

High Refractive Index Resists

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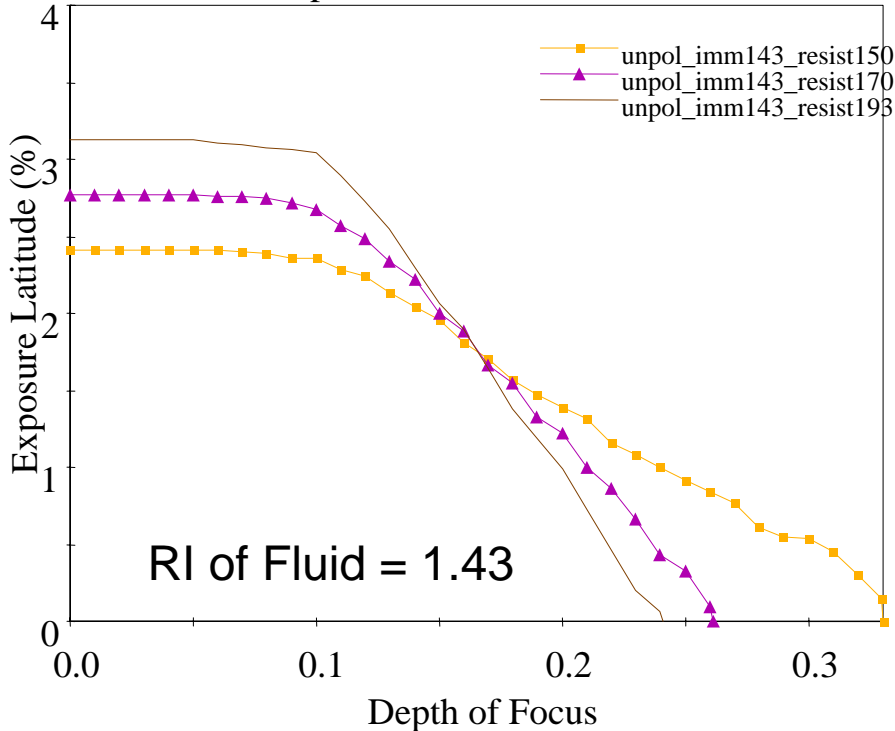
University of Queensland, Australia

Plan of This Talk

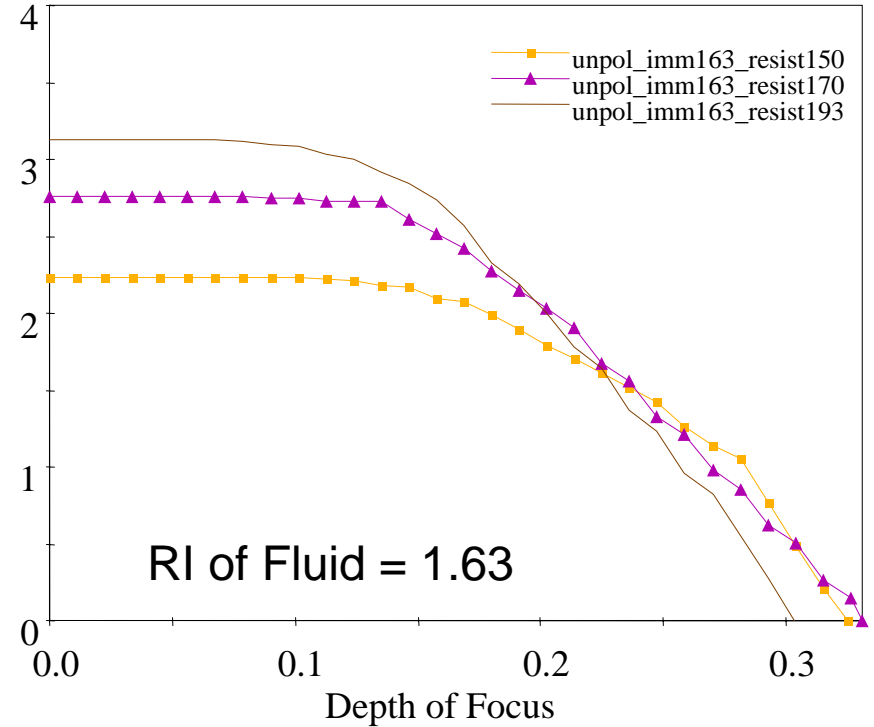
- Brief Introduction to Approach
- Update on QSPR
- Synthesis
 - Thiomethacrylates
 - Michael-addition polymers
- Update on Modelling

Why High RI?

Exposure Latitude vs. DOF



Exposure Latitude vs. DOF



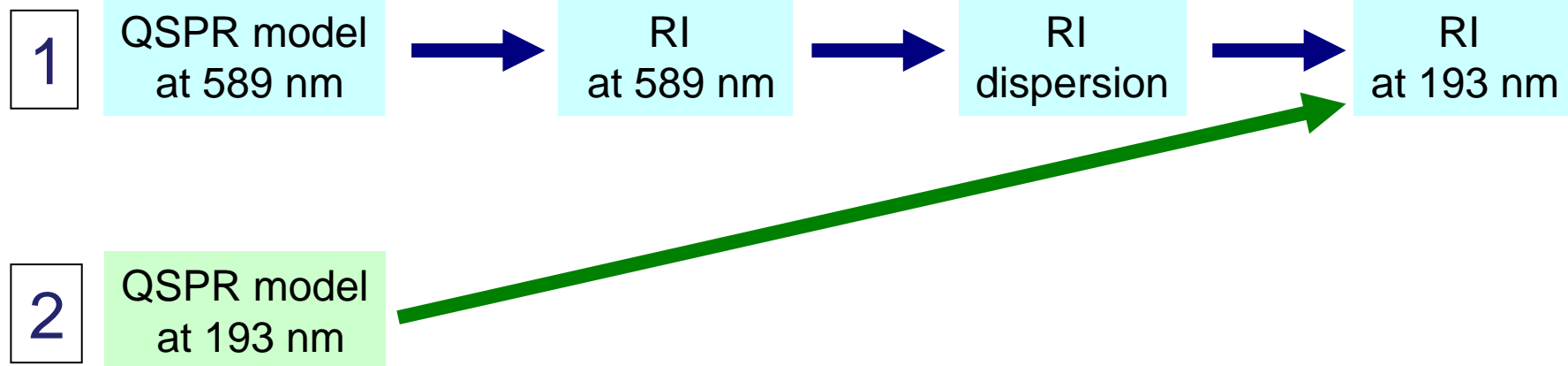
- Fluid RI of 1.43 and 1.63 (32nm on 100nm pitch, binary, unpolarized)
- Resist index of 1.5, 1.7 and 1.93

Conley, SPIE, Feb 2006

Approach to High RI Resists

- Examination of the literature showed that highly-polarizable groups confer high RI
- Initial candidates have high sulfur content
 - RI of a-PP = 1.474 and PPS = 1.596 @ 589 nm
- Refine selection with a quantitative model
 - QSPR model
- Synthetic program

QSPR Approach



Route	Advantages	Disadvantages
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1

