

# **Optimising the thickness determination of homopolymers and diblock copolymers using optical spectral reflectance during solvent vapour annealing**

INM - RUC 2019 - Master's Thesis

Supervisor: Dorthe Posselt

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7/5/2019

Roskilde University

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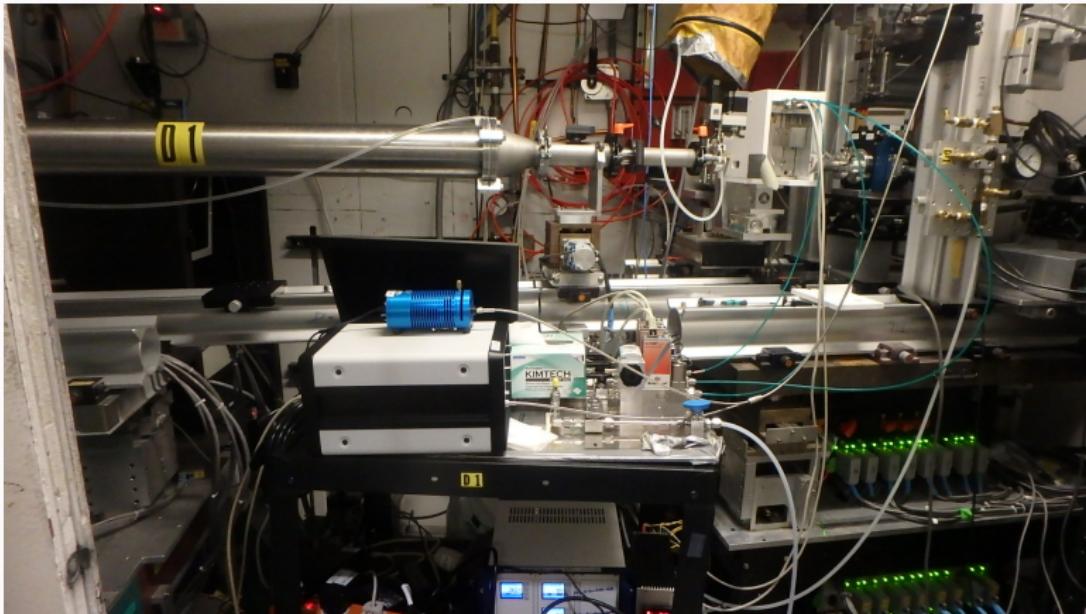
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- 3. Experimental Setup
- 4. Polymers
- 5. Fresnel Models
- 6. Solvent vapour Annealing
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- 9. Conclusion
- 10. Results - 2 polymer layers
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# Master Thesis Prelude

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# D-Line

December '17 and May '18



# Problems with the reflectance measurements during swelling



Figure 1: Polystyrene - SVA run used in Master Thesis

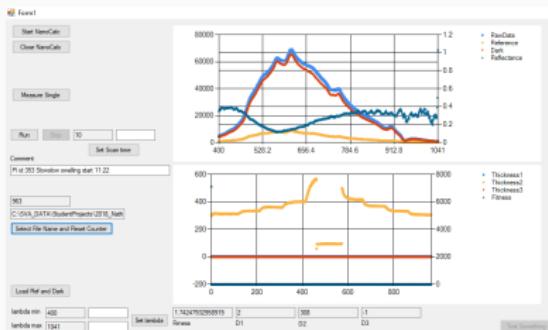


Figure 2: Polyisoprene - SVA run used in Master Thesis

# **Master Thesis Problem Formulation**

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## Problem Formulation

What are the advantages and limitations when using optical spectral reflectance for determining the thickness of thin polymer films during solvent vapour annealing?

What is the optimal modelling and fitting method for the optical spectral reflectance measurements and thickness determination of the homopolymers, polystyrene and polyisoprene thin films during solvent vapour annealing?

Can the same thickness determination be used on thin films with a horizontal nano scale structure such as the diblock-copolymer Polystyrene-b-Polyisoprene?

## Experimental Setup

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# Experimental Setup Overview

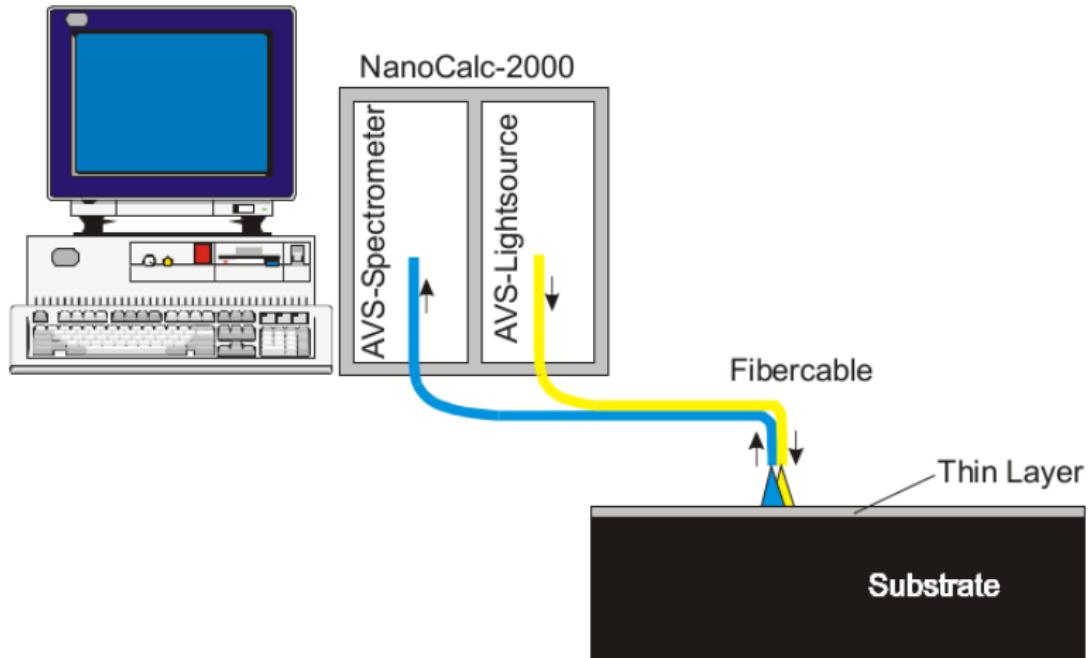
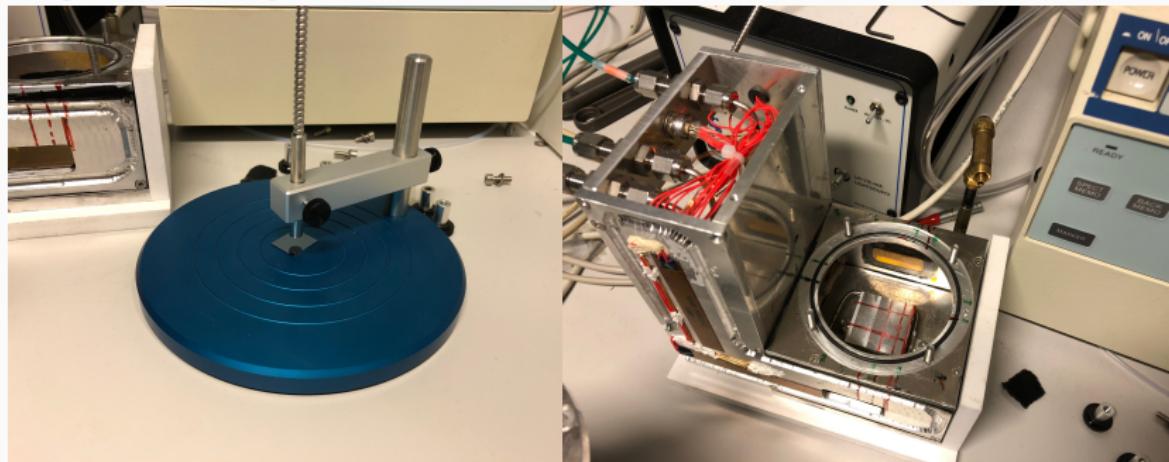


