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Spectroscopic studies of organosilane-organogermane copolymer photosensitivity for write-as-needed patterning applications

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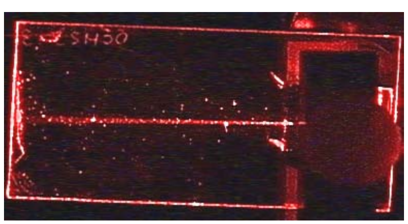
OUTLINE

- **Introduction**
  - Photosensitive materials - application
  - Molecular hybrid materials: Polysilane and Ge-Si co-polymer
- **Experimental**
- **Results**
  - Effect of composition and local environment
    - Refractive index
    - Absorption spectroscopy (near-UV)
    - Vibrational spectroscopy (FTIR)
- **Conclusion**

Photosensitive materials

- **Photosensitivity**: stable photoinduced optical property changes – Δn
- **Application**: Write-as-needed photopatterning
  - Engineered material response to enable photosensitive response with integrable sources (incident λ compatibility)
  - High Δn response with low fluence exposure
  - Reliable photoresponses under different environmental condition
- *Molecular hybrid materials (polysilane-based materials)*



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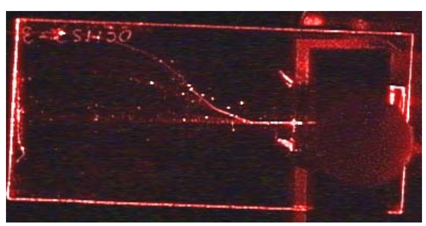

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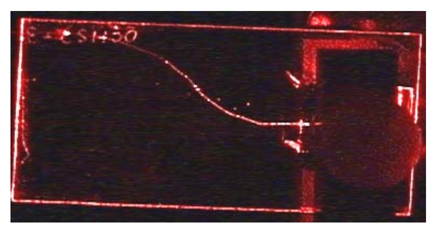


t = 3 min

Molecular hybrid materials – Linear chain polysilane (polysilylenes)

- σ-bond conjugation provides electron delocalization along backbone and **high sensitivity to structural modification or disruption.**
- Lowest energy absorption associated with σ– σ* transition (HOMO-LUMO) of backbone structure.

Structural influence on optical absorption:

R-group selection:

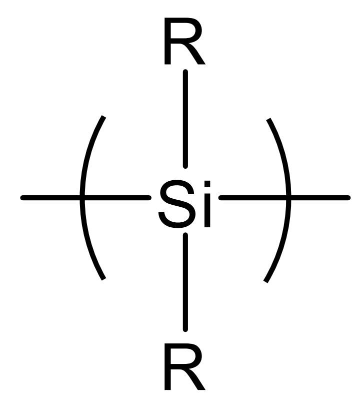
✓ *backbone conformation through steric effects*

✓ *contributions to $\sigma - \sigma^*$ energy state character*

Backbone identity:

✓ $\sigma - \sigma^*$ *energy*

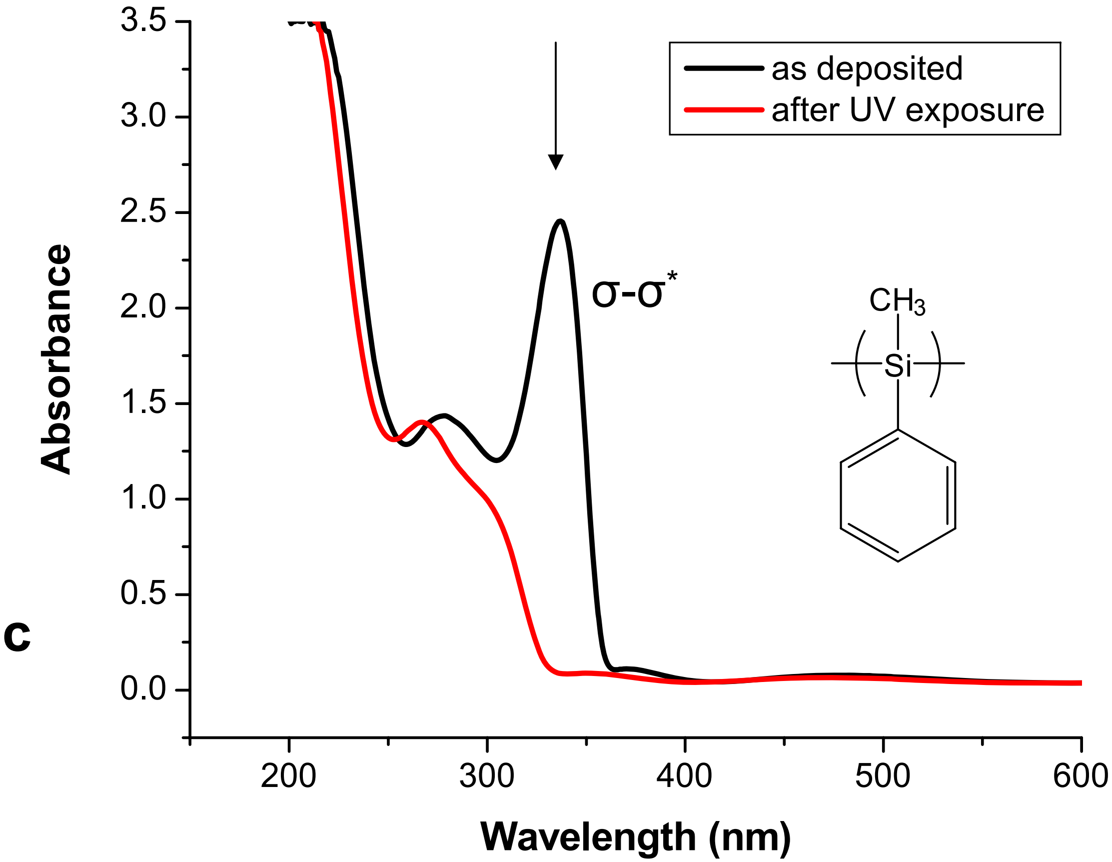
Chain length (MW):



Miller, R.D., *Chem. Rev.*, **89**, 1359 (1989)
Potter *et al*, *J. Non-cryst. Sol.* **352**, 2618 (2006)

Poly(methyl)(phenyl) silylene (PMPS)

- **Responsive to UV irradiation from nitrogen laser (λ_{inc} = 337 nm) and excimer laser (λ_{inc} = 248 nm)**
- **$\Delta n_{632.8nm}$= – 0.04 to – 0.14**
- **Previously studied under different local atmospheric environments**



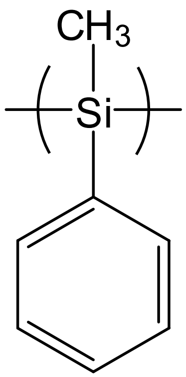
Potter *et al.*, *Eur. J. of Glass Sci. and Tech. Part B.* **47**, 105-109 (2006).
Potter *et al.*, *J. Non-cryst. Solid* 352(23-25), 2618-2627 (2006).

