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

INM - RUC 2019 - Master's Thesis

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Roskilde University

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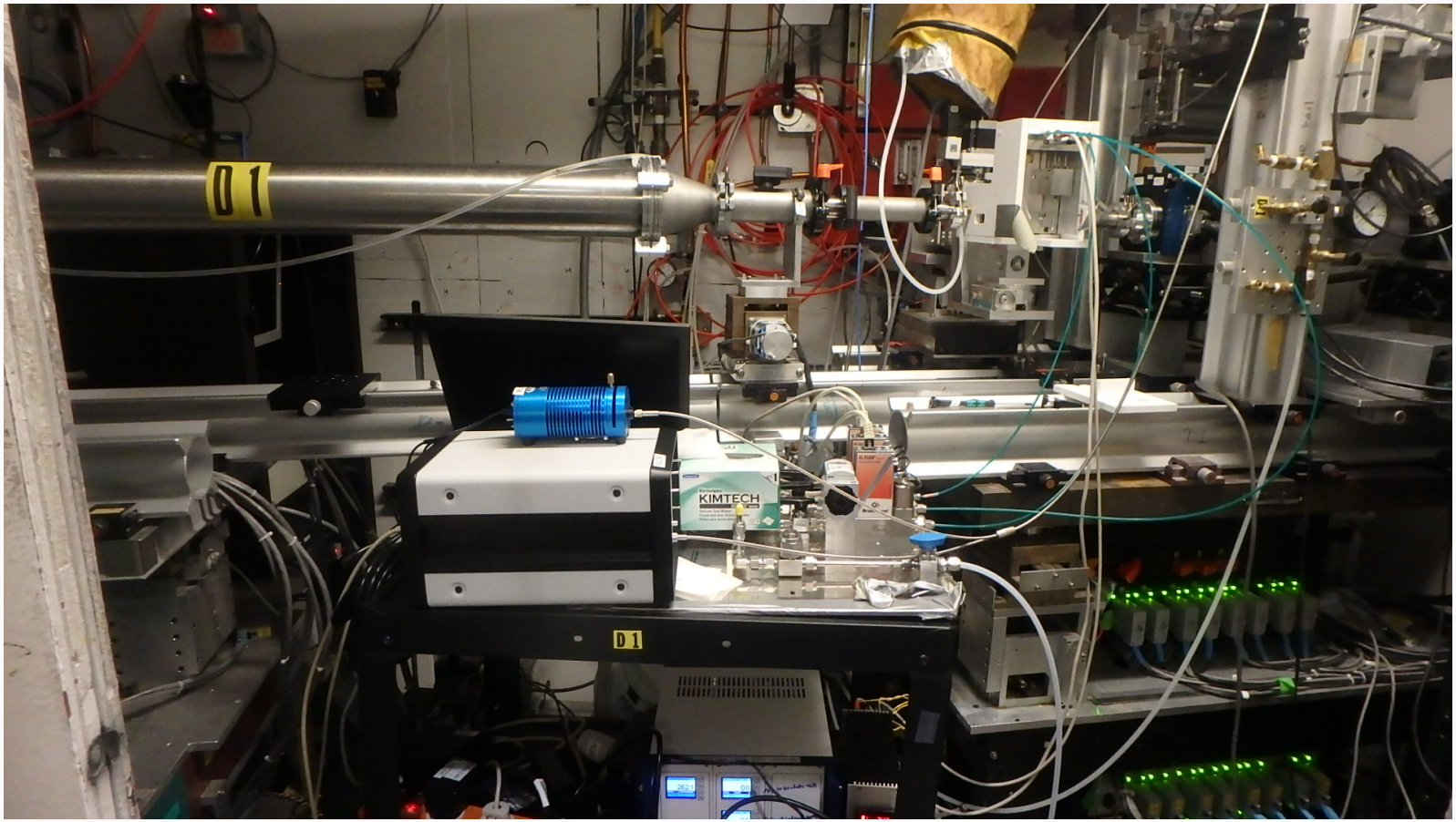
Master Thesis Prelude