Large amount of RI data available
Accurate QSPR model

Multiple steps
Depends on knowledge of RI dispersion

QSPR Model at 589 nm

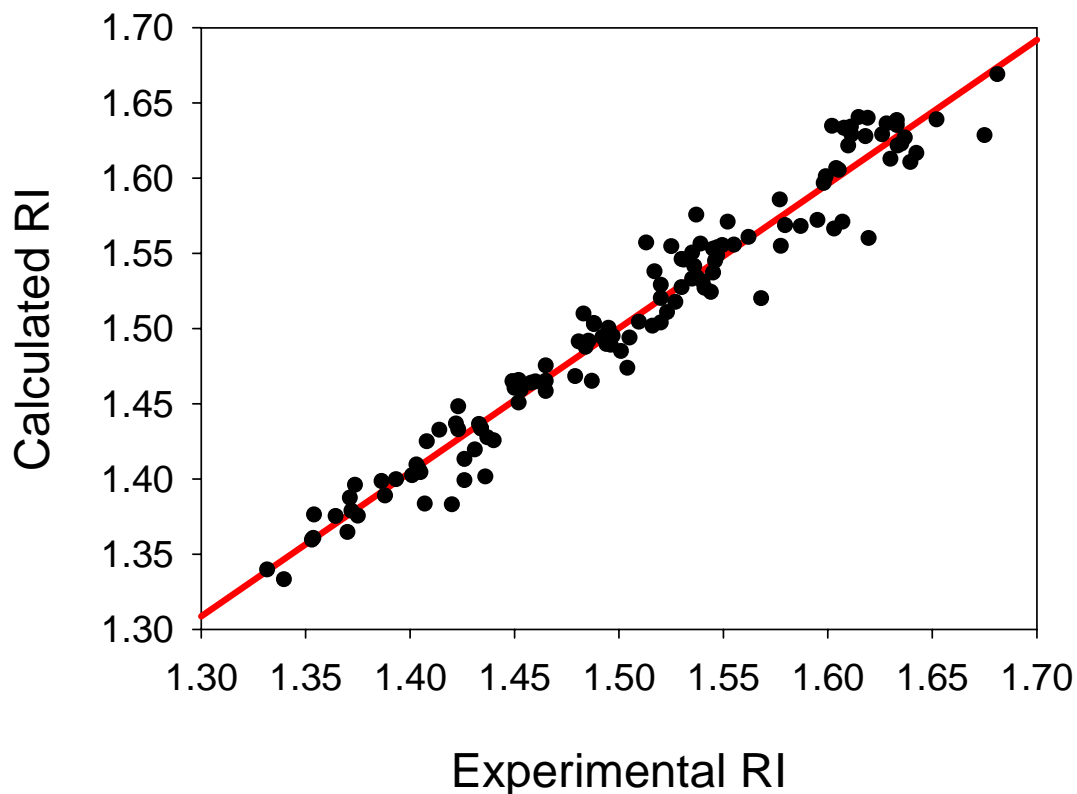
Diverse set of 126 model compounds were used

$$RI = \sum_{i=1}^9 k_i \cdot \text{Descriptor}_i$$

- 9 parameters
- Stable with high correlation
- $R^2 = 0.96$

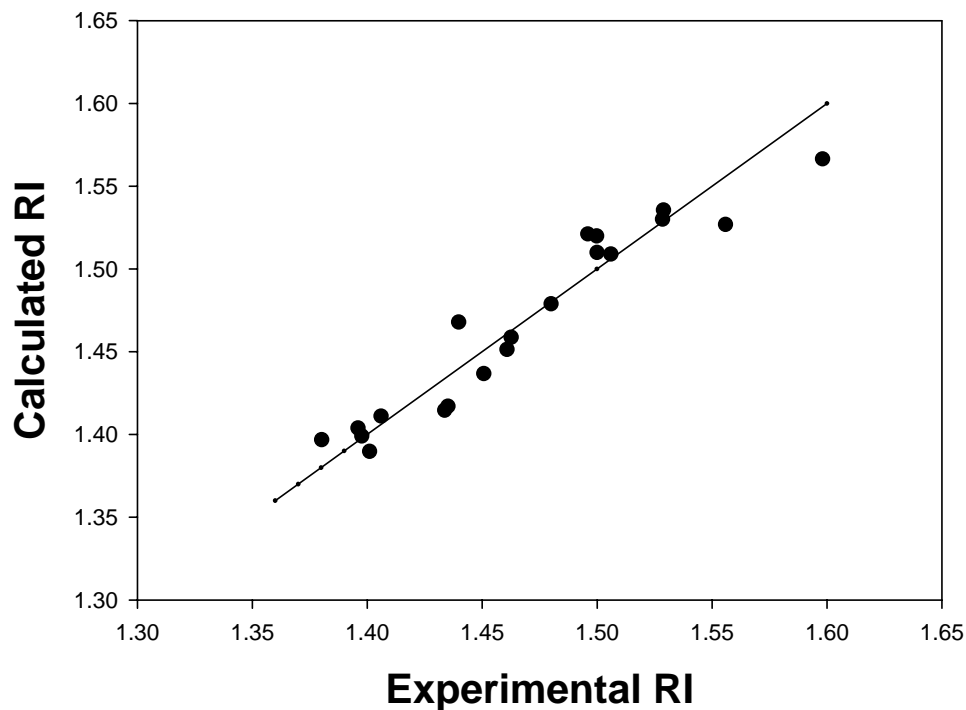
- Cross-validated
- $R^2 \text{ (CV)} = 0.95$

126 Structures
 $R^2=0.9580$ $F=293.8$ $S^2=0.0003$

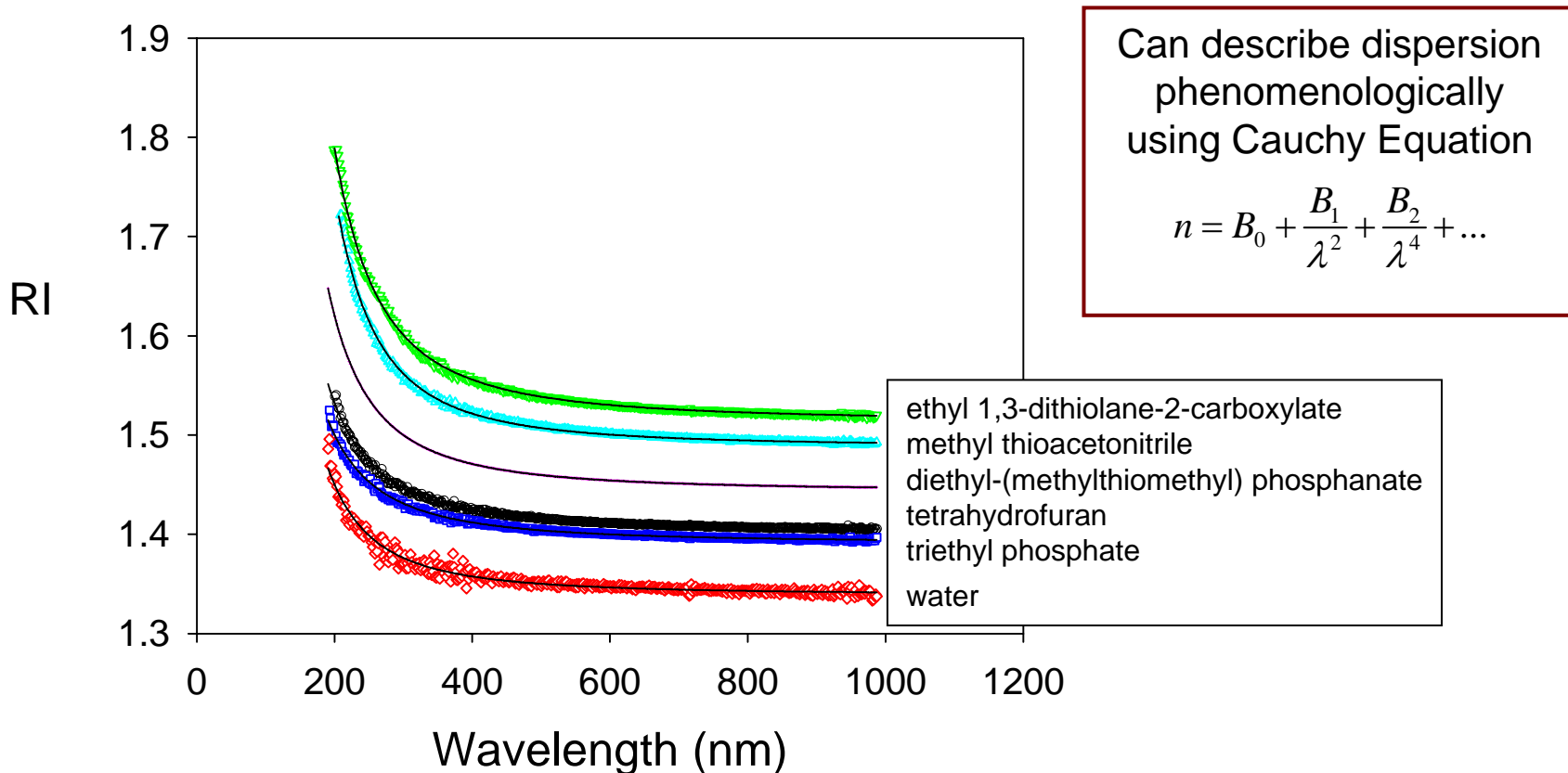


QSPR Model at 589 nm

- 20 compounds were randomly selected to externally validate the model
- These compounds were not used to develop the model
- Included aromatic, Cl, Br, I, S, P, N, O-containing compounds
- The errors were less than 2%