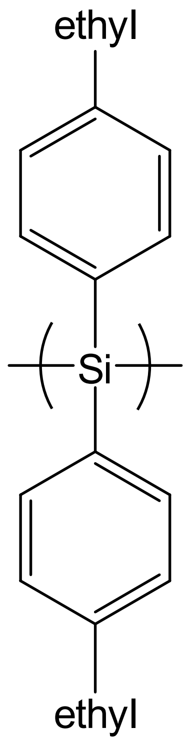
Objectives

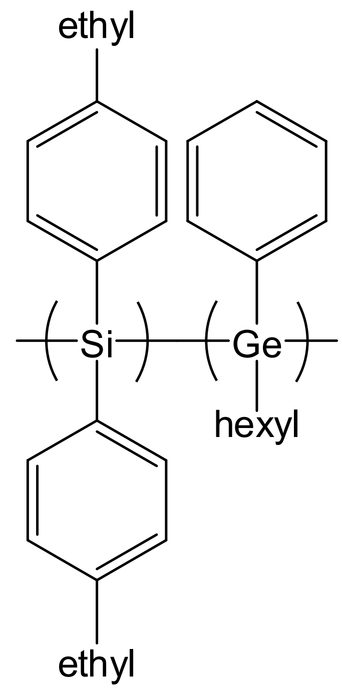
- Engineer polysilane based materials responsive to compact LED sources operating in the 350 – 380 nm range.

- Confirm photosensitive behavior of modified materials under different local atmospheres
  - Optical properties
  - Structural modification

Materials selection







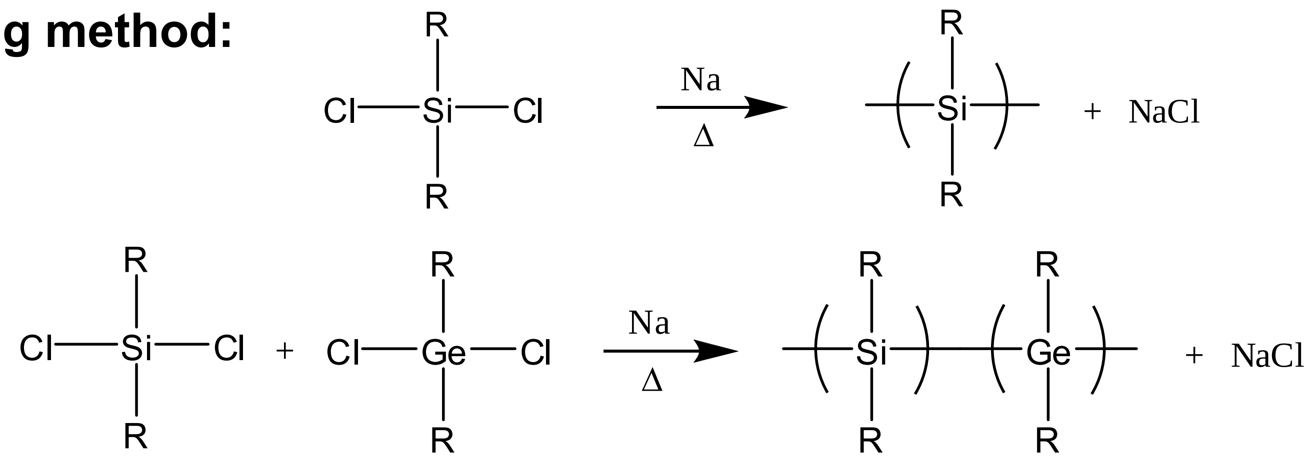
poly(methylphenyl)silane
(PMPS)

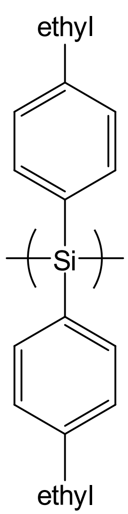
poly(bisphenylethyl)silane
(PBPES)

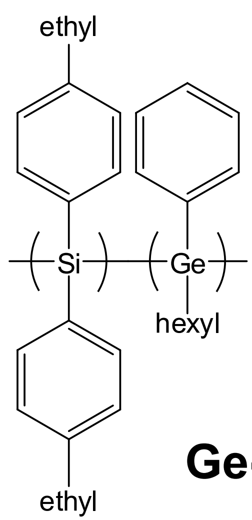
poly(bisphenylethyl)silane-co-(hexyl)(phenyl)germane
(Ge-Si copolymer)
(5 : 95 %mol)

Polymer synthesis

Wurtz Coupling method:







Ge-Si copolymer

PBPES

(Sandia National Laboratories)

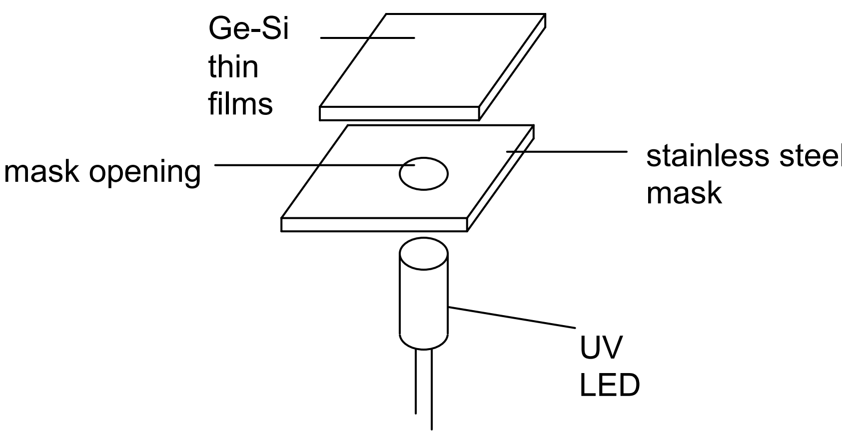
Thin films preparation

- **Ge-Si copolymer**
  - UV-visible absorption
    - ✓ Solution (6.25% wt Ge-Si/THF)
    - ✓ Substrate: SiO_2
  - FTIR
    - ✓ Solution (12.5% wt Ge-Si / THF)
    - ✓ Substrate: KCl
- **PBPES**
  - Solution (0.33% wt. PBEPS / THF)
  - Substrates: SiO_2 (UV-vis) and KCl (FTIR)