Figure 3: Taken from NanoCalc Software Manual v.4

# Experimental Components

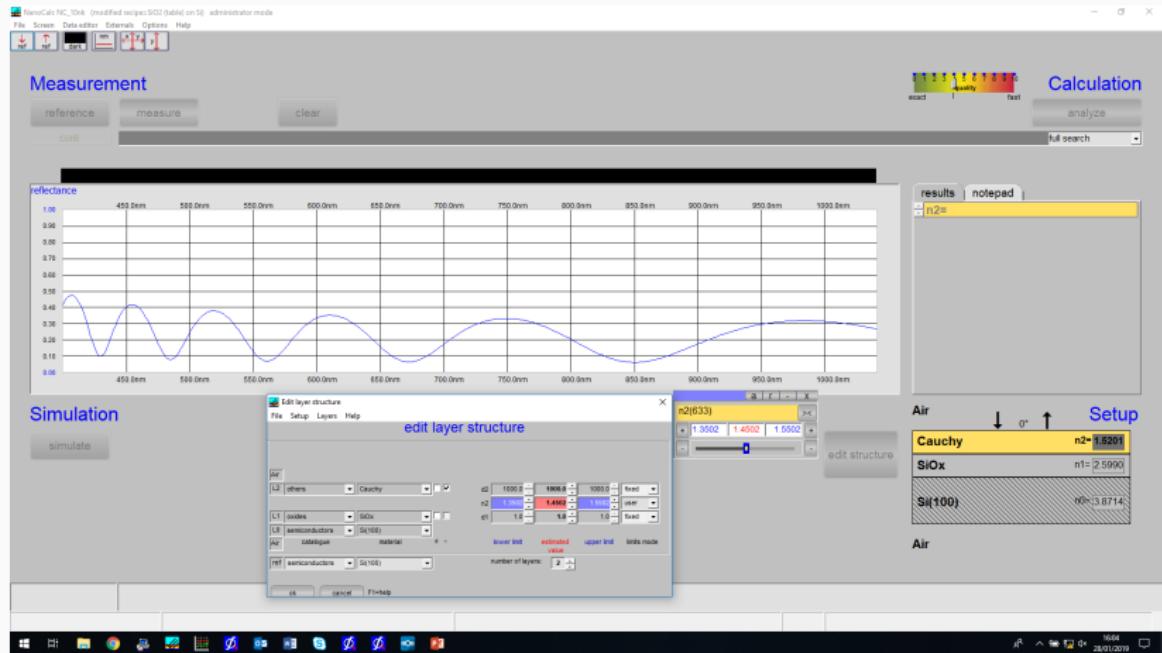
Single Point Stage and SVA test chamber.



## Step Wafer



# NanoCalc Software



# Taking Measurements

$$\text{Reflectance} = \frac{\text{Meas} - \text{Dark}}{\text{Ref}} \cdot R_{\text{sub}}$$

- Dark Measurement - *Dark*
  - Measuring stray light.
- Reference Measurement - *Ref*
  - Measuring light from blank wafer - SiO<sub>x</sub>/Si
  - Ref data - minus dark
- Wafer Measurement - *Meas*
  - Wafer with spin-coated polymer
- Reflectance from ambient/substrate model -  $R_{\text{sub}}$ 
  - Calculation - Fresnel model

# Polymers

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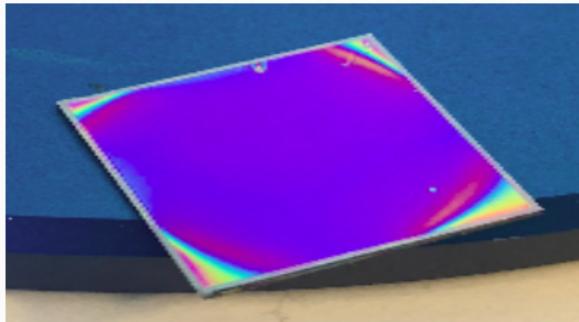
# Polymers used in Master Thesis



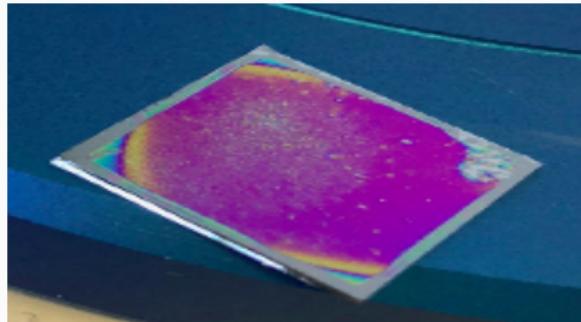
**Figure 4:** Source:[www.isowall.co.za](http://www.isowall.co.za)



