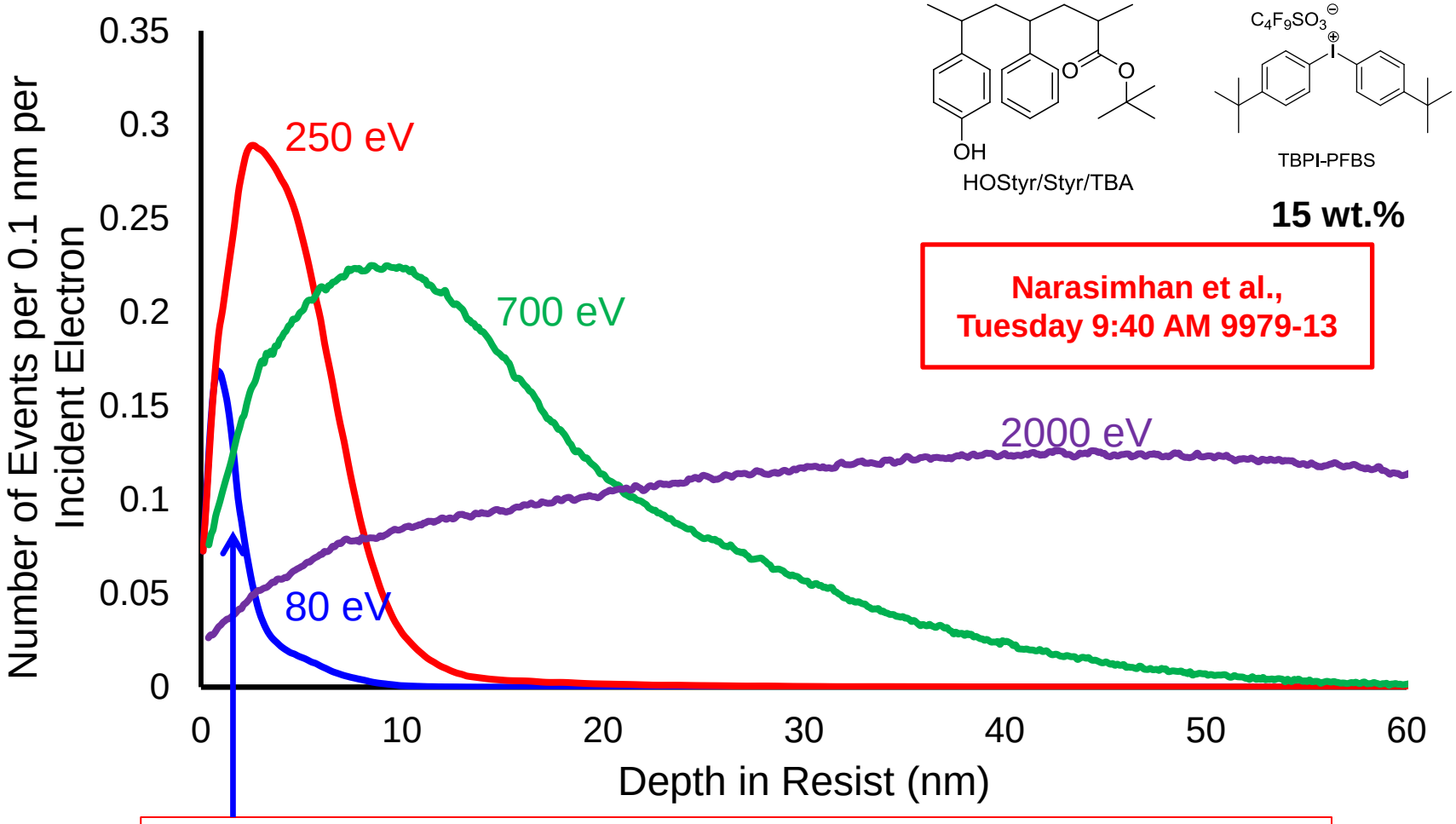
How far does the photoelectron travel?