- **Spin-coating (2500 rpm, 30s) and annealing 50 C / 30 min to remove remaining THF**
- **Solution preparation and depositions performed in dry argon environment under reduced light conditions.**

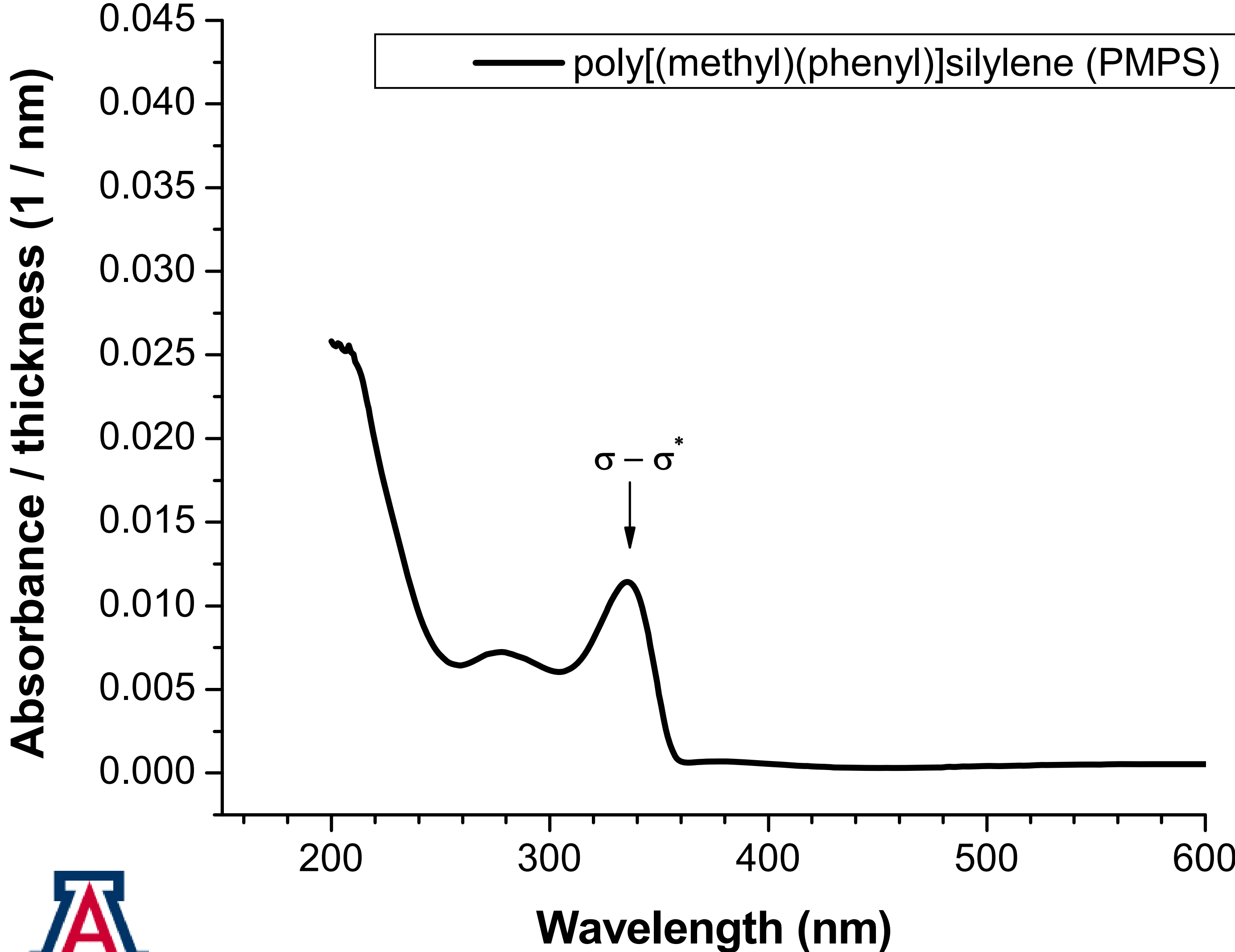
Optical Exposure Conditions

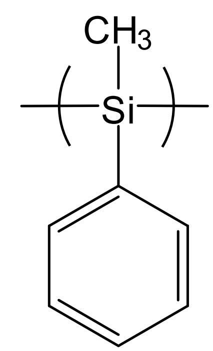
- **UV LED**
  λ = 370 nm (3.35 eV) cw
  P = 1.16 mW/cm^2.
- **Local environment during exposure – air and N_2**