**Figure 6:** Source:[wbcisd.org](http://wbcisd.org)

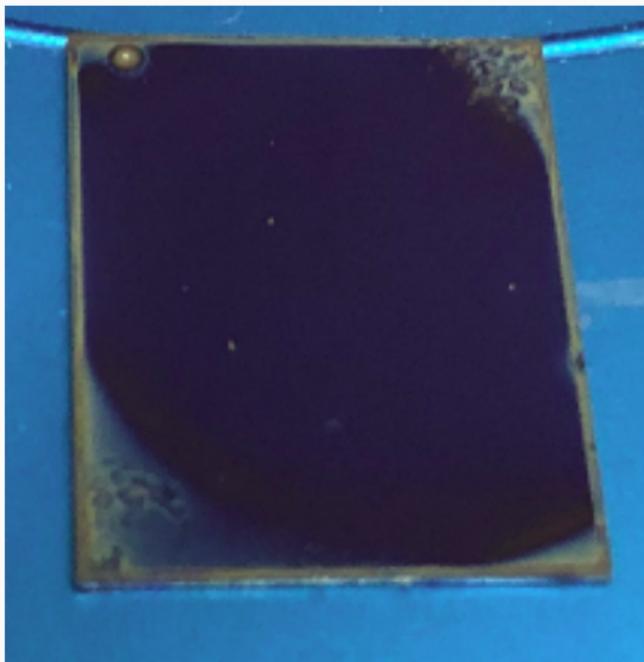


**Figure 5:** Polystyrene wafer



**Figure 7:** Polyisoprene wafer

## Polymers used in Master Thesis

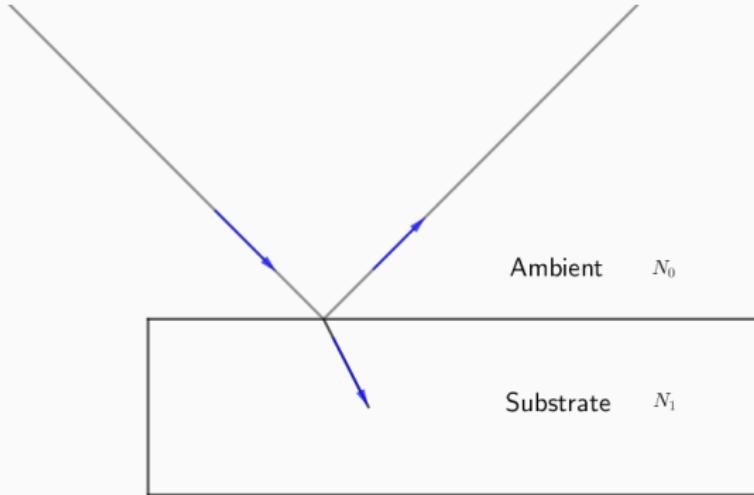


**Figure 8:** Polystyrene-b-polyisoprene

## Fresnel Models

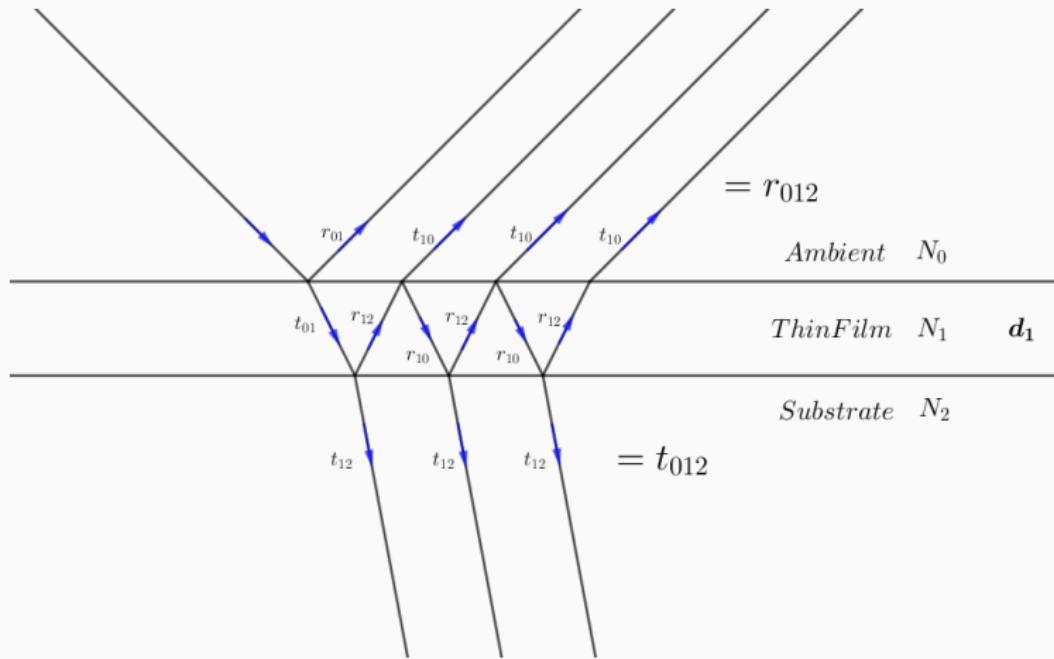
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## Fresnel Equations - Substrate



$$r_p = \frac{E_{r,p}}{E_{i,p}} = \frac{N_1 - N_0}{N_0 + N_1}$$
$$R_p = | r_p |^2$$

## Fresnel Equations - One layer



$$r_{012} = r_{01} + t_{01}t_{10}r_{12} \exp(-i2\beta) + t_{01}t_{10}r_{10}r_{12}^2 \exp(-i4\beta) + \\ t_{01}t_{10}r_{10}^2r_{12}^3 \exp(-i6\beta) + \dots$$

## Fresnel Equations - One layer

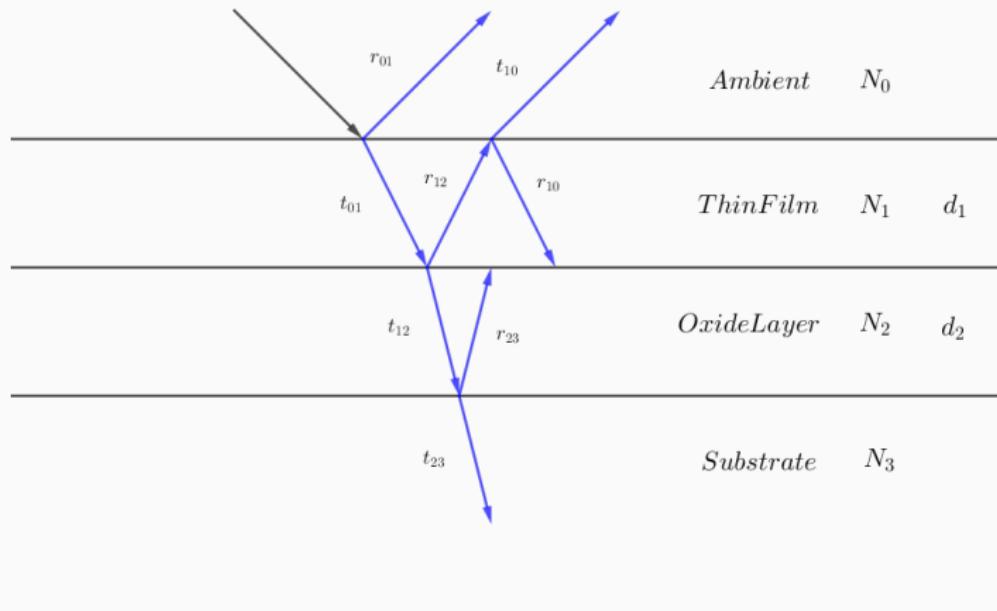
$$r_{012} = \frac{r_{01} + r_{12} \exp(-i2\beta)}{1 + r_{01}r_{12} \exp(-i2\beta)}$$

$$r_{jk} = \frac{N_k - N_j}{N_j + N_k}$$

$$\beta = \frac{2\pi d_1}{\lambda} N_1$$

$$R_{012} = |r_{012}|^2$$

# Homopolymer Fresnel Model



## Homopolymer Fresnel equations

$$r_{0123} = \frac{r_{01} + r_{123} \exp(-i2\beta_1)}{1 + r_{01}r_{123} \exp(-i2\beta_1)}$$

$$r_{123} = \frac{r_{12} + r_{23} \exp(-i2\beta_2)}{1 + r_{12}r_{23} \exp(-i2\beta_2)}$$