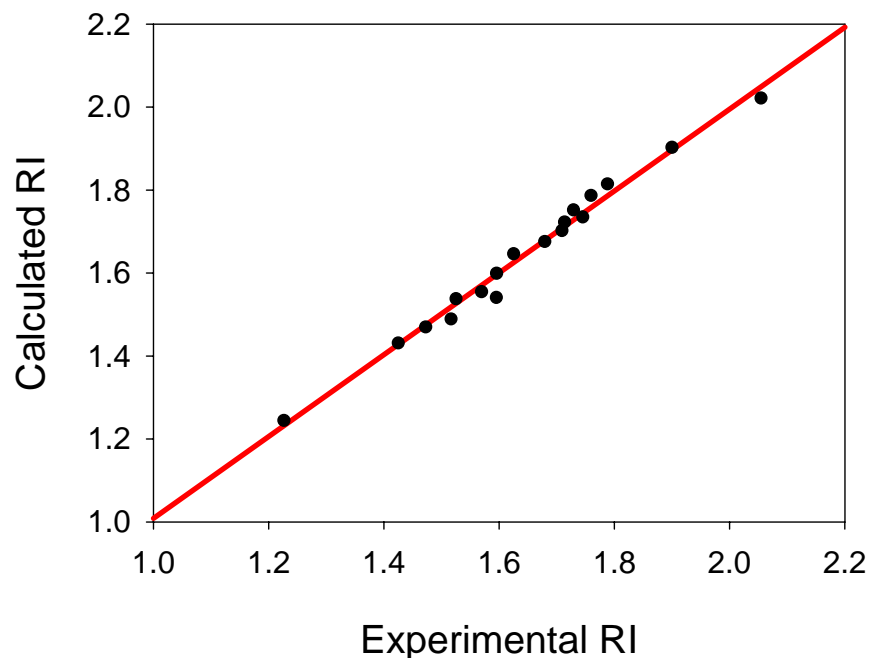


RI Dispersion



QSPR Model at 193 nm

18 Structures
 $R^2=0.9681$ $F=169.75$ $S^2=0.0007$

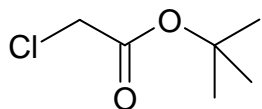


Although the correlation is good, only 18 structures were used, and so it is hard to comment on robustness of the model.

Synthetic Program

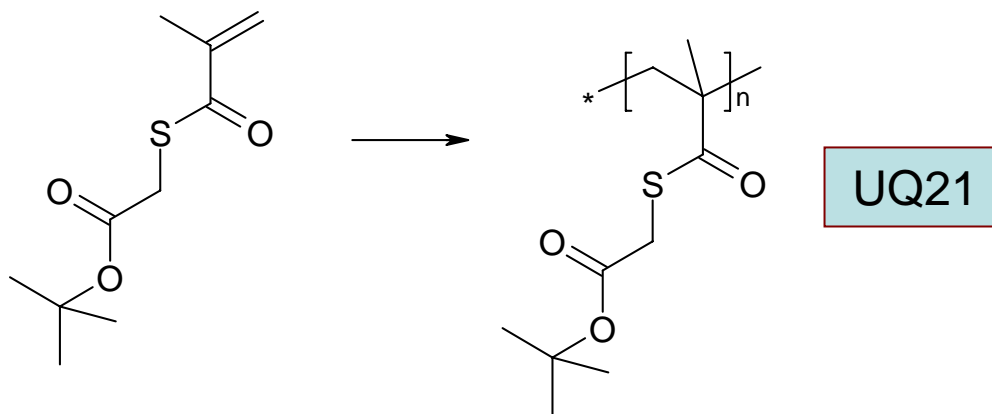
- Two examples to be described:
 - Thio-methacrylates and derivatives
 - Michael addition polymers

Synthesis of Thio-methacrylate



All structures confirmed by
¹H and ¹³C NMR

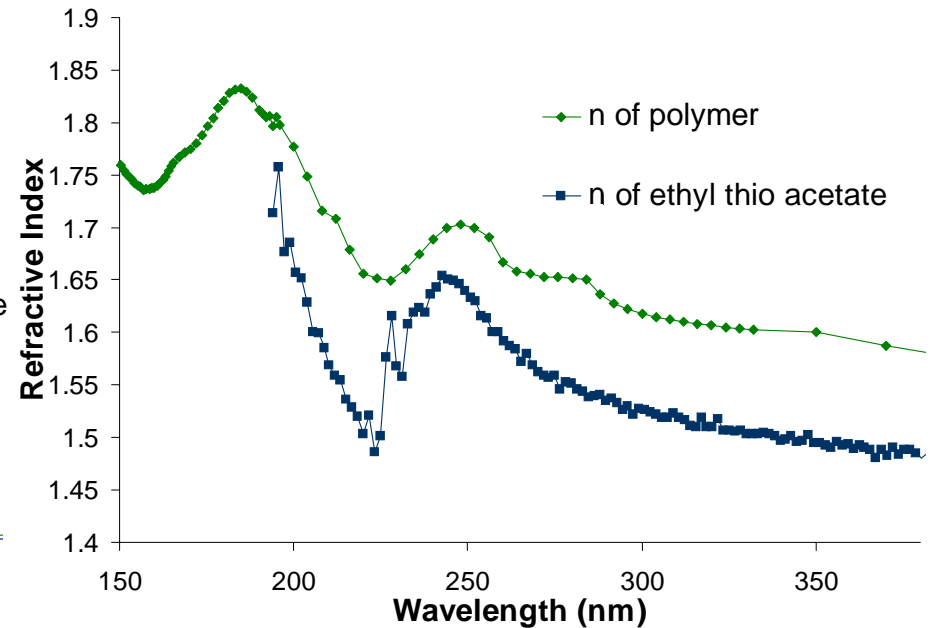
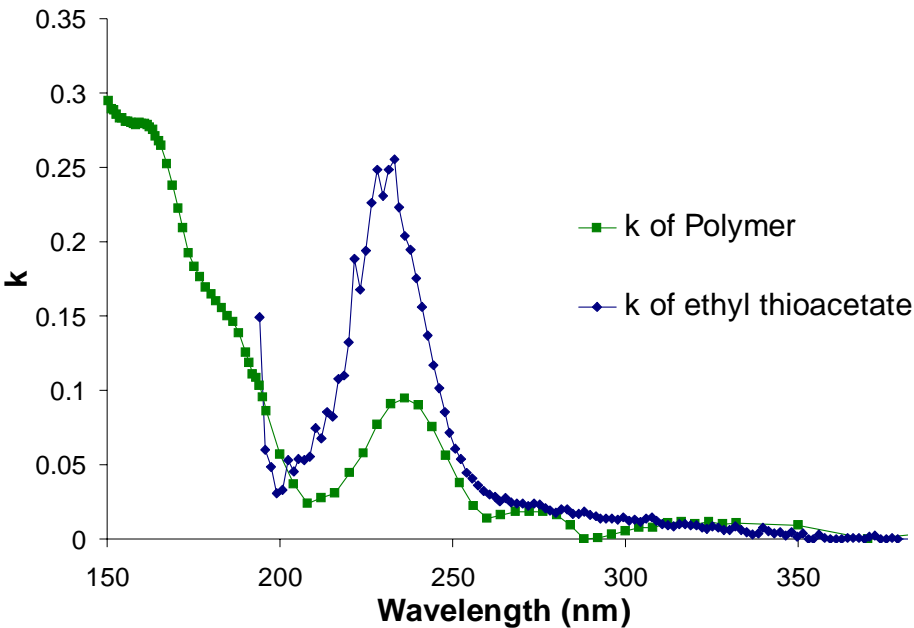
Polymerization of Thio-methacrylate