D-Line

December '17 and May '18



Problems with the reflectance measurements during swelling

Figure 1: Polystyrene - SVA run used in Master Thesis

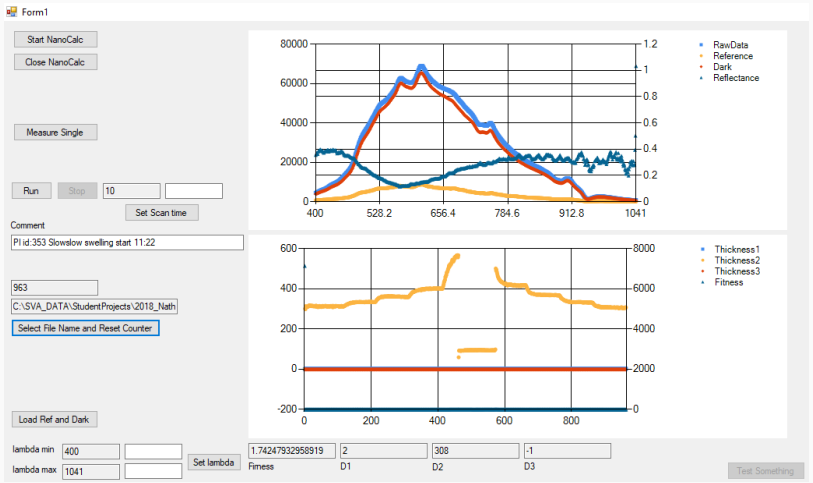


Figure 2: Polyisoprene - SVA run used in Master Thesis

Master Thesis Problem Formulation

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

Experimental Setup Overview

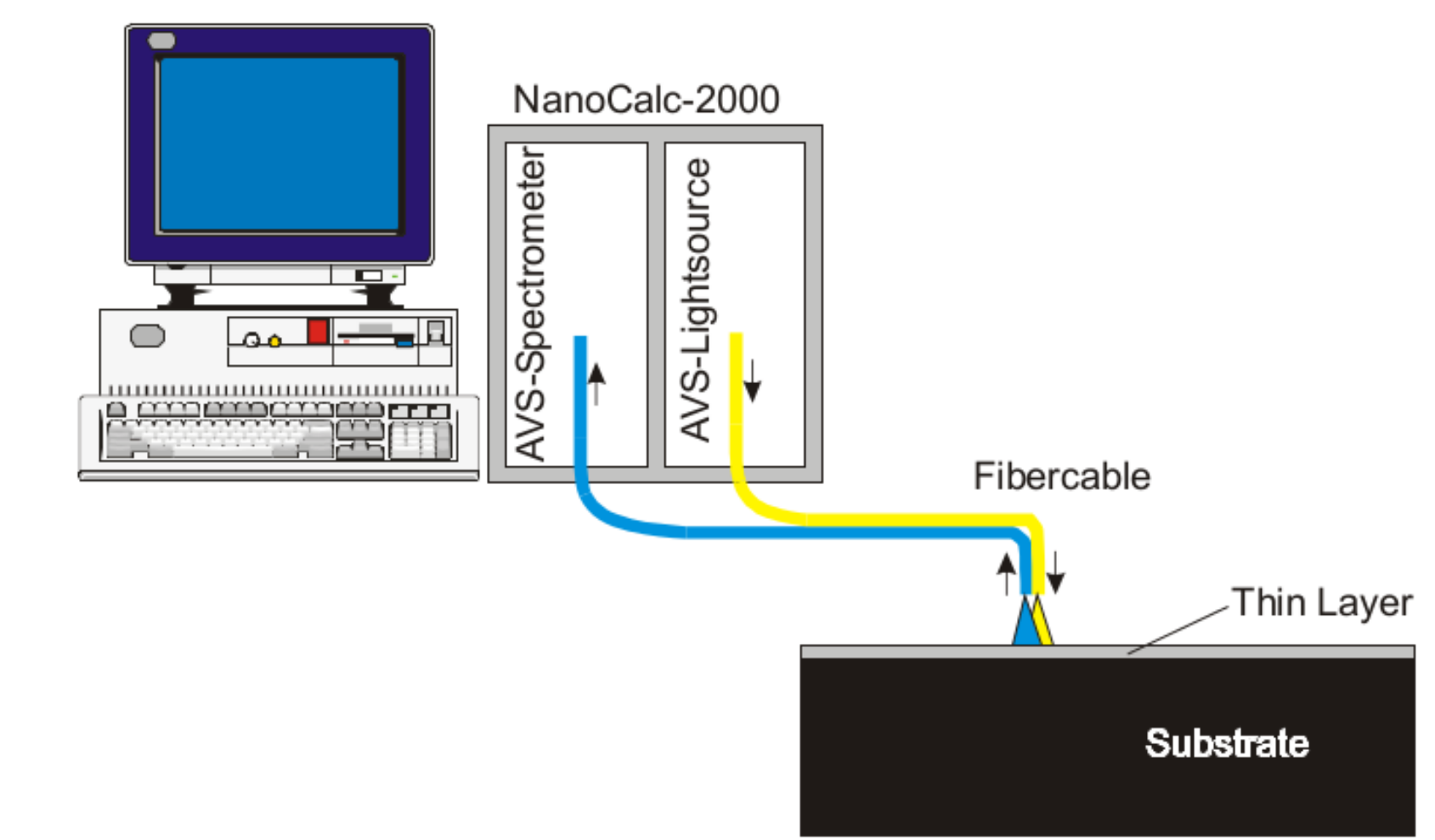
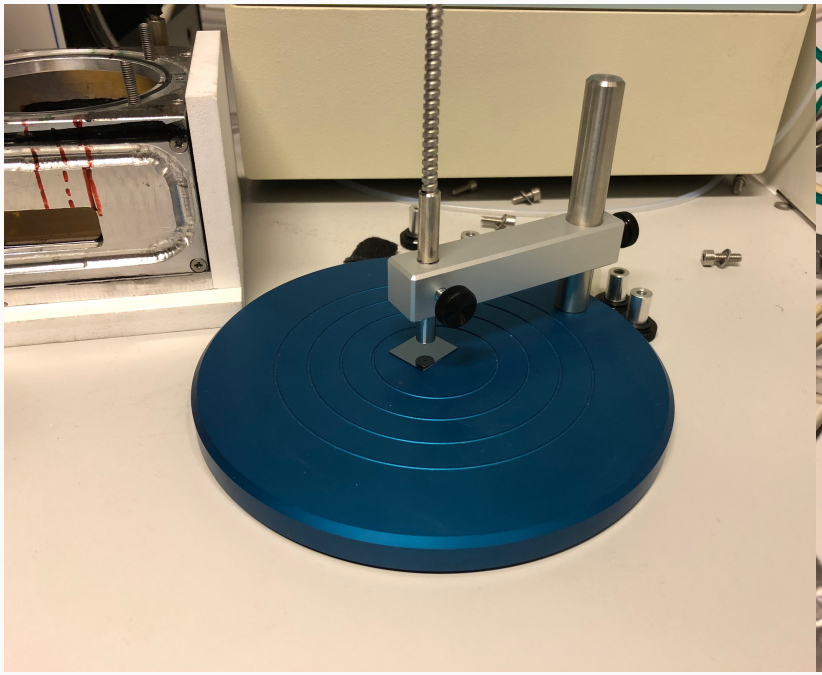
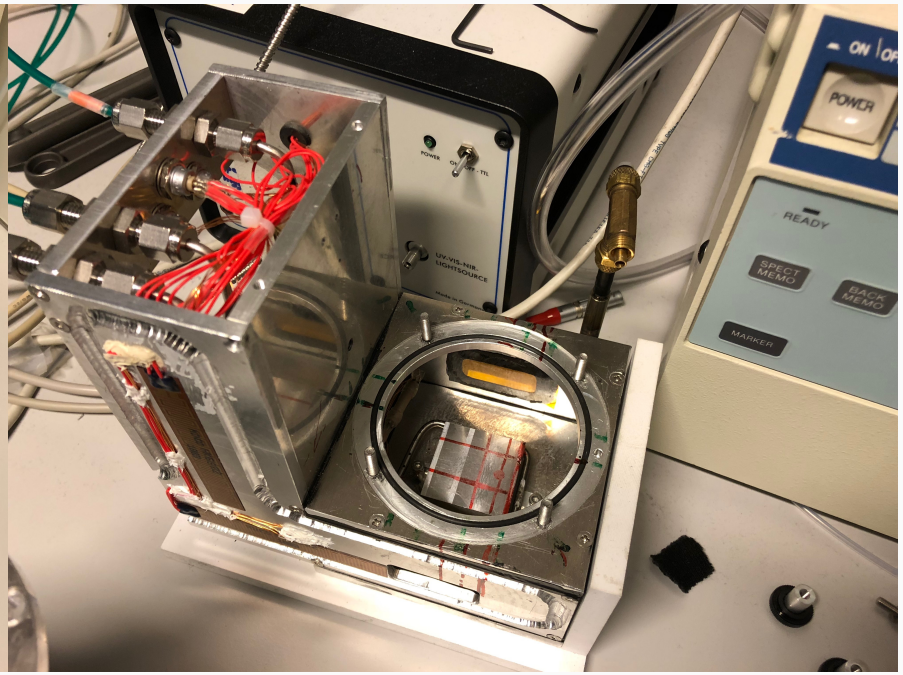