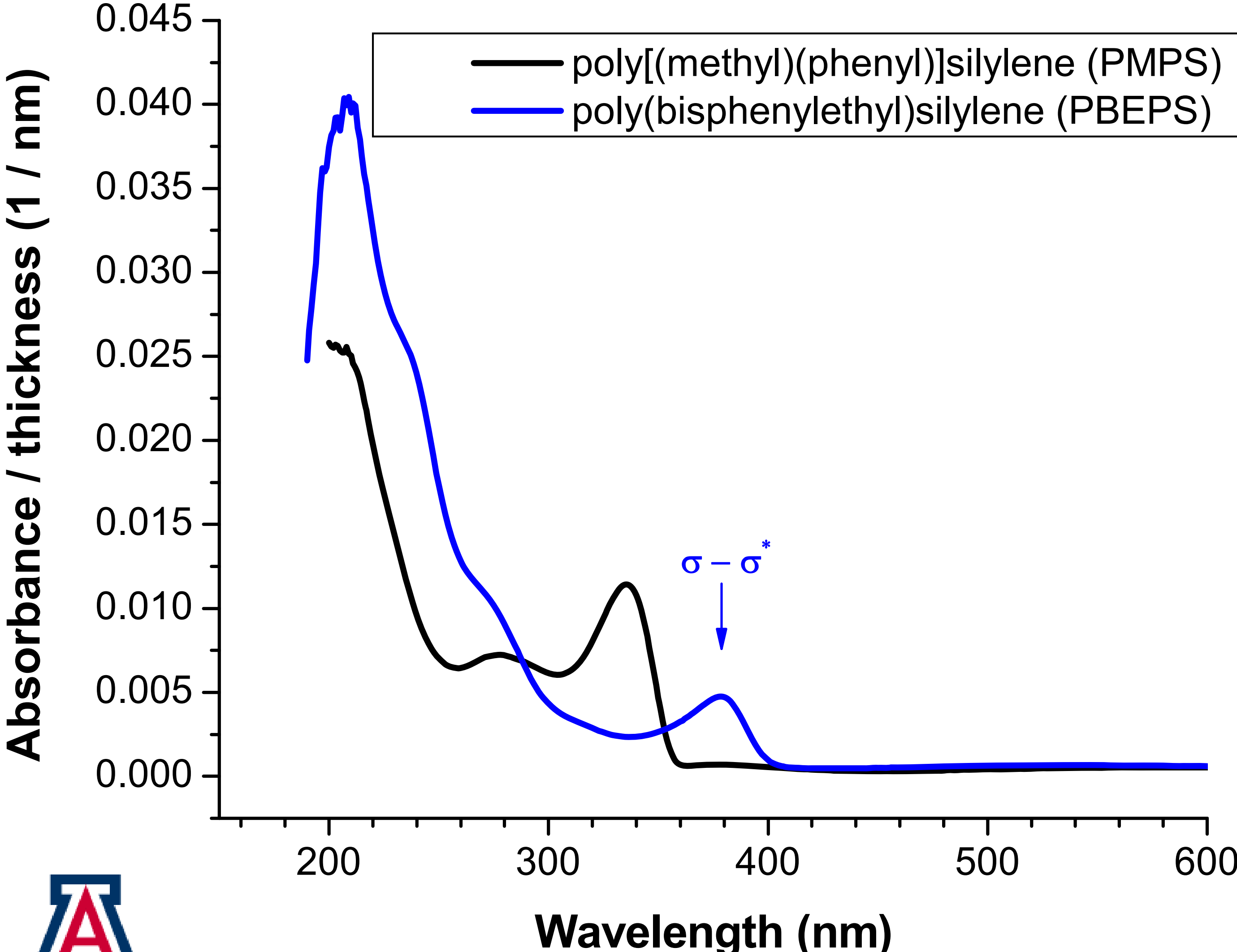
Roithner Lasertechnik

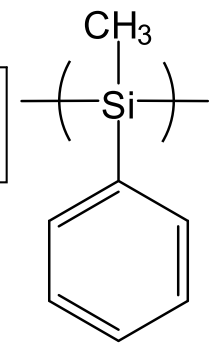
Near-UV absorption

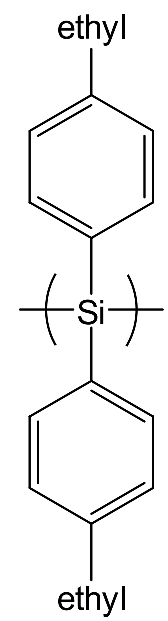




Near-UV absorption