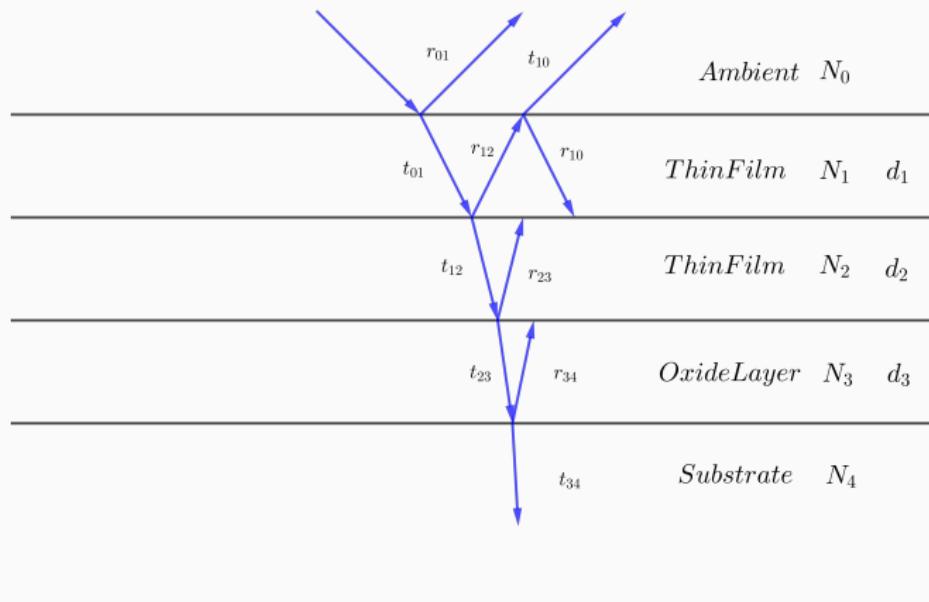
$$r_j k = \frac{N_k - N_j}{N_j + N_k}$$

$$R_{0123} = |r_{0123}|^2$$

$$\beta_i = \frac{2\pi d_i}{\lambda} N_i$$

$N_0, N_1$  and  $d_1$  fitted during solvent vapour annealing.

# Diblock copolymer Fresnel model



## Diblock copolymer Fresnel Equations

$$r_{01234} = \frac{r_{01} + r_{1234} \exp(-i2\beta_1)}{1 + r_{01}r_{1234} \exp(-i2\beta_1)}$$

$$r_{1234} = \frac{r_{12} + r_{234} \exp(-i2\beta_2)}{1 + r_{12}r_{234} \exp(-i2\beta_2)}$$

$$r_{234} = \frac{r_{23} + r_{34} \exp(-i2\beta_3)}{1 + r_{23}r_{34} \exp(-i2\beta_3)}$$

$$r_{jk} = \frac{N_k - N_j}{N_k + N_j}$$

$$\beta_i = \frac{2\pi d_i}{\lambda} N_i$$

$N_0, N_1, N_2, d_1$  and  $d_2$  fitted during solvent vapour annealing.

## Plotted Fresnel models

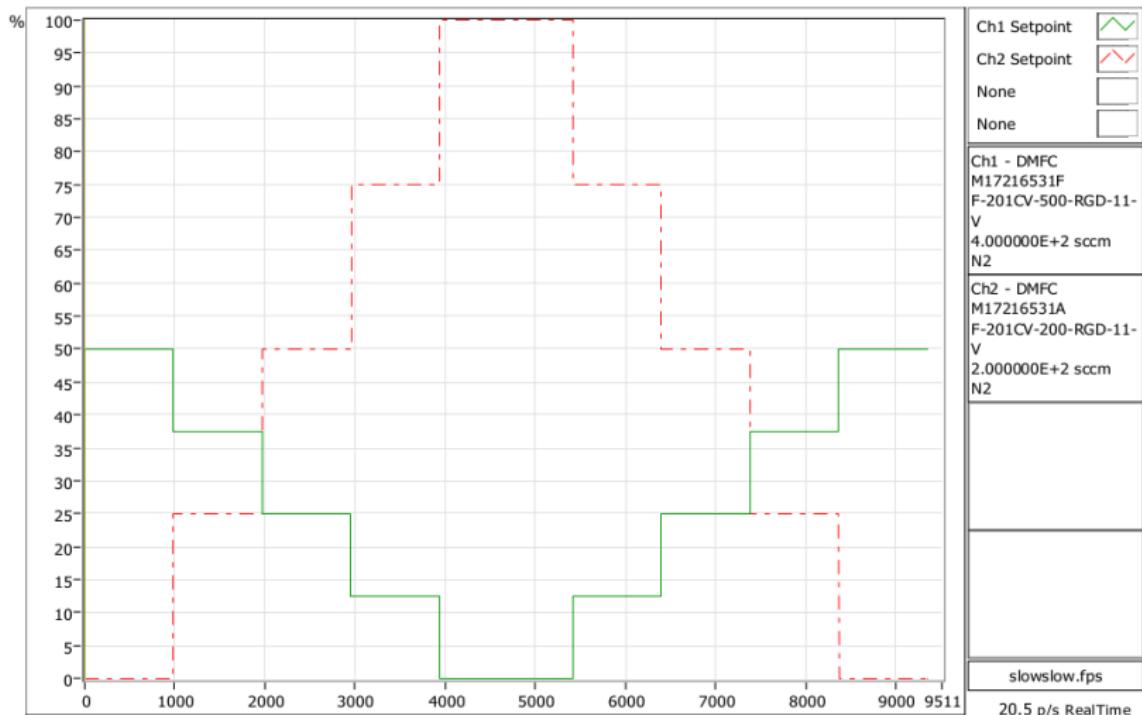
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Movie:varyRI.avi