- Standard conditions were used:
 - 2% AIBN, THF, 60°C
- 70% conversion after 3 days
 - Could be due to chain transfer properties of thioester
 - Mw 31000, Mn 22000, PDI 1.4

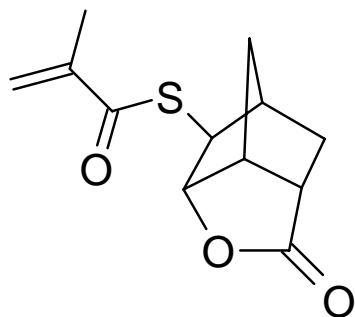
RI of Poly(Thio-methacrylates)

- Similar n and k profiles observed for polymer and model
 - Approximately 0.06 higher for polymer
 - Slight shift in absorption maxima and minima

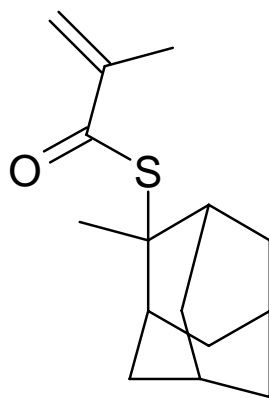


Thio-methacrylate Monomers

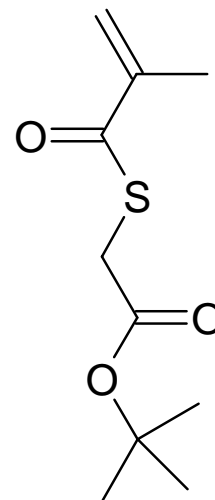
- Initial targets include these monomers
 - Synthesis of A and B is under way using analogous synthetic schemes



A



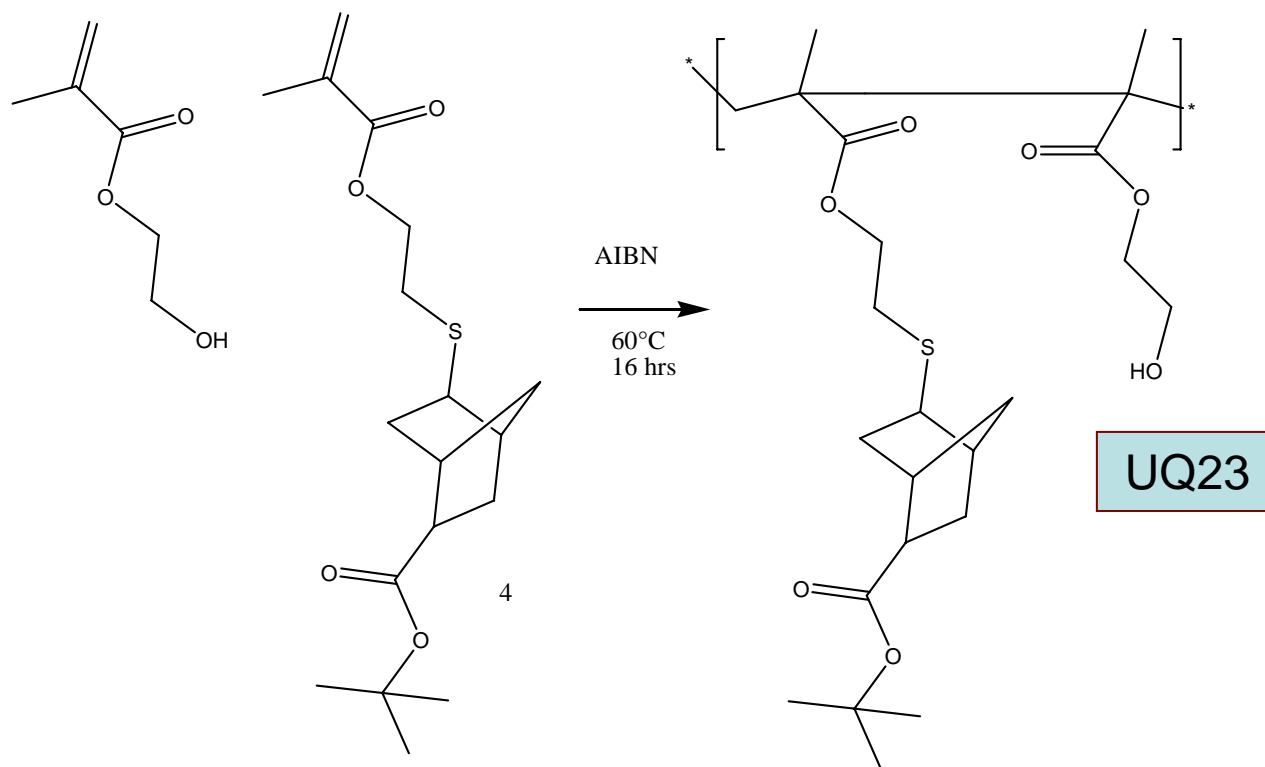
B



C

Imagable Polymer UQ 23

- HEMA copolymer
- SPIE2005, 5753, 592 reported that OH-containing monomers promote adhesion, more so than lactone-containing monomers
- The QSPR model suggests that OH groups might give rise to higher RI
- The hydrophilicity of future resists may need to be tailored to suit non-aqueous immersion fluids