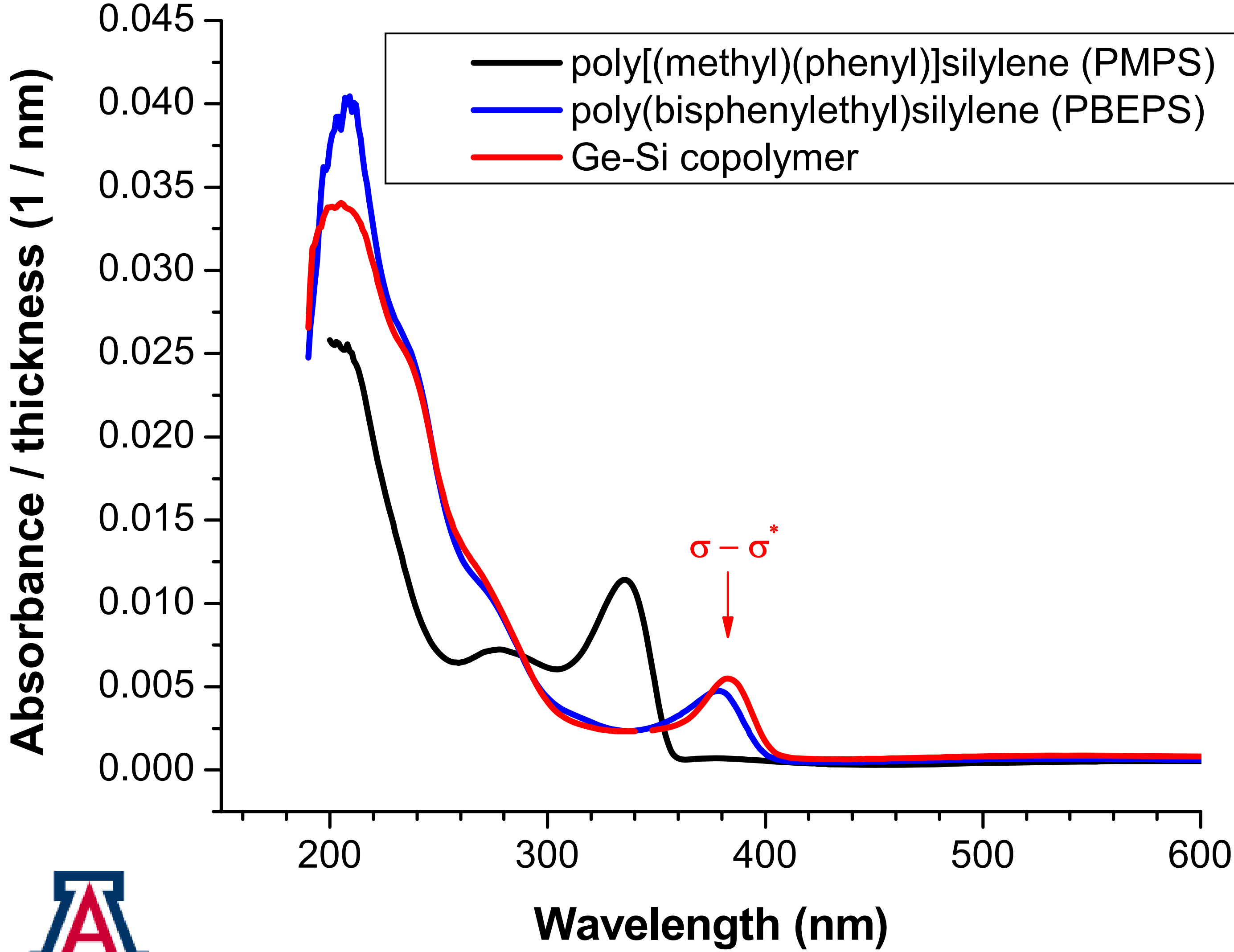


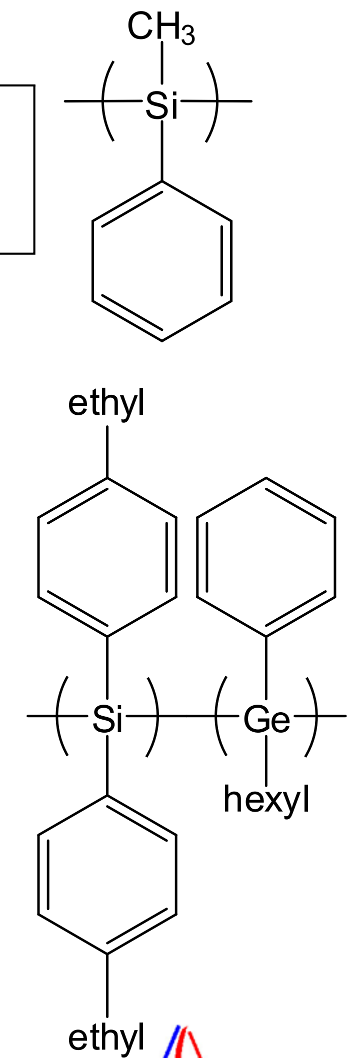




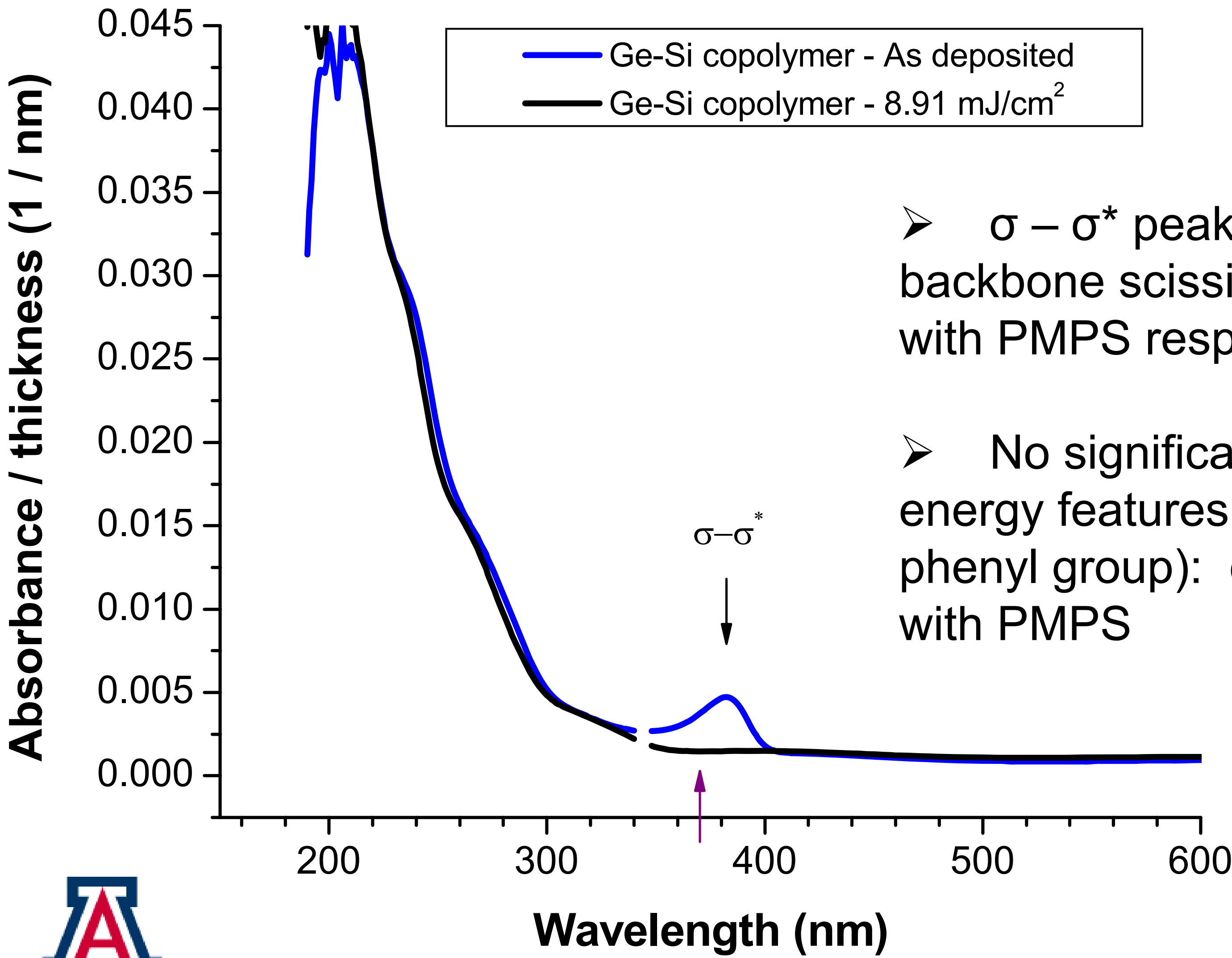
R.D. Miller, *J. Polymer Sci. Part C* **25**, 32 (1987)