## Solvent vapour Annealing

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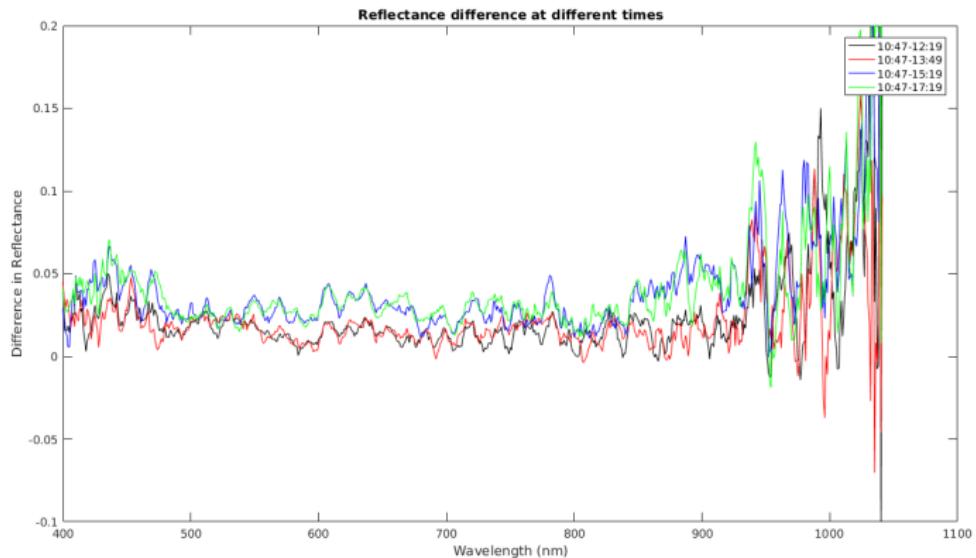
# SVA protocol



## Preliminary Studies

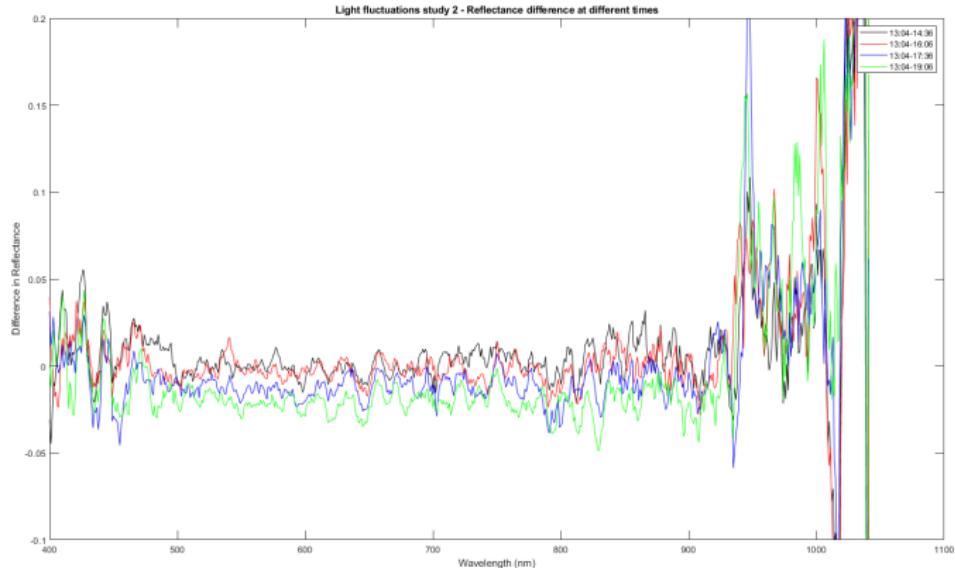
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# Light Fluctuation



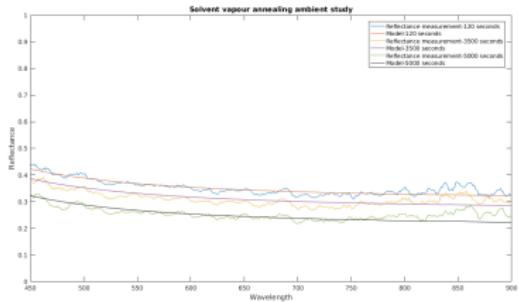
**Figure 9:** Light Fluction study 1

# Light Fluctuation continued

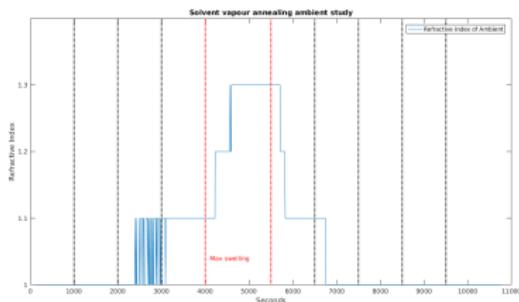


**Figure 10:** Light Fluction study 2

# Solvent vapour annealing ambient study



**Figure 11:** Reflectance curves at different times during SVA



**Figure 12:** Ambient refractive index

## Results - 1 polymer layer

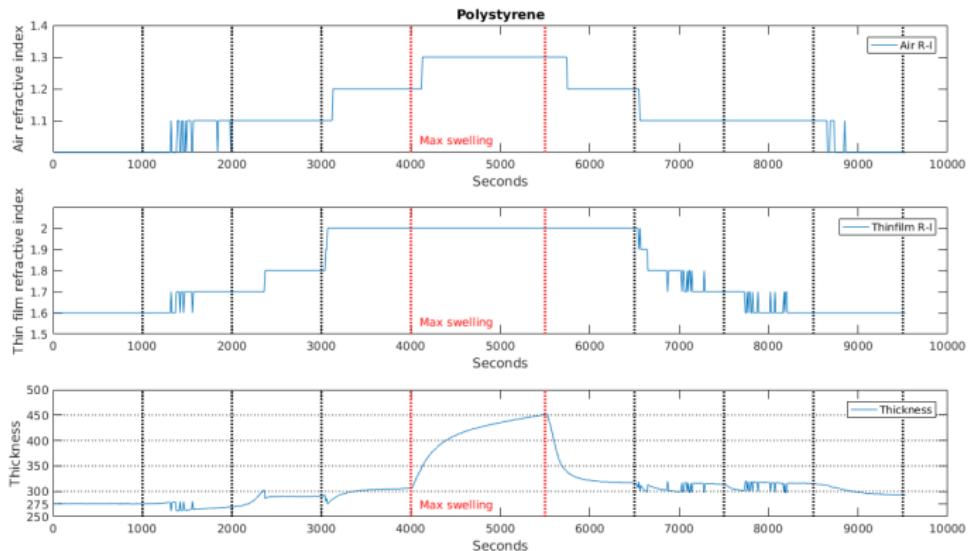
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# Polystyrene