Figure 3: Taken from NanoCalc Software Manual v.4

Experimental Components

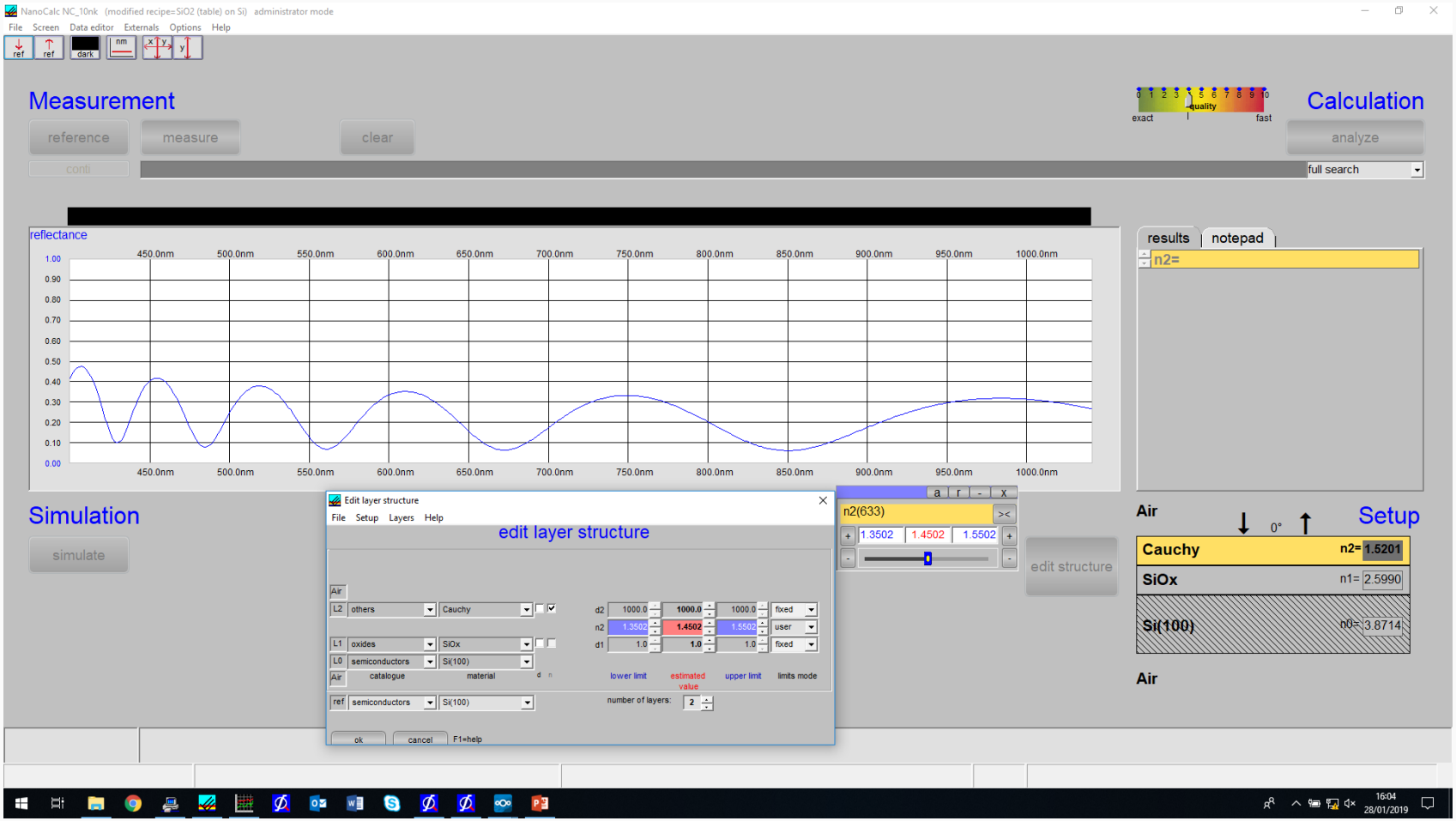
Single Point Stage and SVA test chamber.