Near-UV absorption



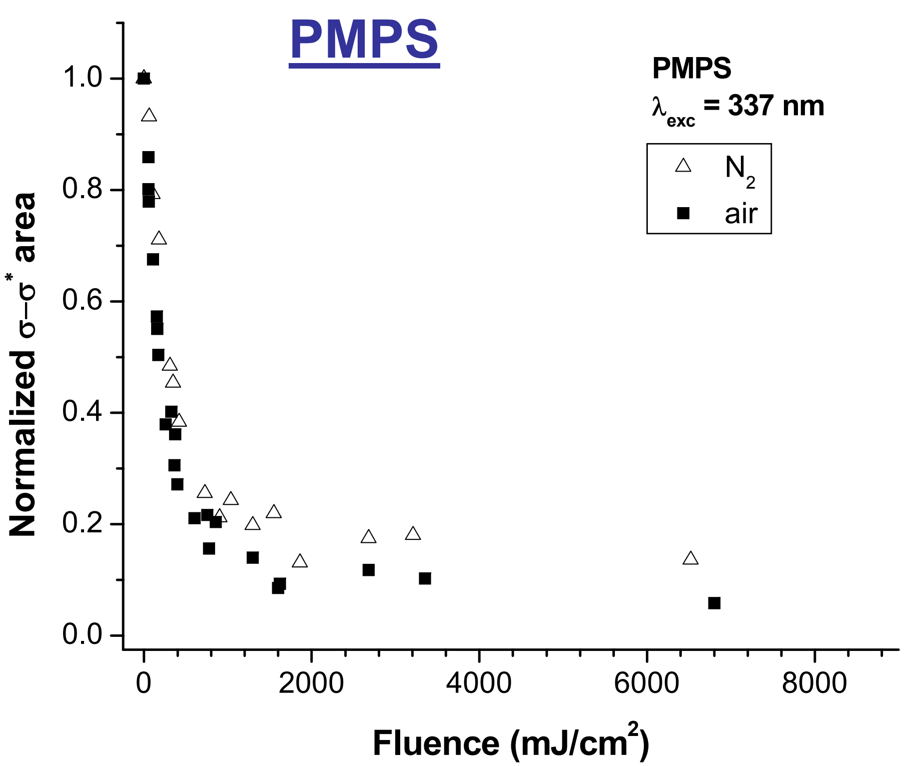


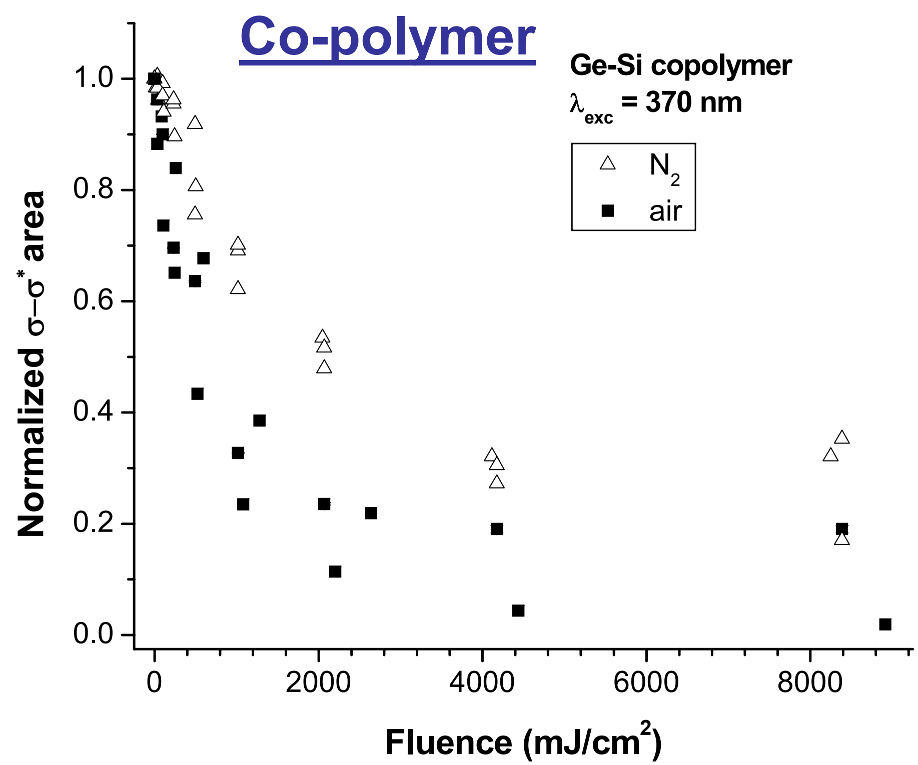
Near-UV absorption – UV-induced bleaching



- σ – σ* peak bleach observed: backbone scissioning consistent with PMPS response.
- No significant impact on higher energy features (associated to phenyl group): contrasts behavior with PMPS