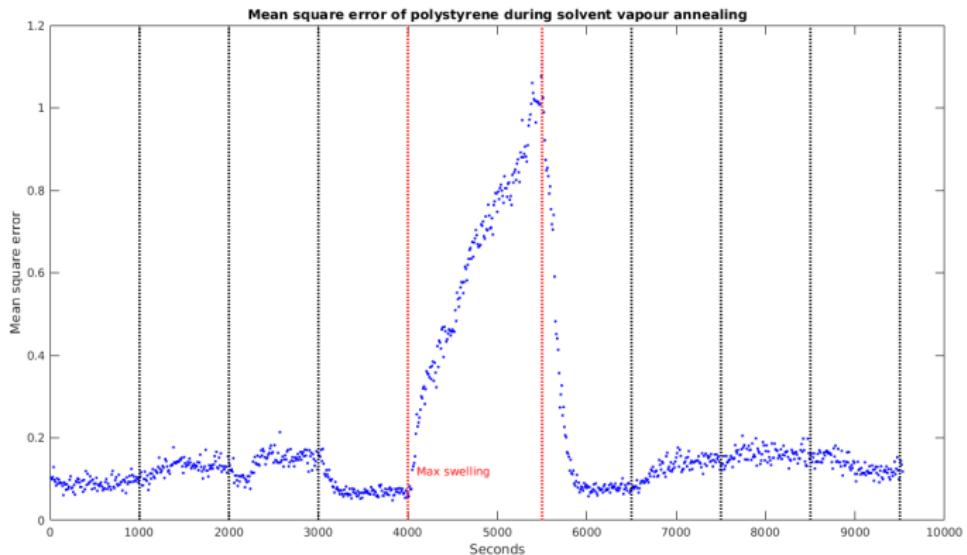
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Movie: PSsva.avi

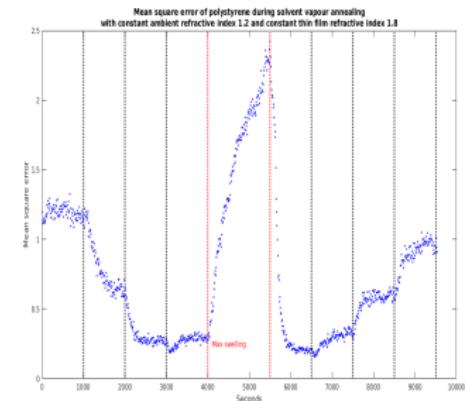
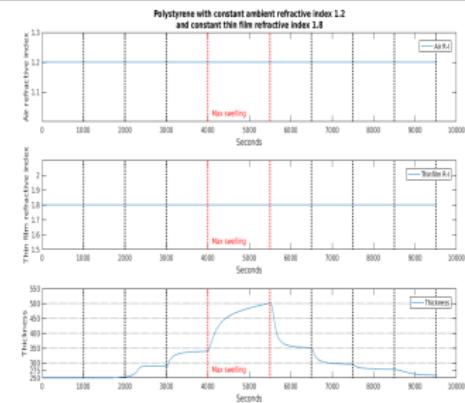
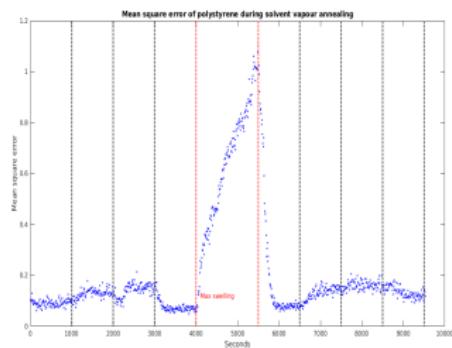
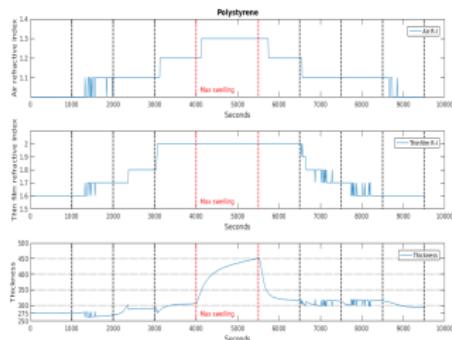
# Polystyrene Results