Step Wafer

NanoCalc Software



Taking Measurements

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

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

Polymers

Polymers used in Master Thesis

Figure 4: Source:www.isowall.co.za

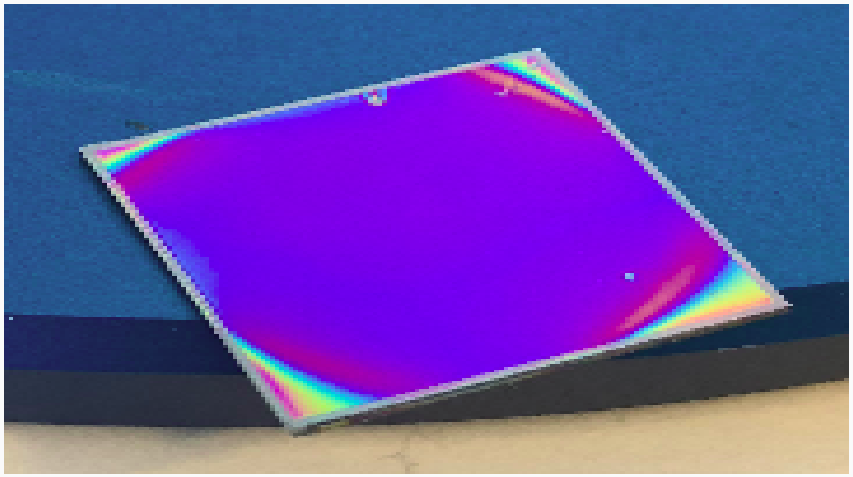


Figure 5: Polystyrene wafer

Figure 6: Source:wbcsd.org

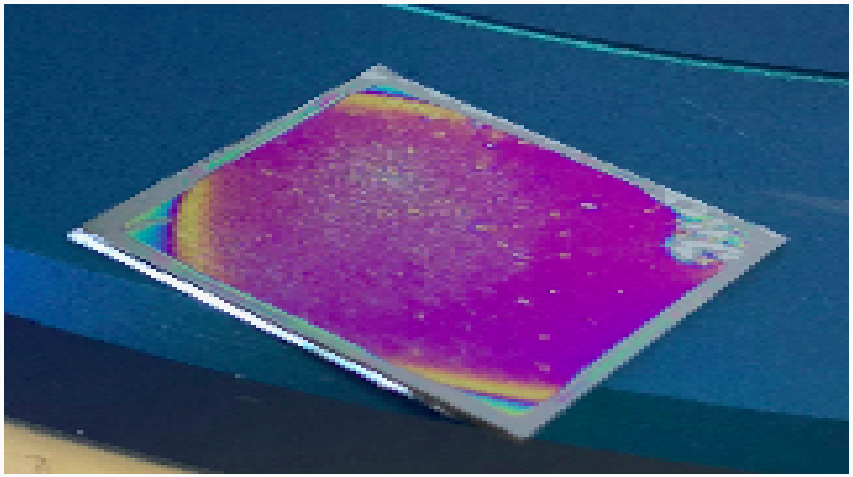


Figure 7: Polyisoprene wafer

Polymers used in Master Thesis

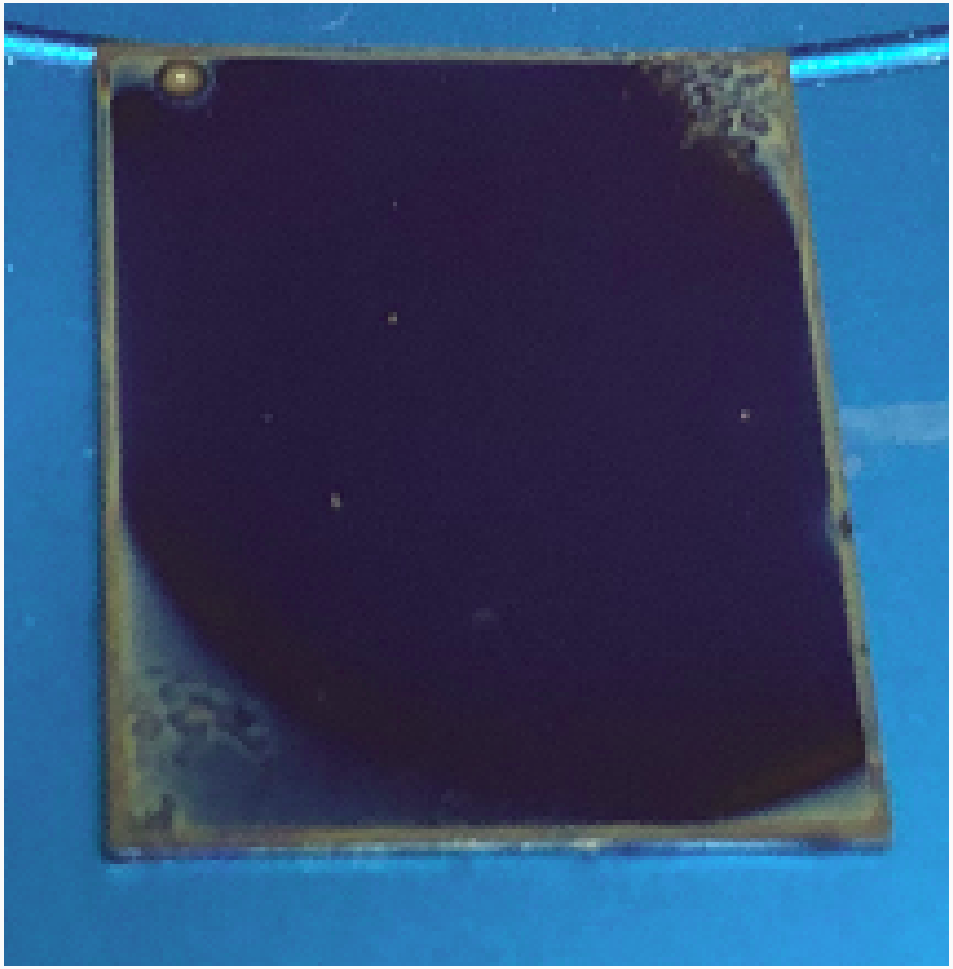
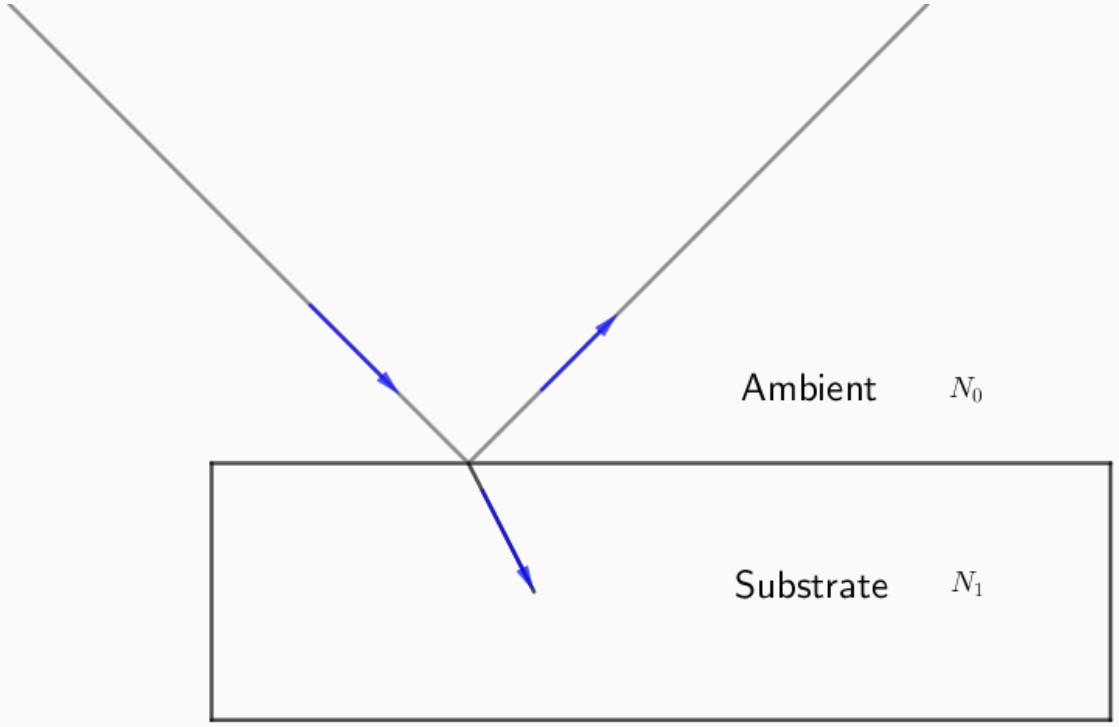