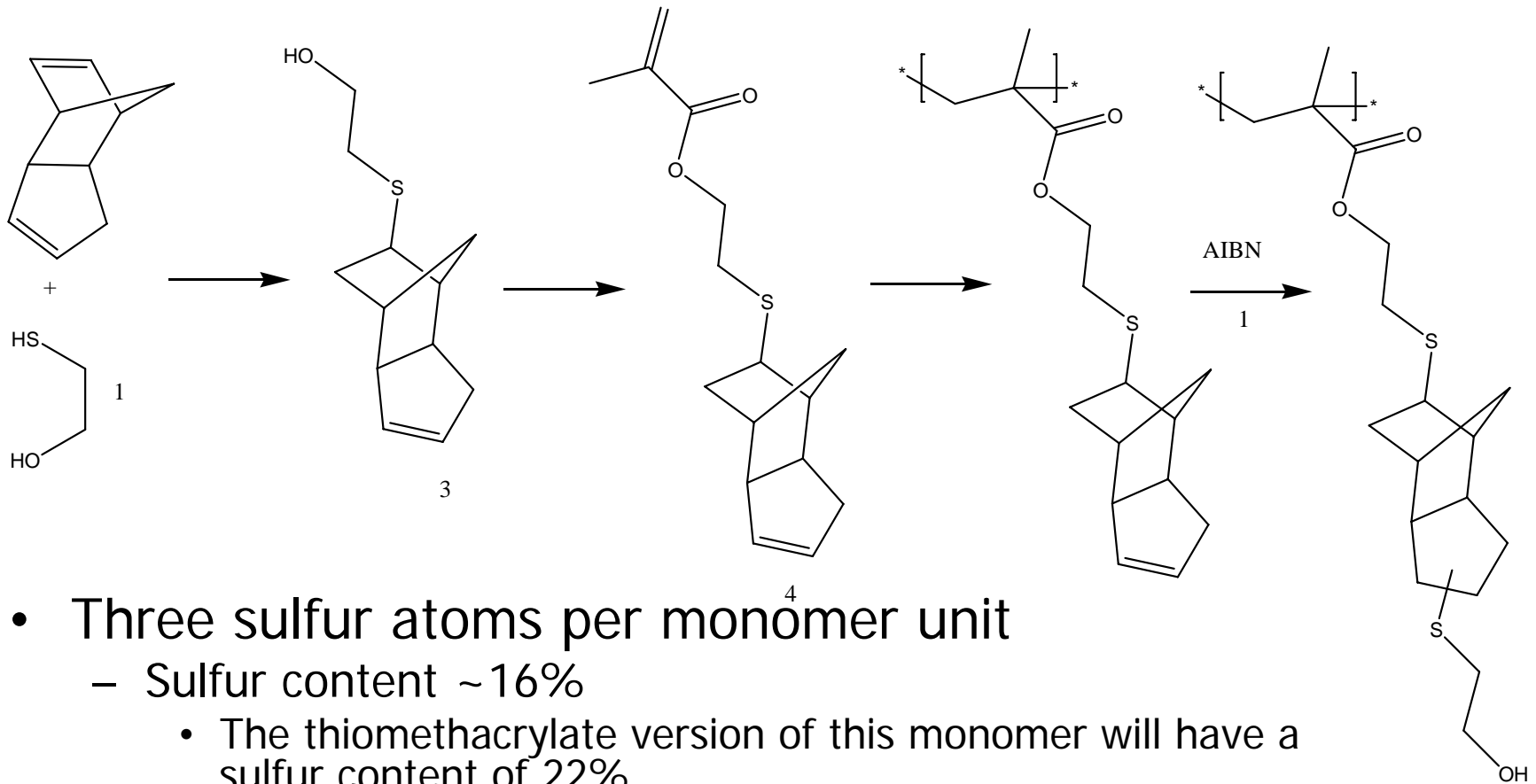


Optical Properties of UQ 22 and 23

- UQ 22
 - Sulfur Content ~ 5%
 - k 0.023
 - n 1.72

- UQ 23
 - Sulfur Content ~ 6%
 - k 0.035
 - n 1.72

Other Possibilities



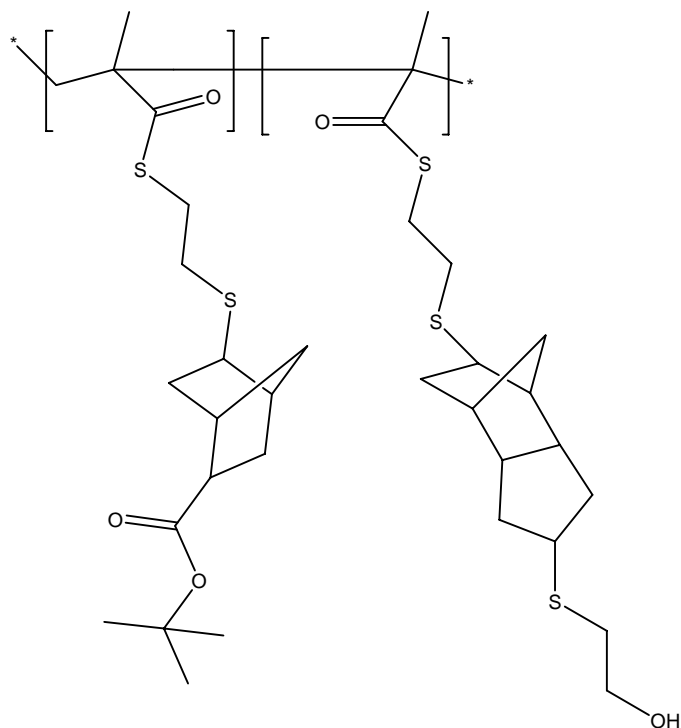
- Three sulfur atoms per monomer unit
 - Sulfur content ~16%
 - The thiomethacrylate version of this monomer will have a sulfur content of 22%
 - Monomer is in the process of being synthesized

What is the Ultimate?

- Using model compound data at 193 nm an estimate of the contribution to RI of different functional groups can be made
- This estimate has been made for thioethers and thioesters
 - Thioether ~ 0.00618 RI units / %S
 - Thioester ~ 0.00738 RI units / %S
- From these values estimates of RI for unknowns that contain those groups can be made

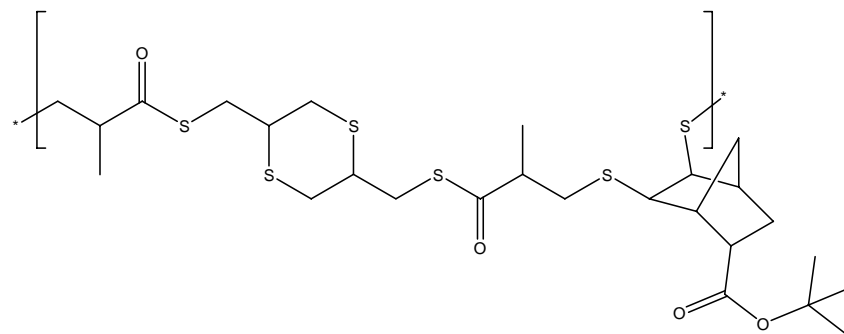
RI of Target Systems

- Target polythiomethacrylate copolymer



1.84

- Target Michael addition copolymer



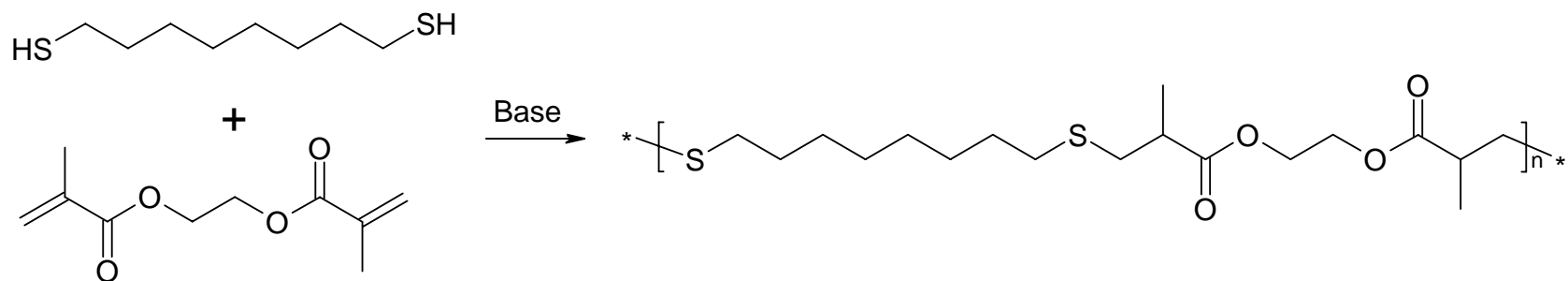
1.93

Michael-Addition Polymerization

- Involves conjugate addition of a nucleophile with an alkene containing an electron-withdrawing group, such as a methacrylate, in the presence of a base
- Generation of low molecular weight polymers ($M_n \sim 9000$ $M_w \sim 22500$) has been demonstrated for HEA and HEMA (Gibas *et al. Polym. Bull.*, 2003: **51**, 17)
- *Aim of this program is to utilize thiols as the nucleophilic group*