Absorption Bleaching: σ – σ* peak area

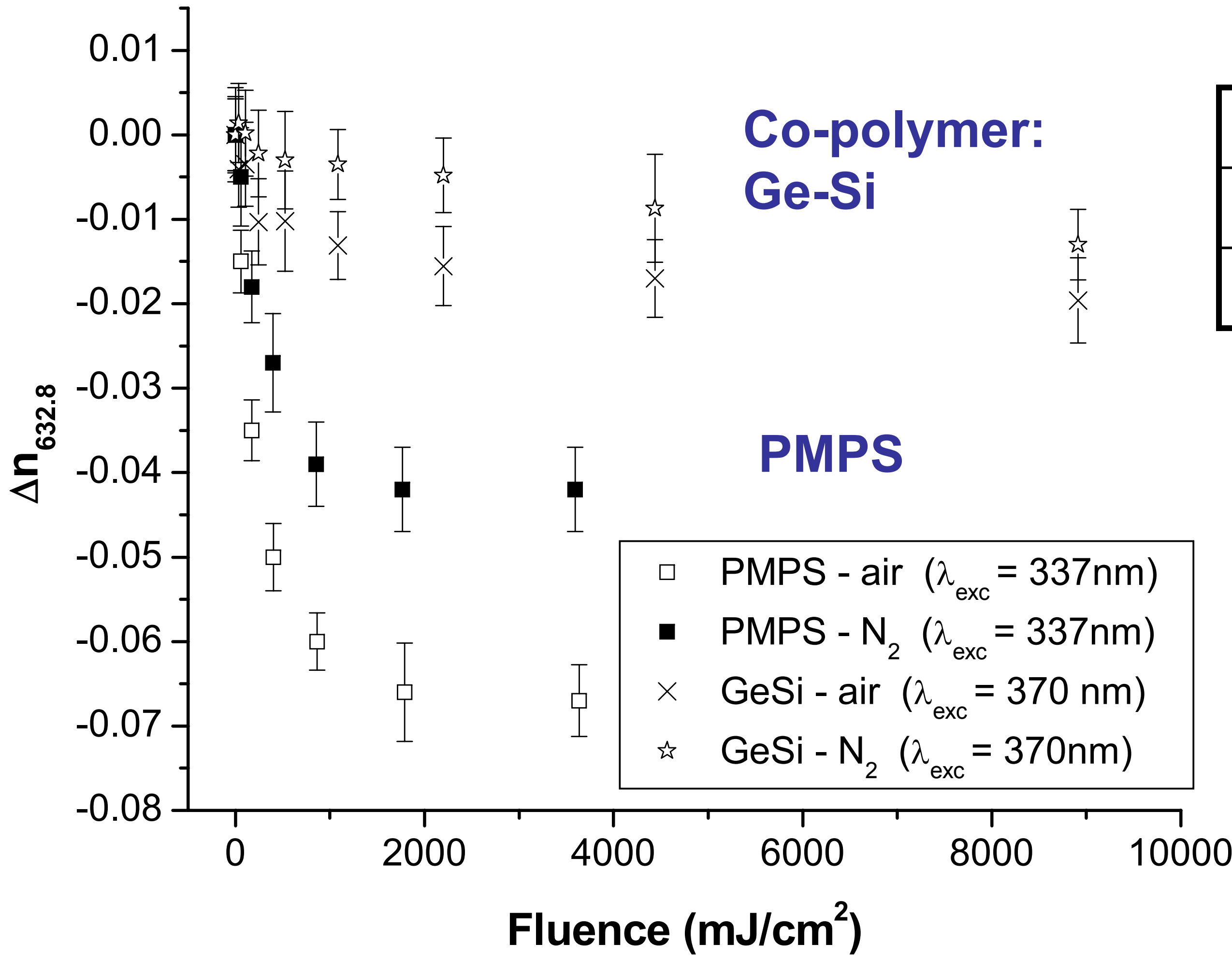




- UV-bleaching of co-polymer system slower (with UV-fluence) compared to PMPS
- Effect of atmosphere more pronounced in co-polymer

Potter *et al*., Materials *Letter* **59**, 326-329 (2005)

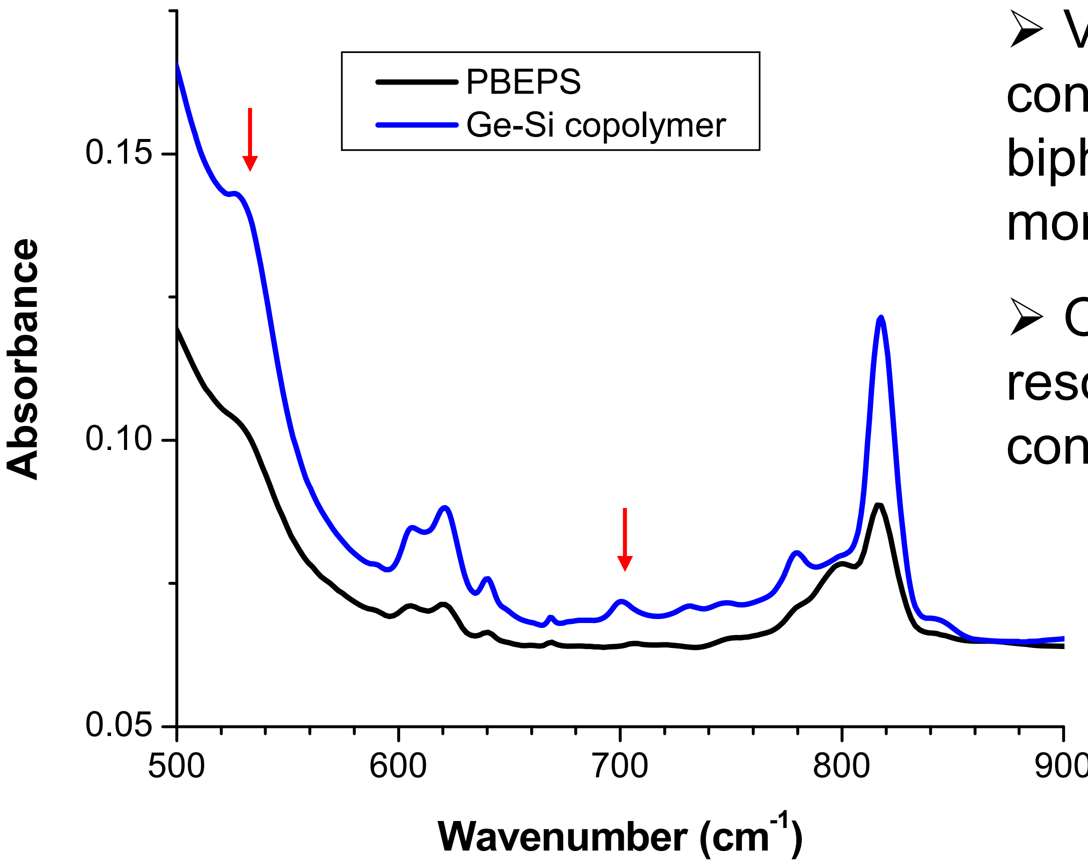
Photoinduced Refractive Index Change



$\Delta n_{632.8}$	Air	N_2
PMPS	-0.07	-0.04
Ge-Si	-0.02	-0.01

Potter *et al.*, *Materials Letter* **59**, 326-329 (2005)