Figure 8: Polystyrene-b-polyisoprene

Fresnel Models

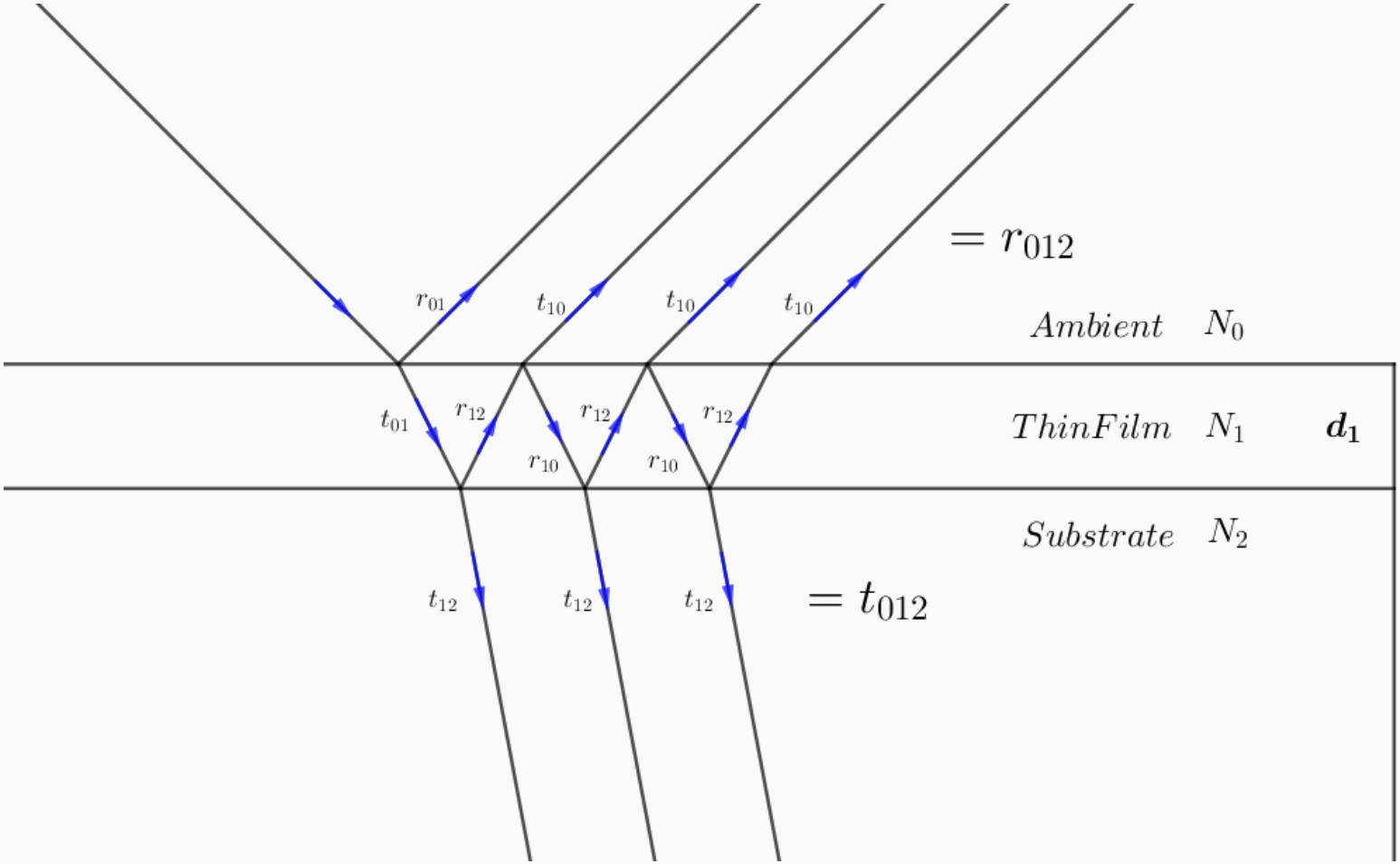
Fresnel Equations - Substrate



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

$$R_p = \mid r_p \mid^2$$

Fresnel Equations - One layer



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

Fresnel Equations - One layer

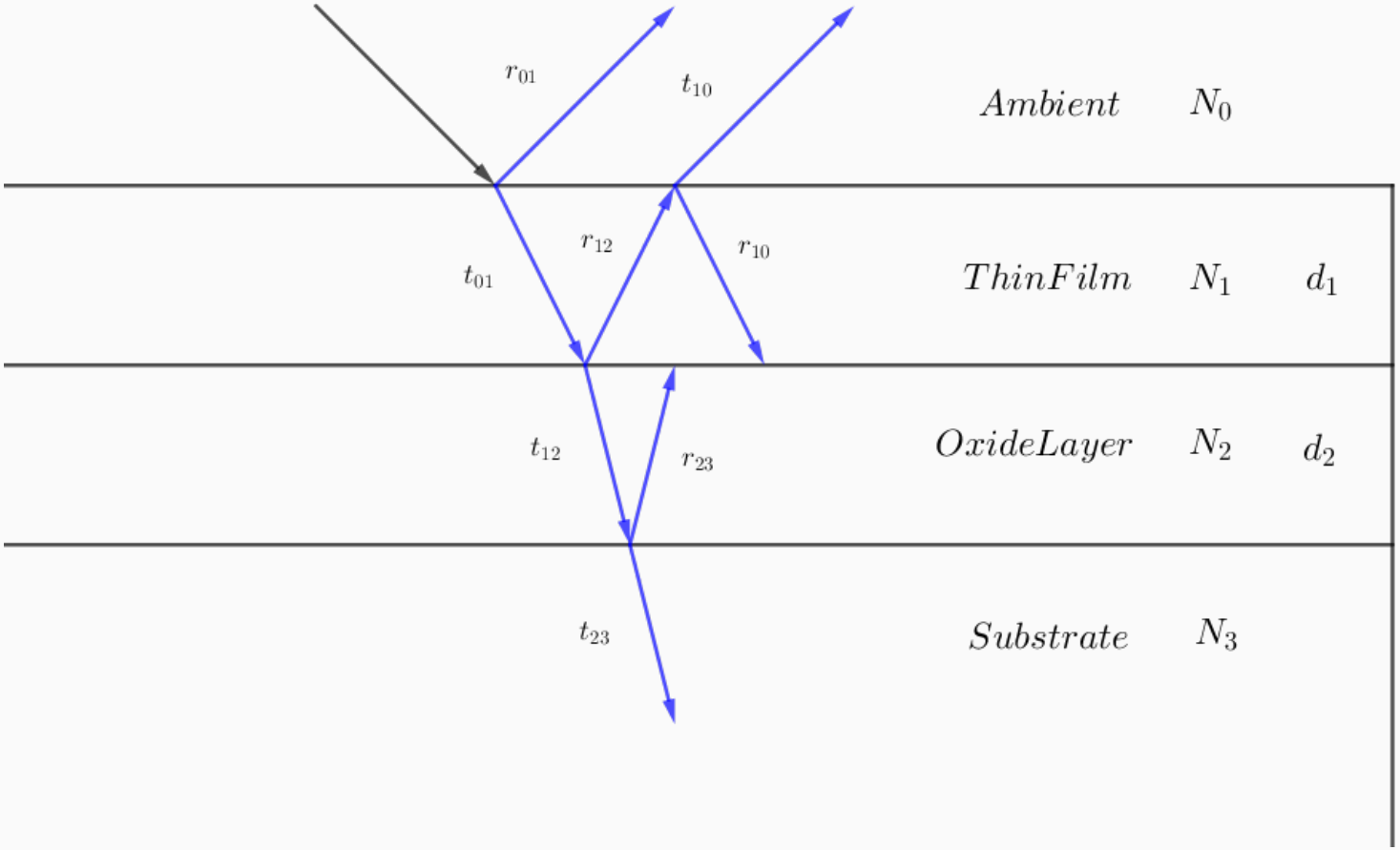
$$r_{012} = \frac{r_{01} + r_{12}\exp(-i2\beta)}{1 + r_{01}r_{12}\exp(-i2\beta)}$$

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

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

$$R_{012} = \mid r_{012} \mid^2$$

Homopolymer Fresnel Model



Homopolymer Fresnel equations

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

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

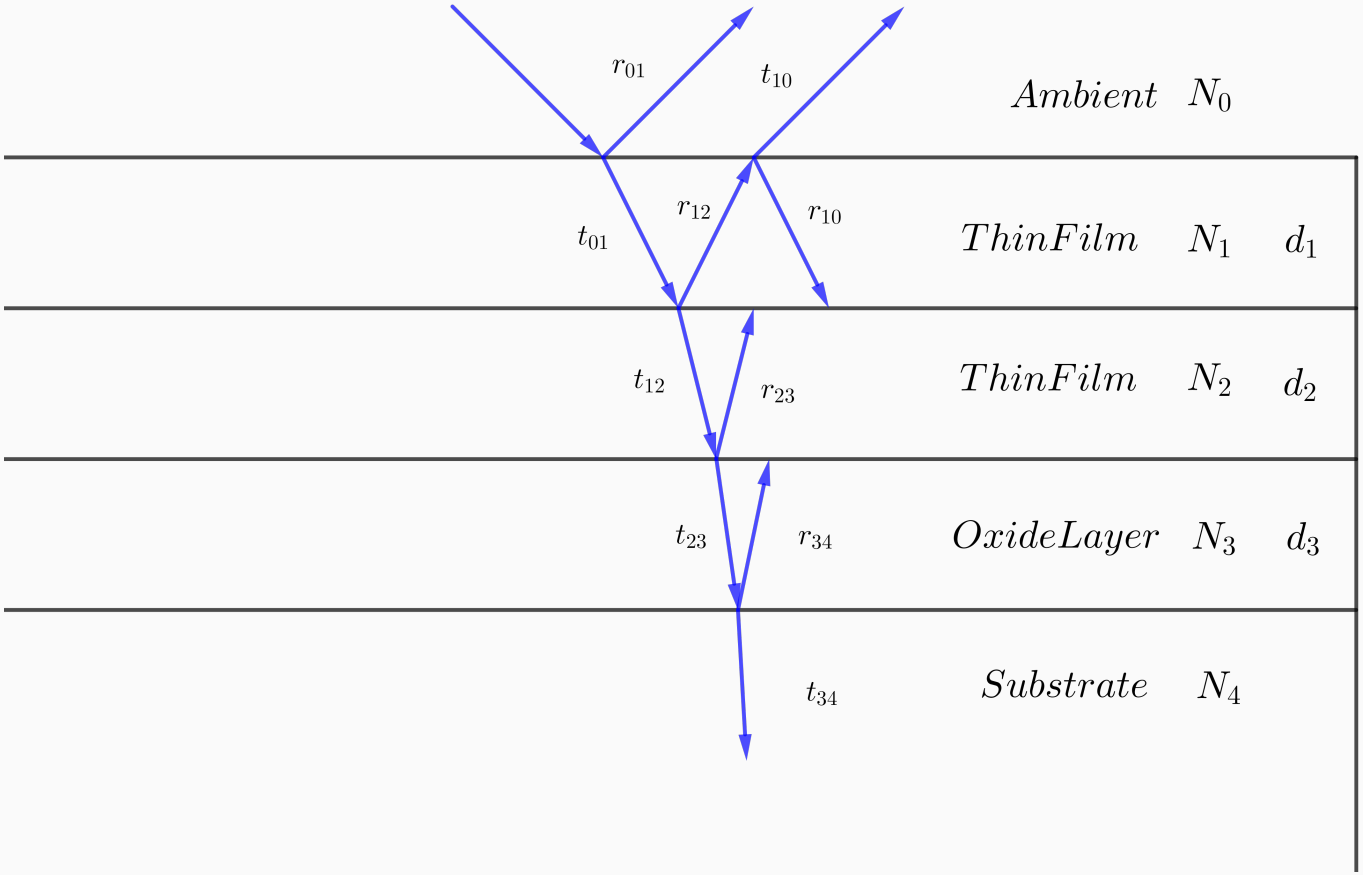
$$r_j k = \frac{N_k - N_j}{N_j + N_k}$$

$$R_{0123} = \left| r_{0123} \right|^2$$

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

N_0, N_1 and d_1 fitted during solvent vapour annealing.