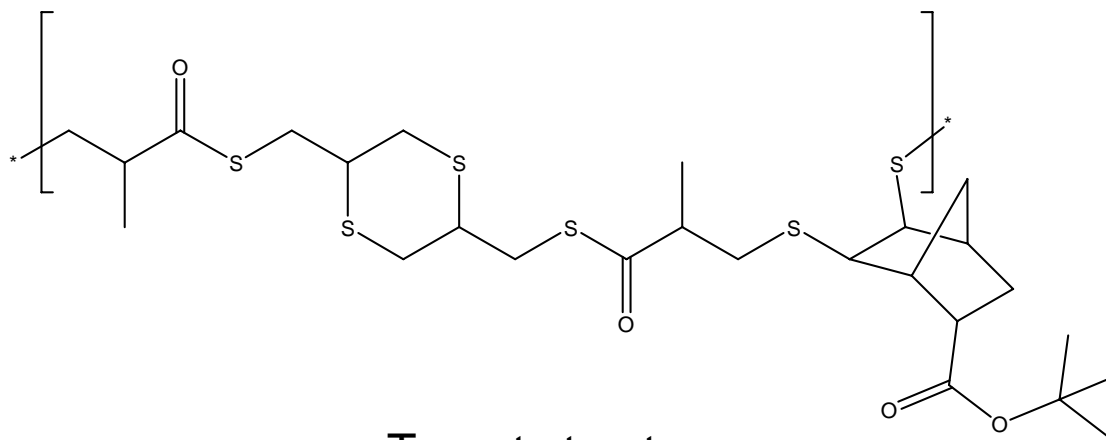
Proof-of-Concept Polymer

- Michael addition polymer
 - This method generates S in the polymer chain
 - UQ24 was made to demonstrate that a polymer could be made in this fashion
 - Sulfur content 17%
 - The polymer is of low molecular weight and a viscous liquid at room temperature
 - More rigid polymers are required



Michael-Addition Polymerization

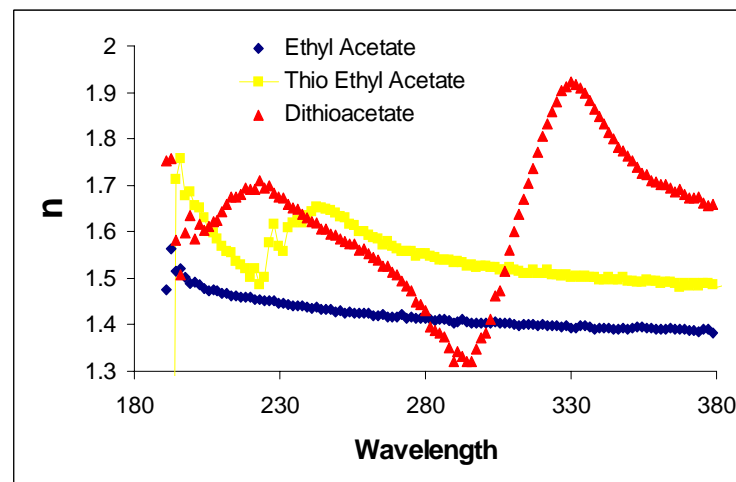
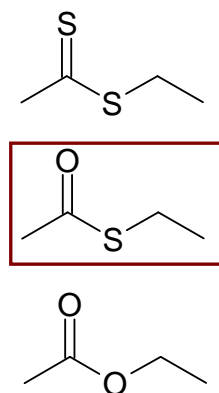
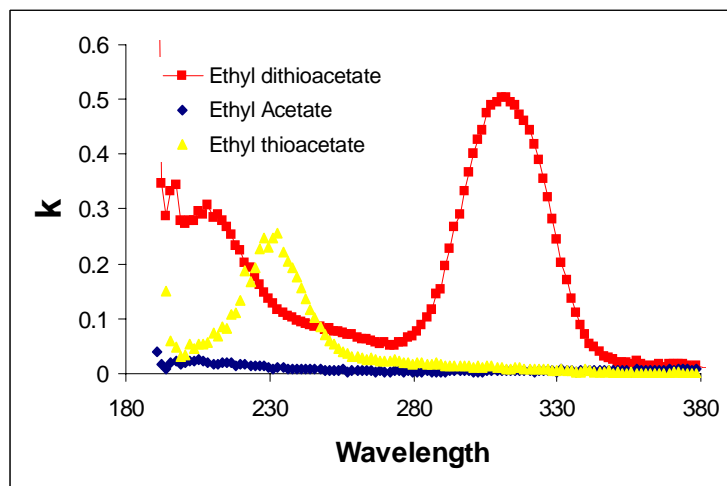
- More rigid targets are currently being pursued
 - In the long term targets will be synthesized that will have a sulfur content of 32% using this methodology



Target structure

A Closer Look at Model Compound Data

- Recent measurements of n & k dispersion indicate:
 - Dithioesters have high absorbance at 193 nm
 - Thioesters seem to be on the edge of an absorbance band near 193 nm
 - According to French *et al.* this should have a positive effect on RI, providing that k is not too high
 - Experimental RI is high (~ 1.75) at 193 nm
 - Polymers containing thioester groups should also have a high RI
 - For a polymer this should be more pronounced due to higher density

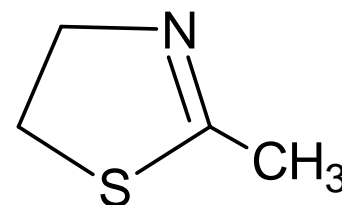
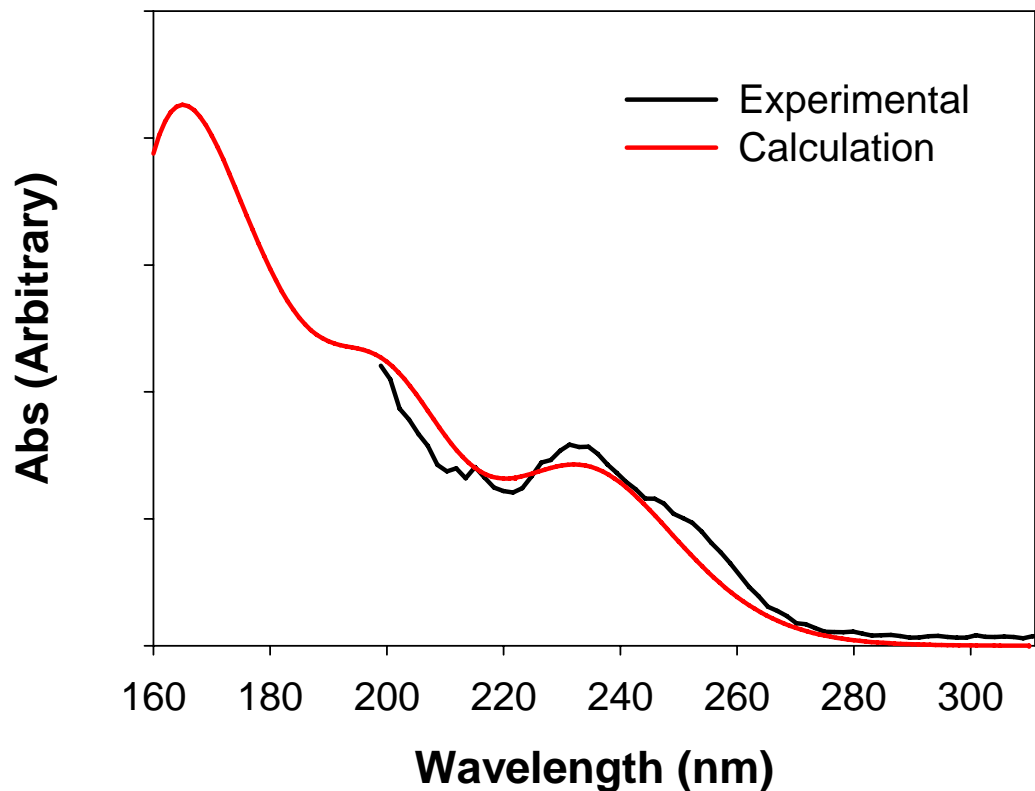