# Polystyrene MSE

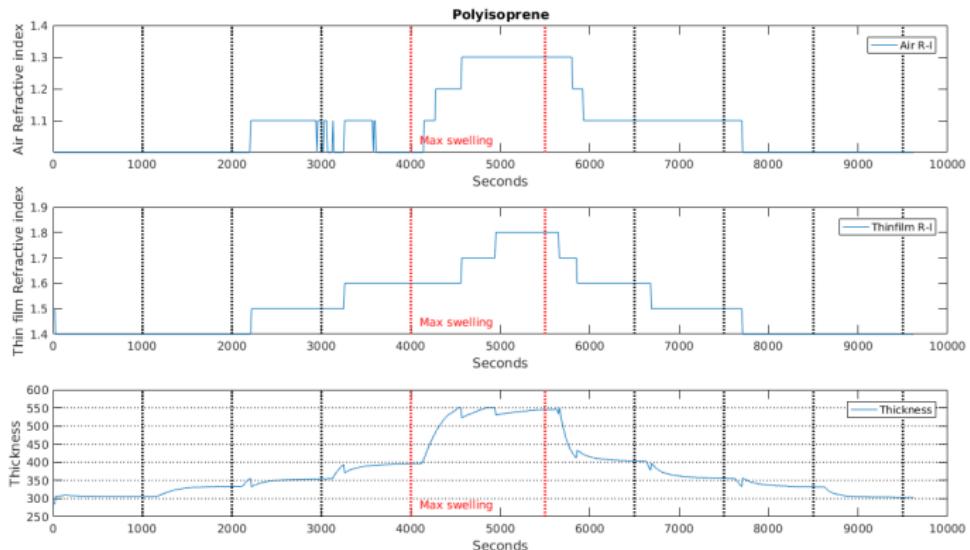


# Polystyrene comparison

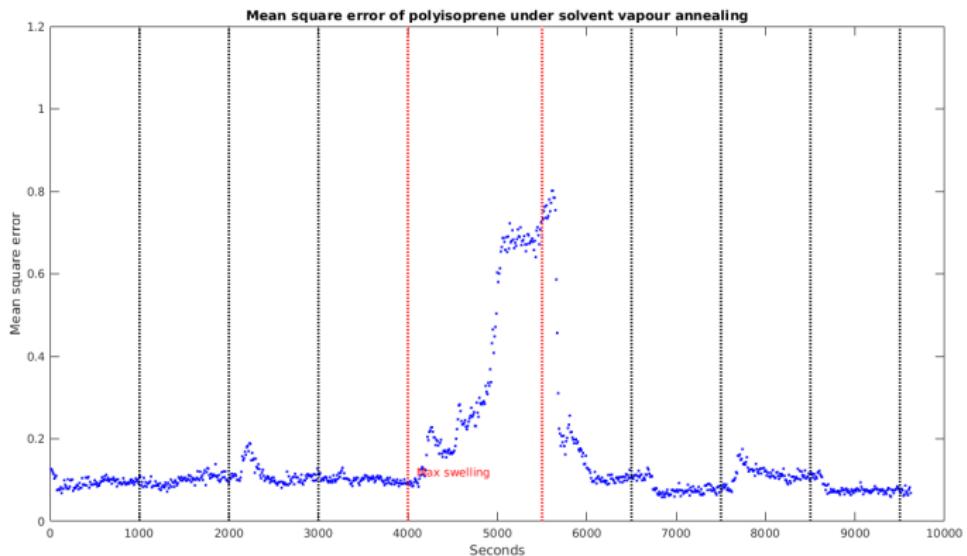


Movie:PIsvalframevalue2.avi

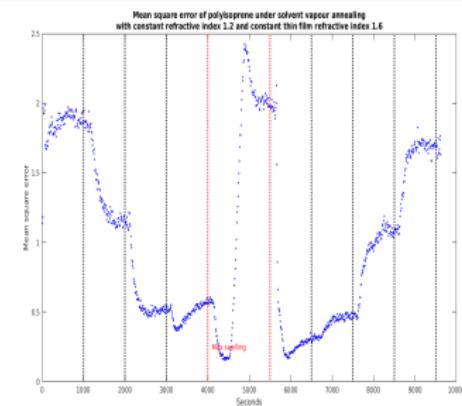
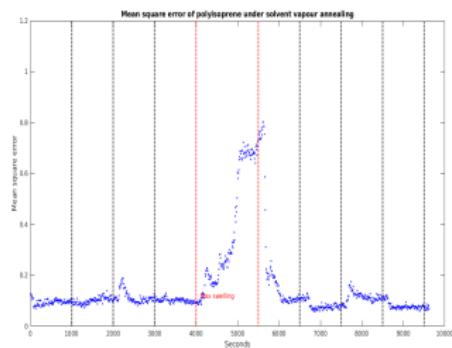
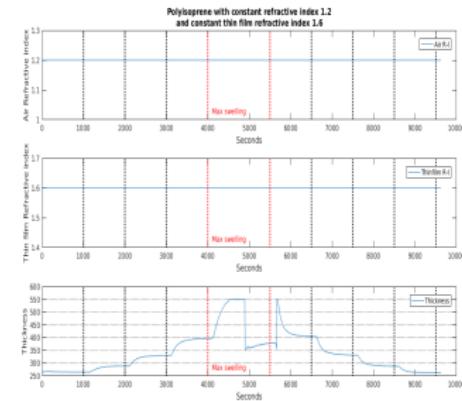
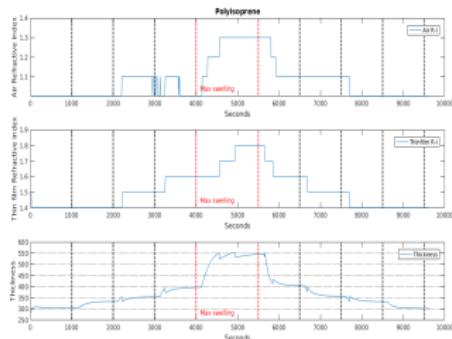
# Polyisoprene Results



# Polyisoprene MSE



# Polyisoprene comparison

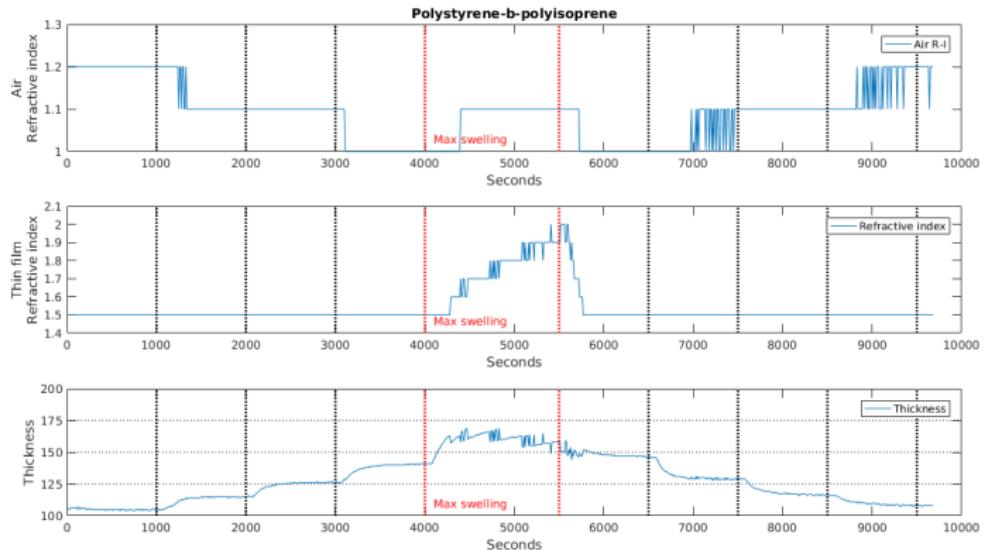


## Polystyrene-b-polyisoprene

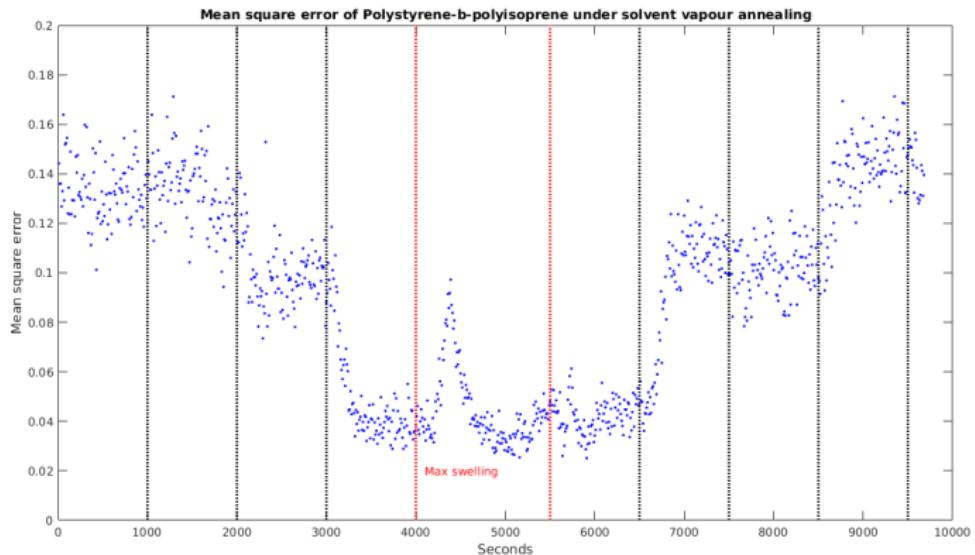
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Movie: PSbPIsinglemodel.avi