Includes Electron Trapping
When electron reaches 5 eV



HOStyr/Styr/TBA

TBPI-PFBS

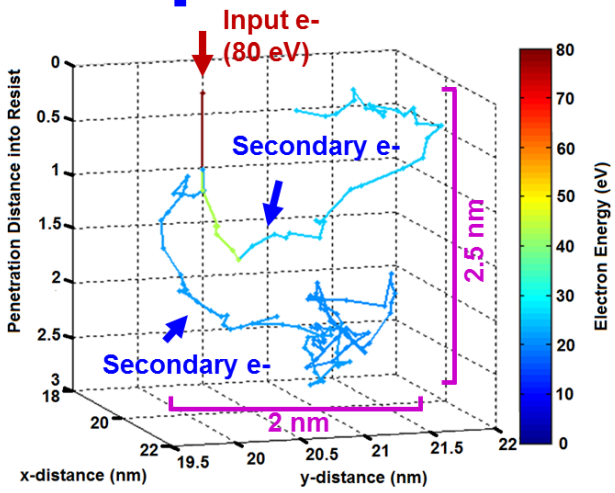
15 wt.%

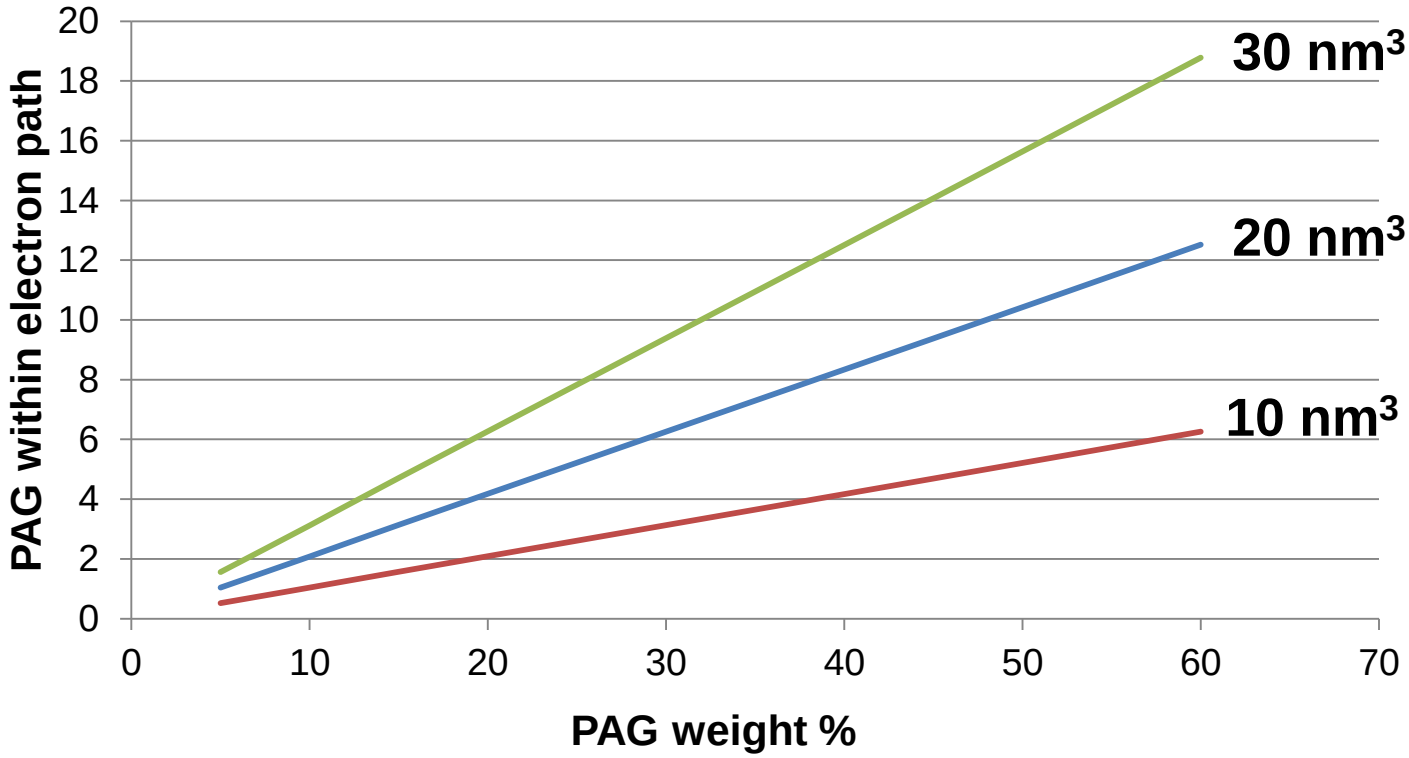
Narasimhan et al., Tuesday 9:40 AM 9979-13

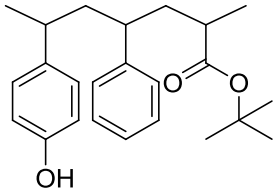
Typical range about 3 nm for a primary 80 eV photoelectron

Are there enough PAG molecules present?

- Electron has net range of about 3 nm. How much volume of resist does the electron interact with?
- If assume approximately 3 nm diameter sphere, then 15 nm^3
- What about secondary electrons, do they add to the total volume or overlap same volume?







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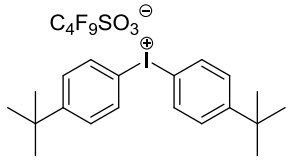

TBPI-PFBS

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What is the Quantum Yield Limit?

Of course, first absorb as many photons as possible

Then, what are the limits to using those that are absorbed:

- Energy – sufficient for >30 reactions/photon
  - Use the energy for the right reactions
- Polymer absorption ~ 80% of ionization events
  - Find system with efficient energy transfer to PAG
- Number of electrons and holes ~4-8 per photon
  - Relevant if internal excitation not efficient process
  - Use material which generates more secondary electrons?
- PAG within path of electron ~10-20
  - Use higher PAG loading

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