French *et al.*, Intl. Symp. Immersion and 157 nm Lithography Vancouver 2004

Gaussian Calculations

- Aim is to extend QSPR modelling to prediction of the absorption spectrum
- Looking for materials with $\lambda_{\max} \sim 180$ nm
- In-silico screening will help get around bottle-neck with acquisition of n & k
- Aim is to develop model by end 2006

2-Methyl-2-Thiazoline



Optimisation:

B3LYP/AUG-cc-pVTZ

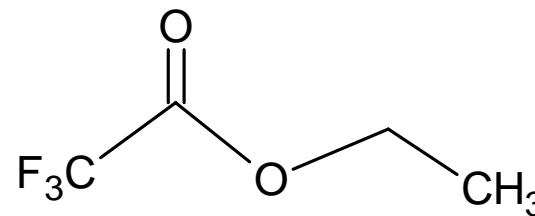
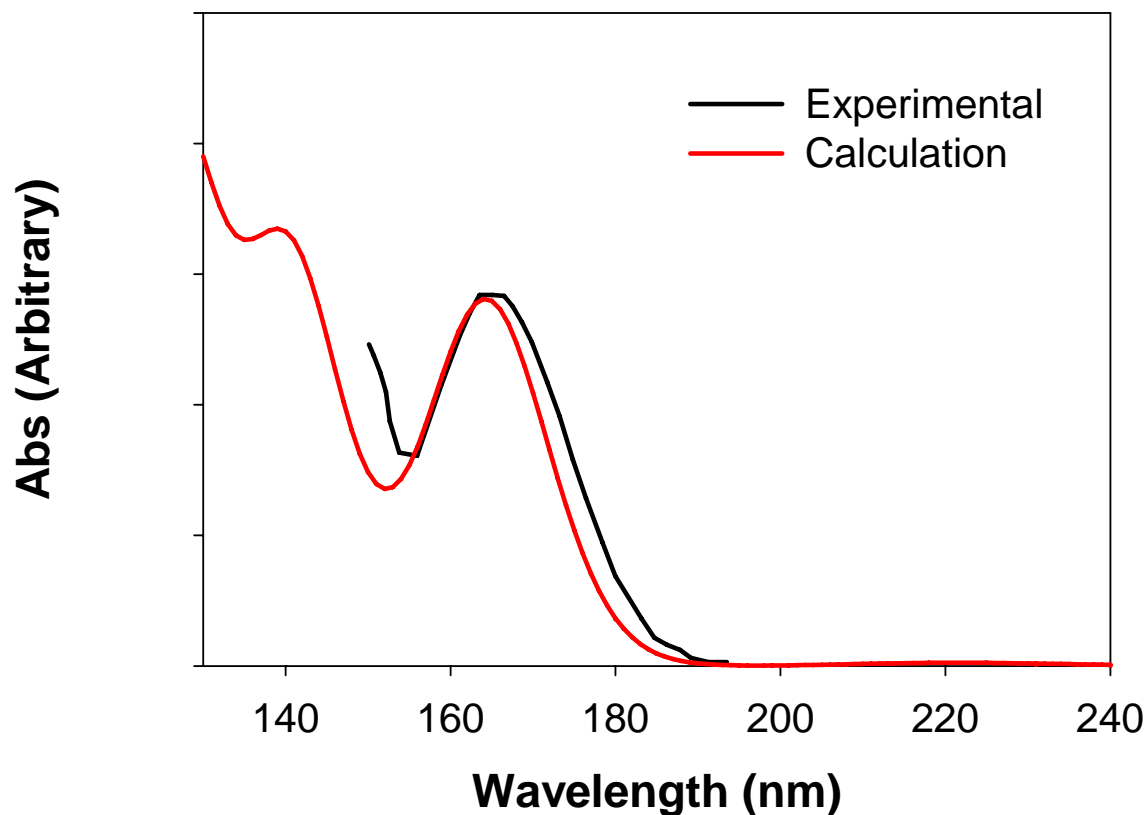
Excited States:

B3LYP/AUG-cc-pVTZ +

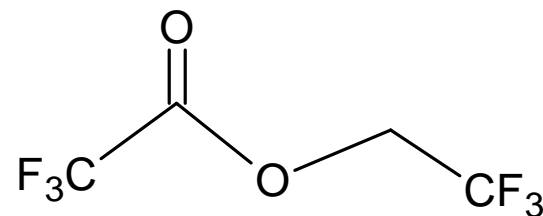
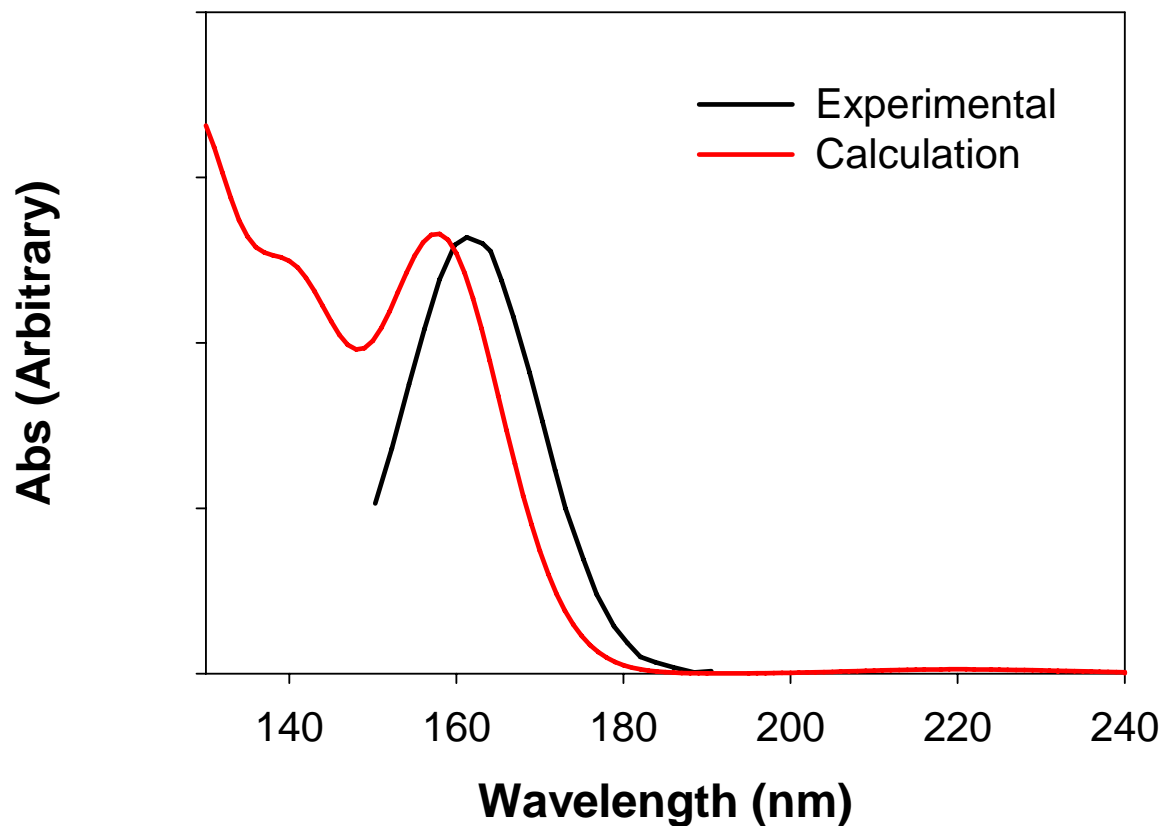
Rydberg function on C, N, S