Vibrational Structure

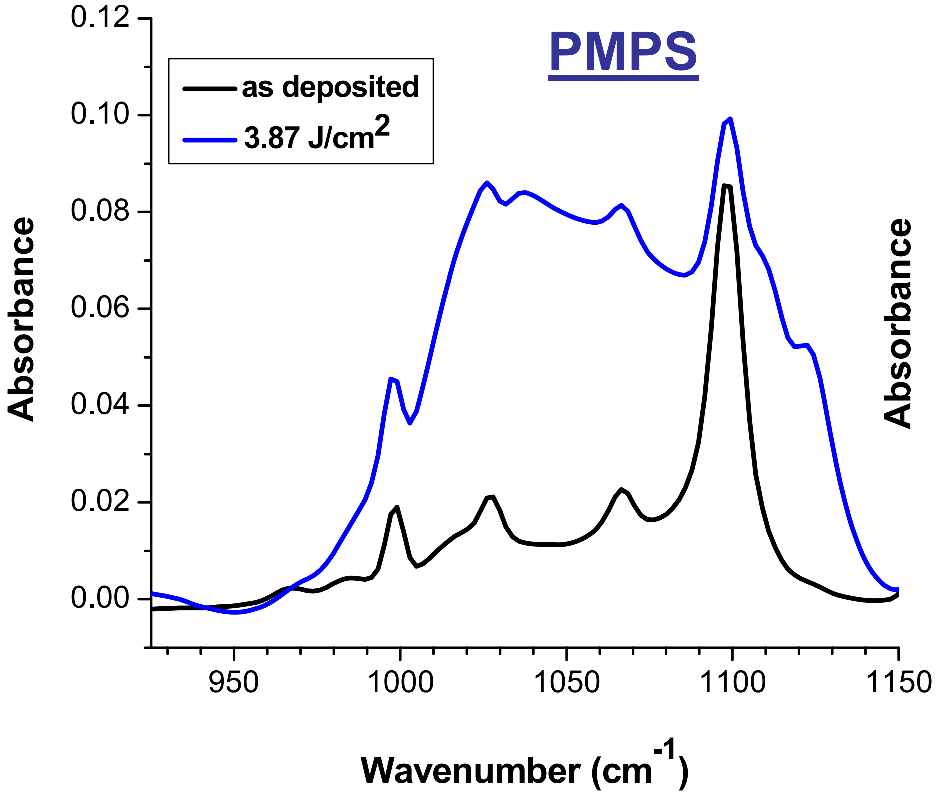


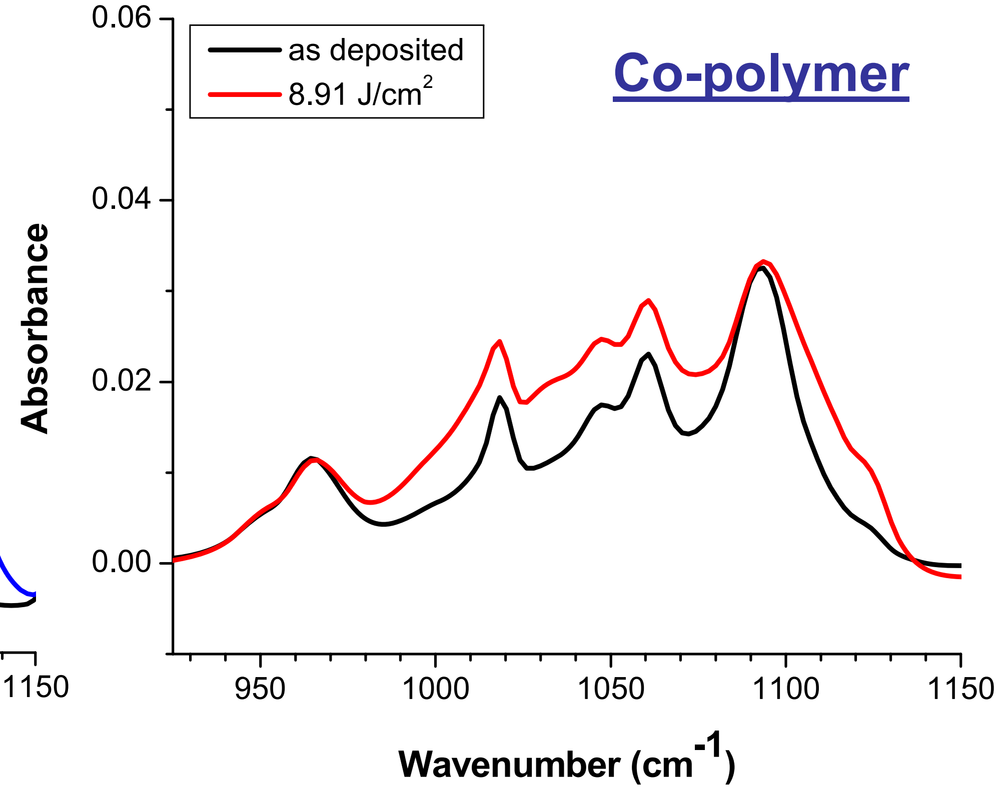
- Vibrational resonances consistent with the presence of biphenyl group associated with Si monomer
- Observation of hexyl-based resonances in co-polymer consistent with Ge repeat unit
  - ✓ 540-485 cm^{-1}: straight chain alkanes (str.)
  - ✓ ~700 cm^{-1}: $–(CH_2)_n–$, n > 3 (rocking vib)

G. Socrates, Infrared and Raman Characteristic Group Frequencies, 3rd Edition, (John Wiley & Sons, 2001)

M. Gazicki, *Thin Solids Film* **256**, 31 (1995)

FTIR: Siloxane formation





- Si-O-Si asymmetric stretch vibration evolves in co-polymer with resonant excitation of Si-Si σ-σ* backbone transition
- *Photosensitive modification linked to backbone scissioning and siloxane formation – Consistent with PMPS*

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Conclusions

- **Modified photosensitive response of polysilane material system through changes in side-group and backbone chemistries.**

- **Lowest excited state absorption (σ– σ*) red-shifted approximately 45 nm to 380 nm.**
  - Anticipated due to all-*trans* backbone conformation enforced by large side group

- **Photoinduced refractive index change in modified material reduced below that observed in PMPS under consistent excitation conditions (resonant excitation, atmospheric composition).**
  - Aerobic environment provide more effective photoinduced modification
  - Rate of absorption bleaching and Δn evolution with fluence lower in co-polymer system.
  - Magnitude of Δn lower in co-polymer system compare to PMPS (-0.02 compared to – 0.07)
  - Lower absorbance exhibited in copolymer system at σ– σ* wavelength likely contributed to reduced rate of UV-induced response with fluence compared to PMPS

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Conclusions, con'd.

- **Photostructural mechanisms accompanying Δn in co-polymer consistent with those observed in PMPS system**
  - Backbone chain scissioning with siloxane bond formation
  - Limited impact on side group vibrational structure – likely contributes to reduced magnitude of saturated Δn
- **Limited spectroscopic evidence for significant effect of Ge in backbone on photosensitive response in the 5% Ge-content co-polymer.**
  - Modifications in $\sigma - \sigma^*$ transition in the co-polymer system appear largely the result of side-group effects to enforce backbone conformation

Acknowledgement

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  - a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.
- **State of Arizona TRIF Optics Initiative**