Diblock copolymer Fresnel model



Diblock copolymer Fresnel Equations

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

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

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

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

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

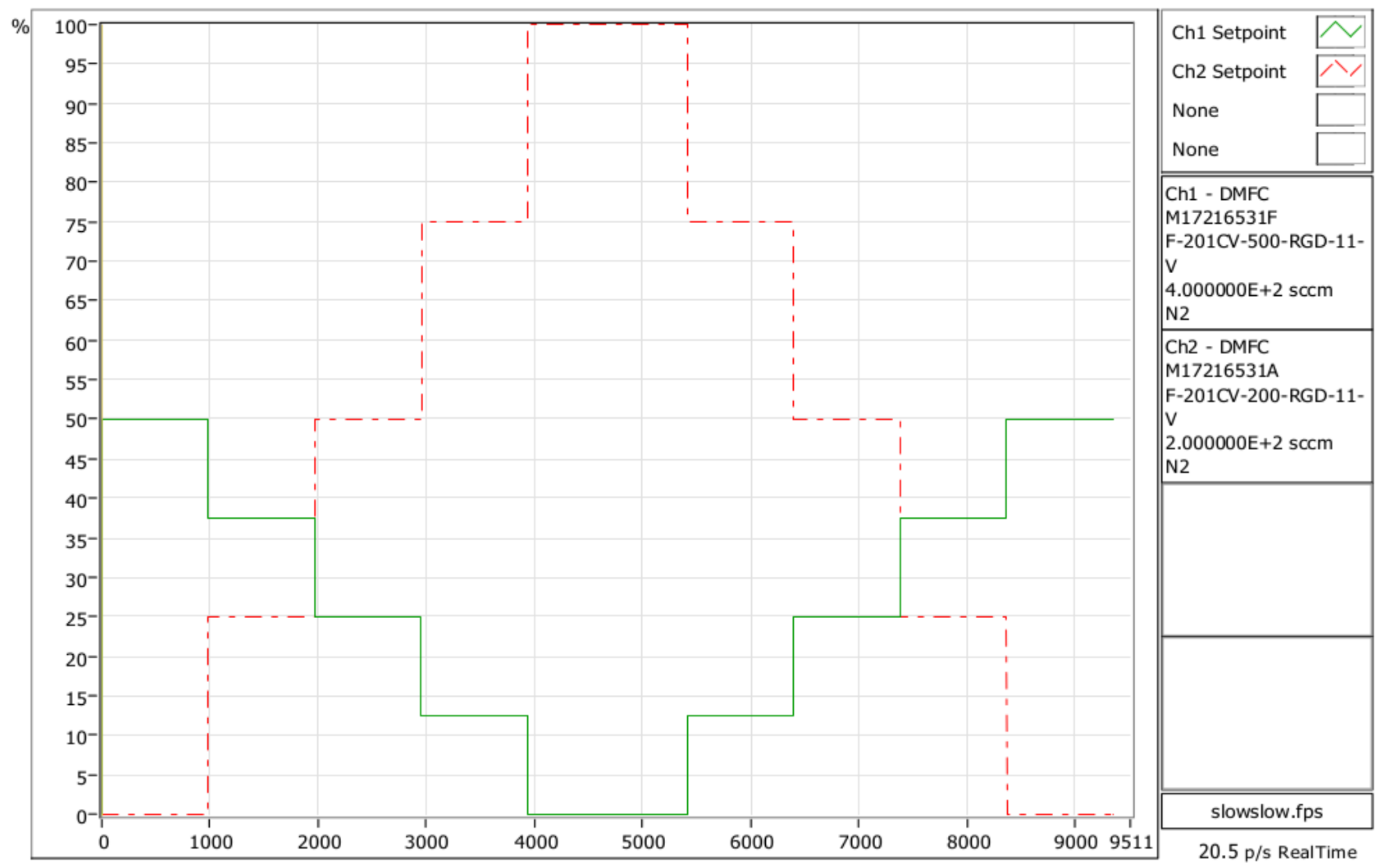
N_0, N_1, N_2, d_1 and d_2 fitted during solvent vapour annealing.