FWHM: 6000 cm^{-1}

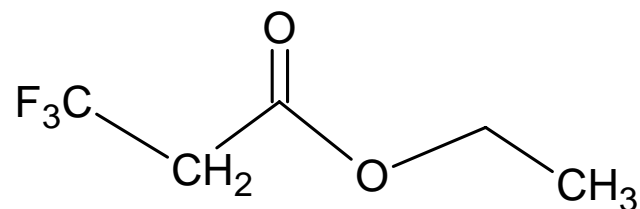
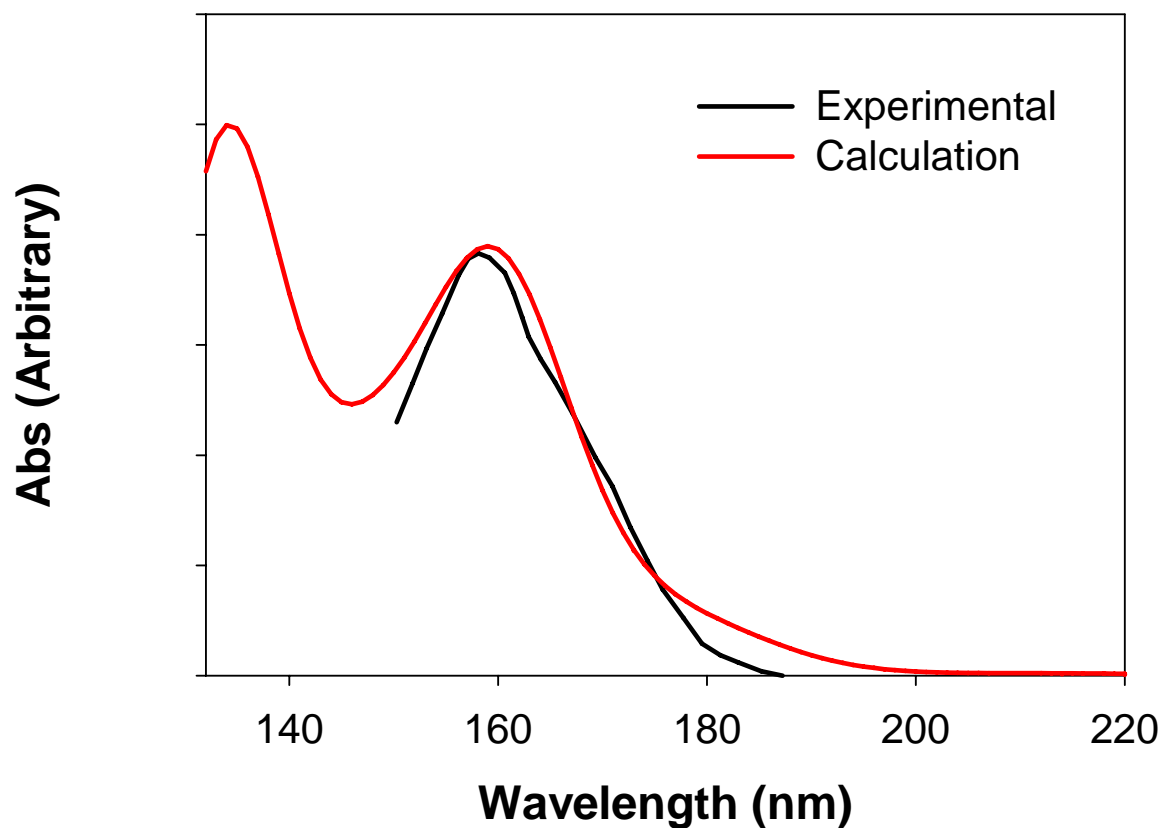
Trifluoroethylacetate



Trifluoroethyltrifluoroacetate



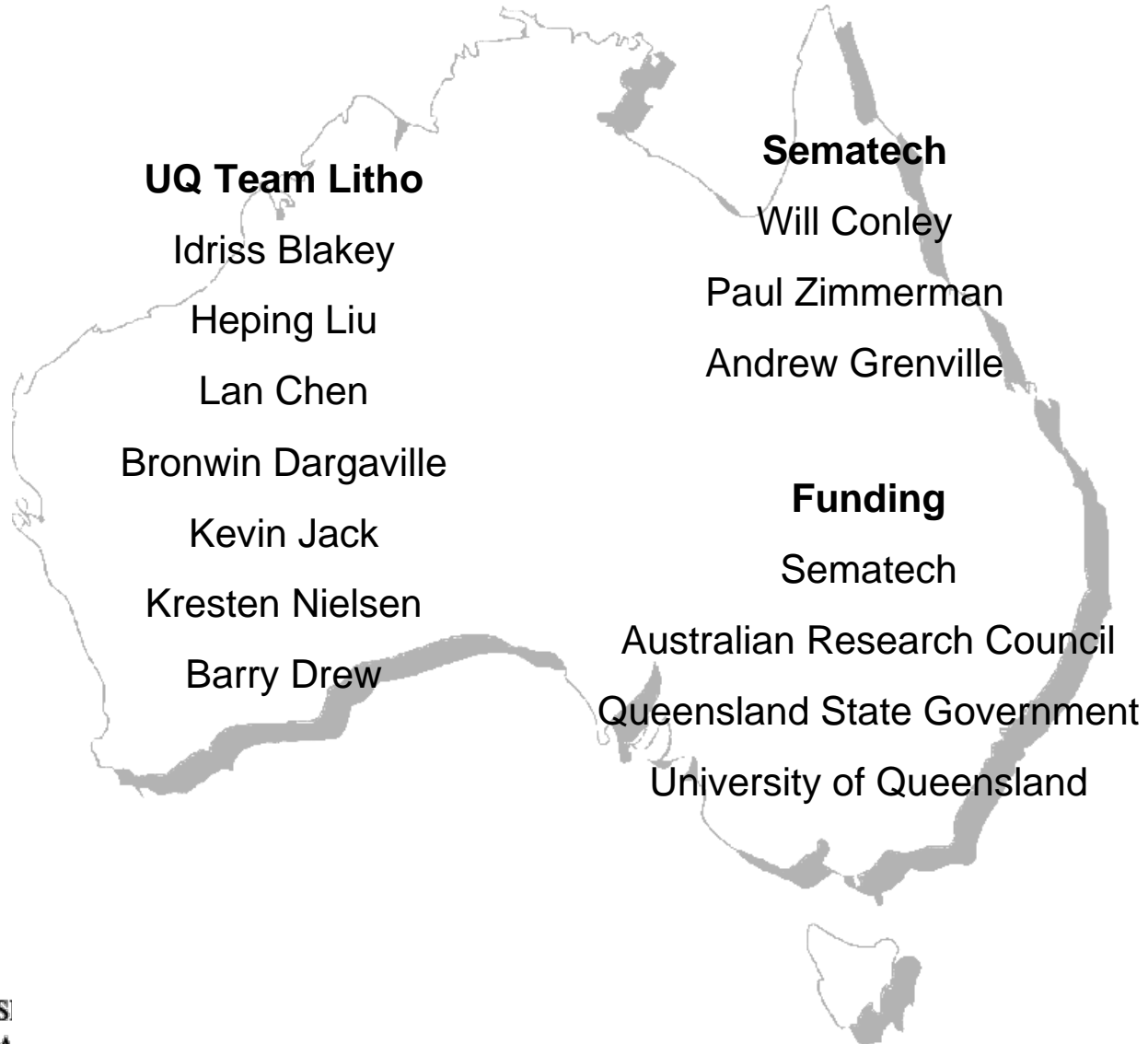
Ethyl Trifluoropropionate



Summary

- A strong theoretical/predictive basis for synthetic strategy is being built
- A broad range of candidate materials have been identified and are being prepared
- QSPR approach has broad applications
- Modelling of absorption proceeding

Acknowledgements



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