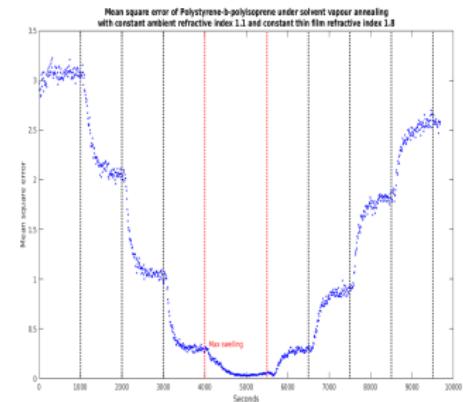
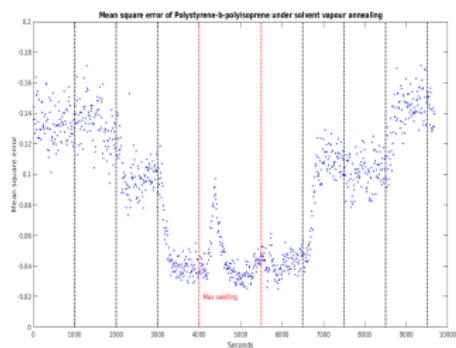
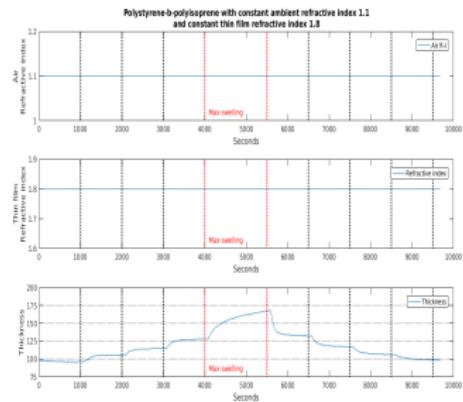
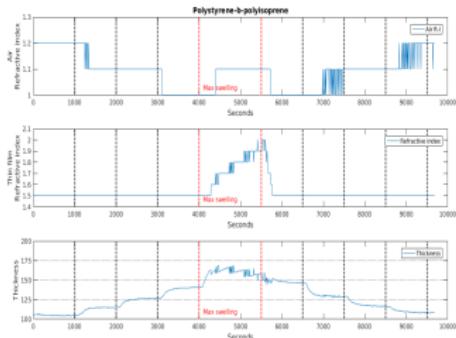
# Polystyrene-b-polyisoprene Results



# Polystyrene-b-polyisoprene MSE



# Polystyrene-b-polyisoprene comparison



## Conclusion

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# Conclusion

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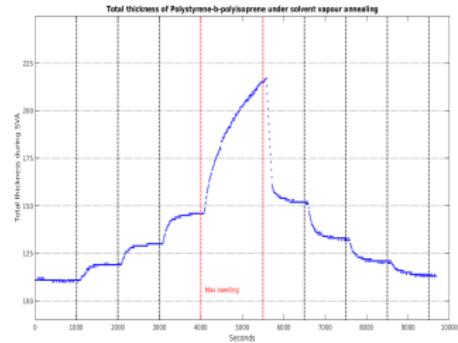
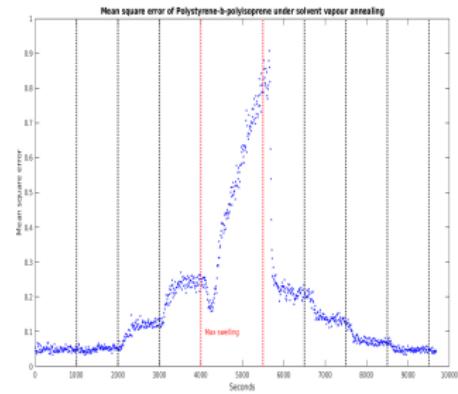
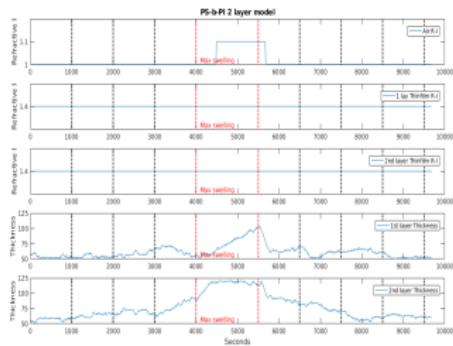
- Fresnel equations easily calculated
- Care when taking dark measurements
- Homopolymer Fresnel model seems optimal for polystyrene and polyisoprene

## Results - 2 polymer layers

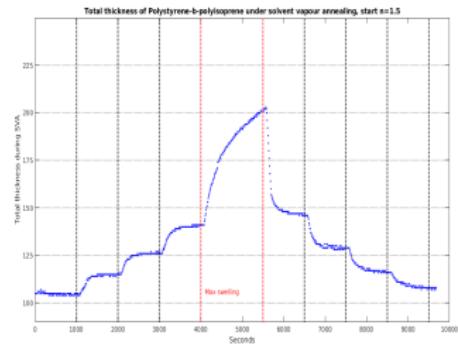
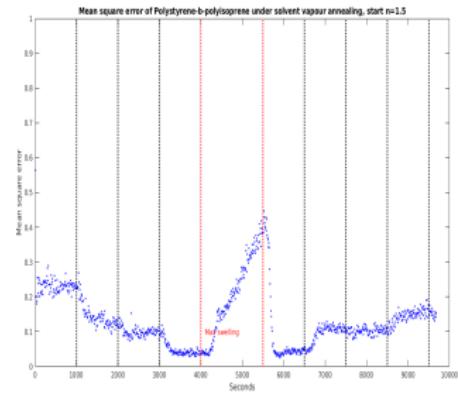
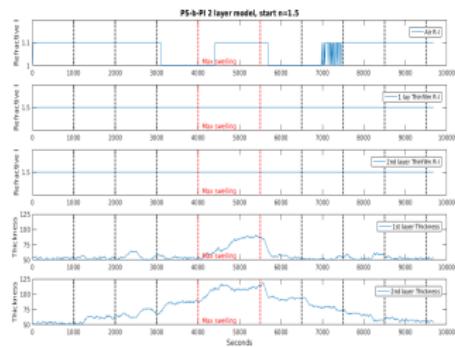
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Movie: PSbPIfit2layermodelV2.avi

# PS-b-PI - 2 layer model



# PS-b-PI - 2 layer model



## Perspective

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