Plotted Fresnel models

Movie:varyRI.avi

Solvent vapour Annealing

SVA protocol



Preliminary Studies

Light Fluctuation

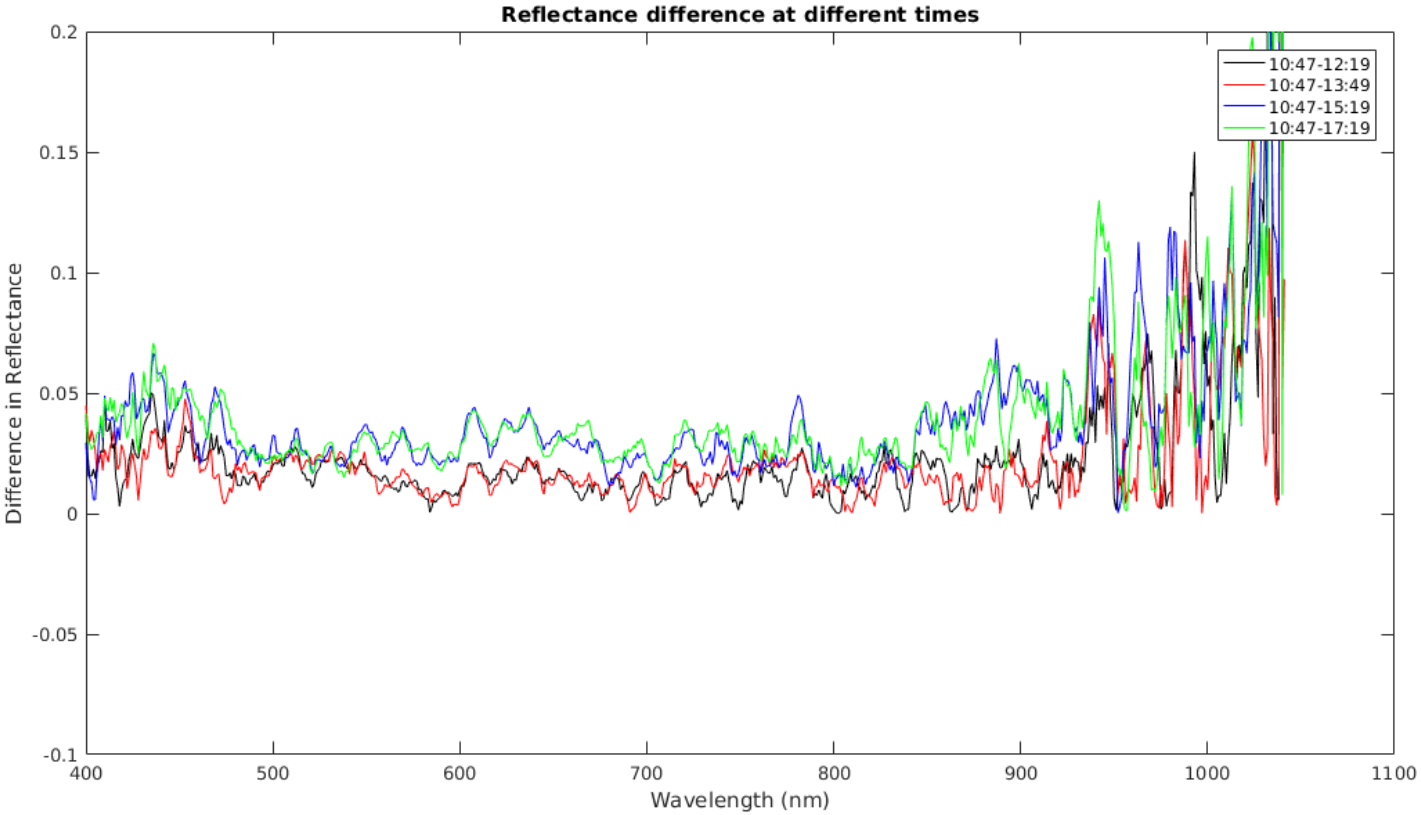


Figure 9: Light Fluction study 1

Light Fluctuation continued

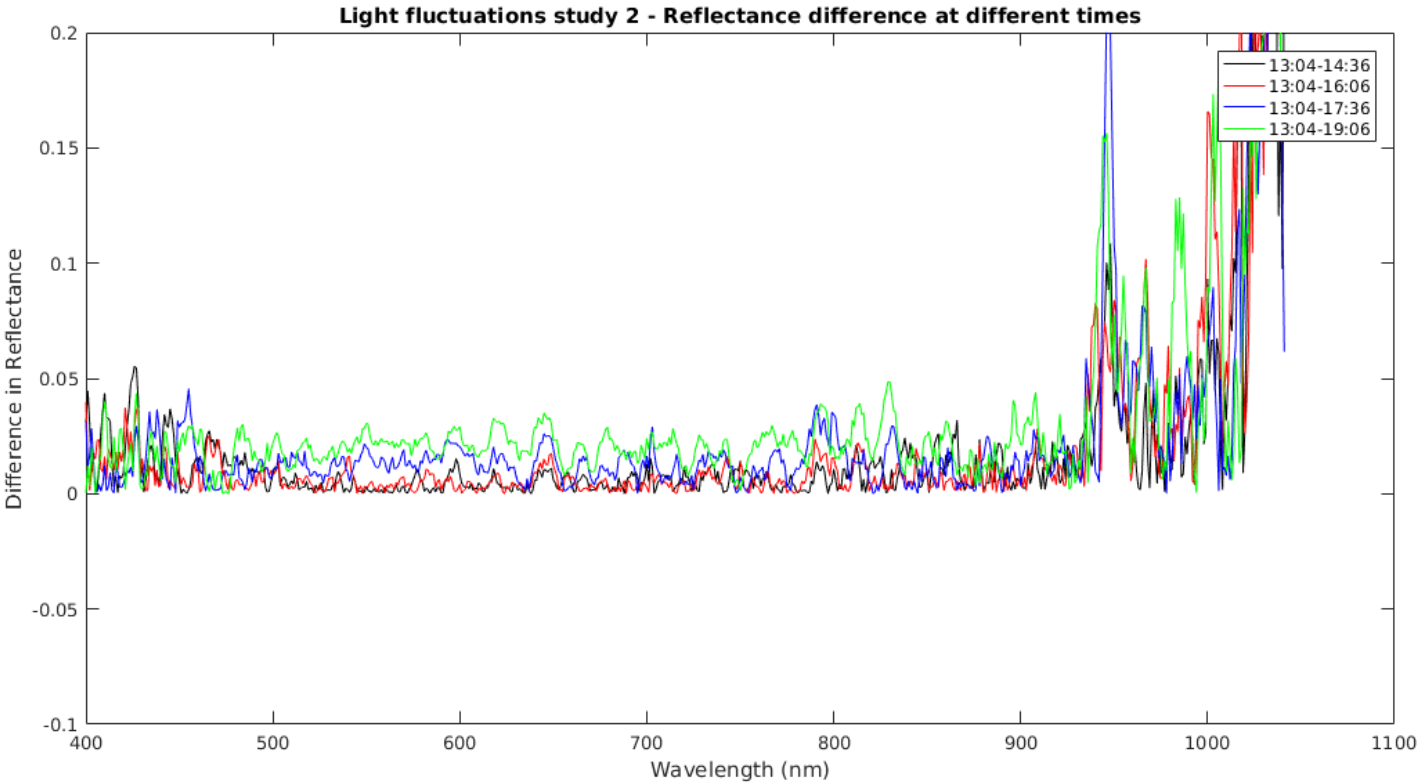


Figure 10: Light Fluction study 2

Solvent vapour annealing ambient study

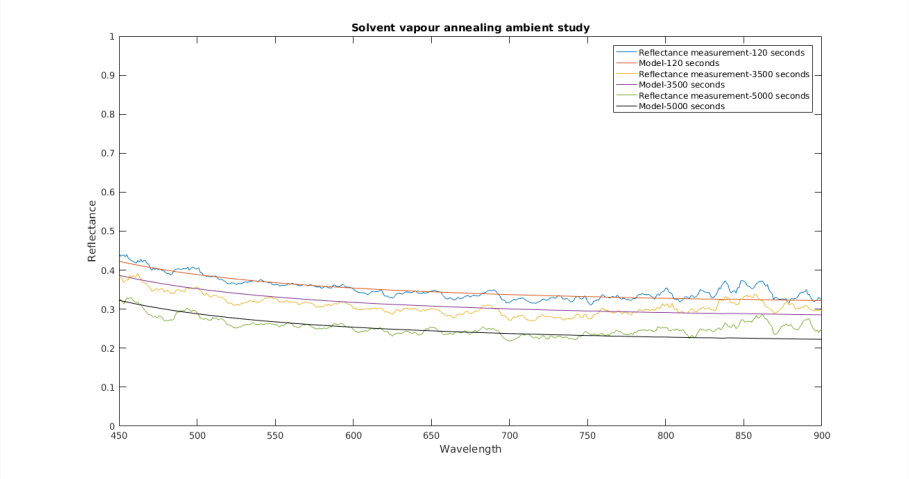


Figure 11: Reflectance curves at different times during SVA -120s,3500s,5000s.

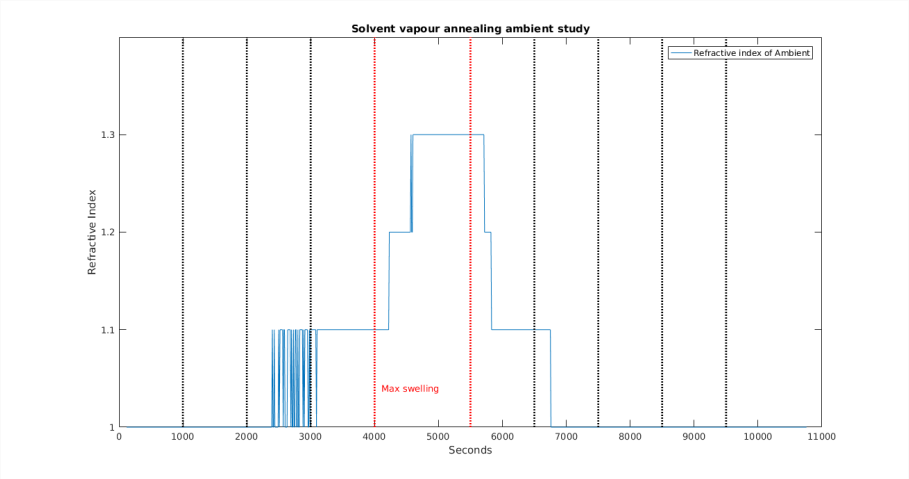
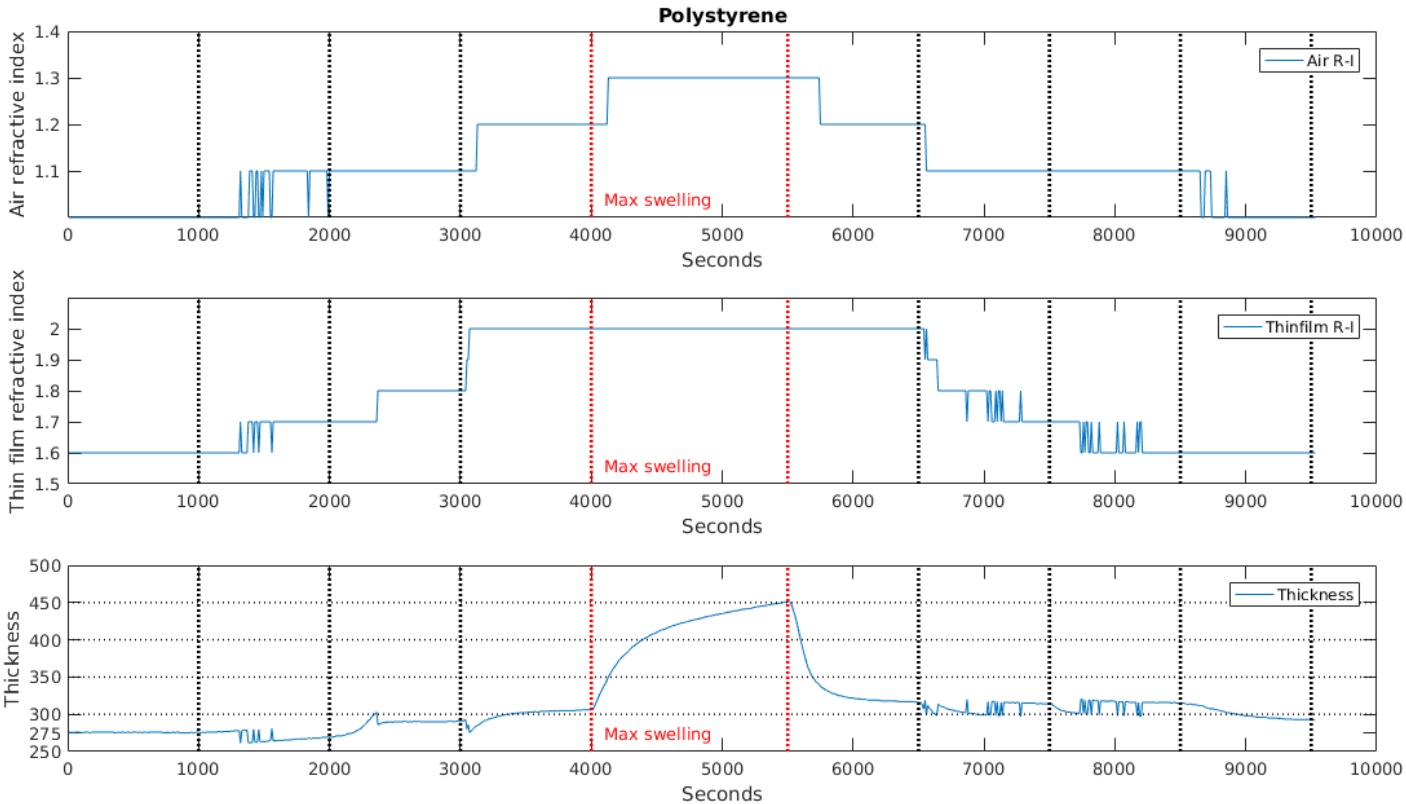


Figure 12: Ambient refractive index

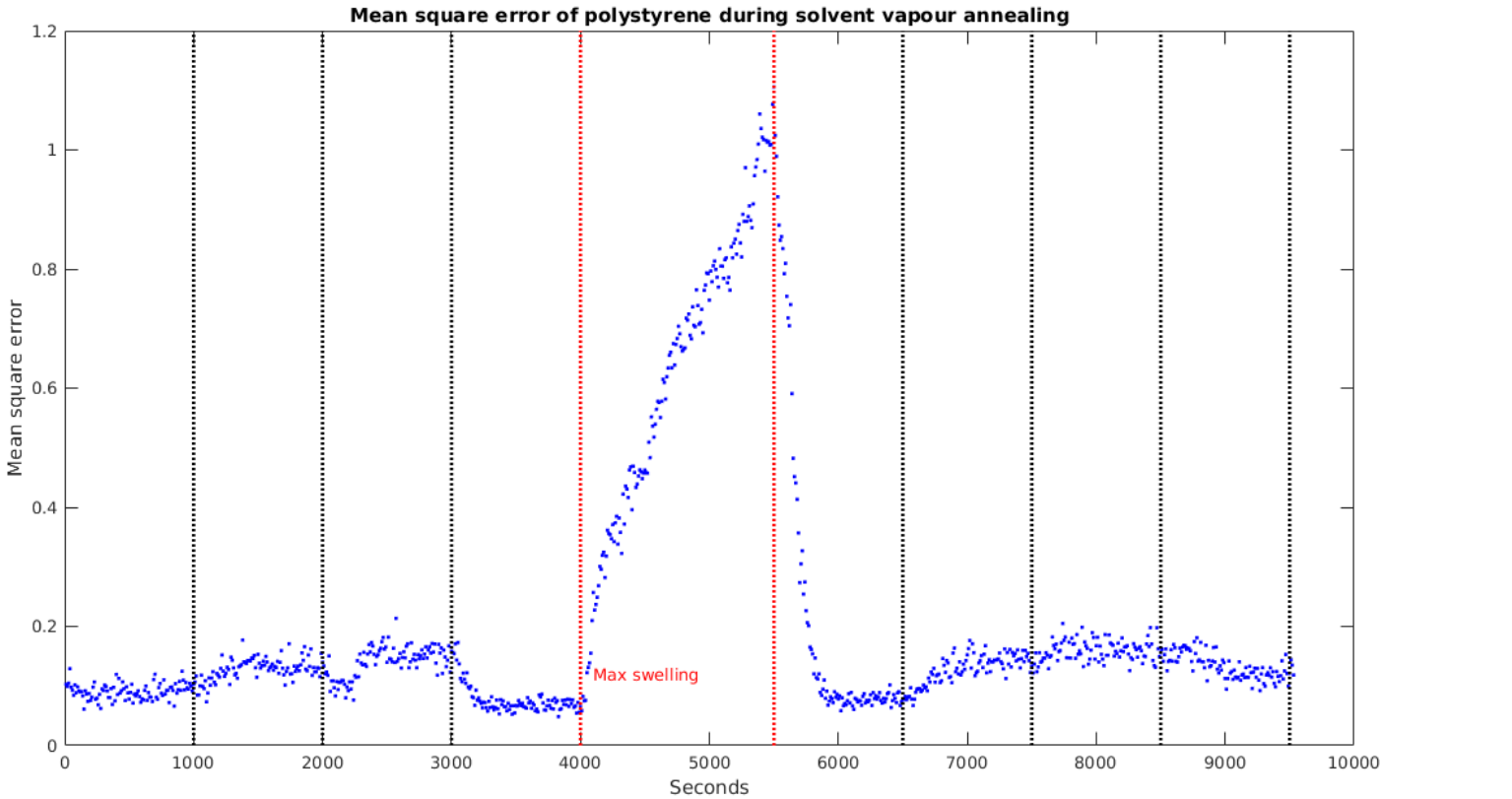
Results - 1 polymer layer

Movie: PSsva.avi

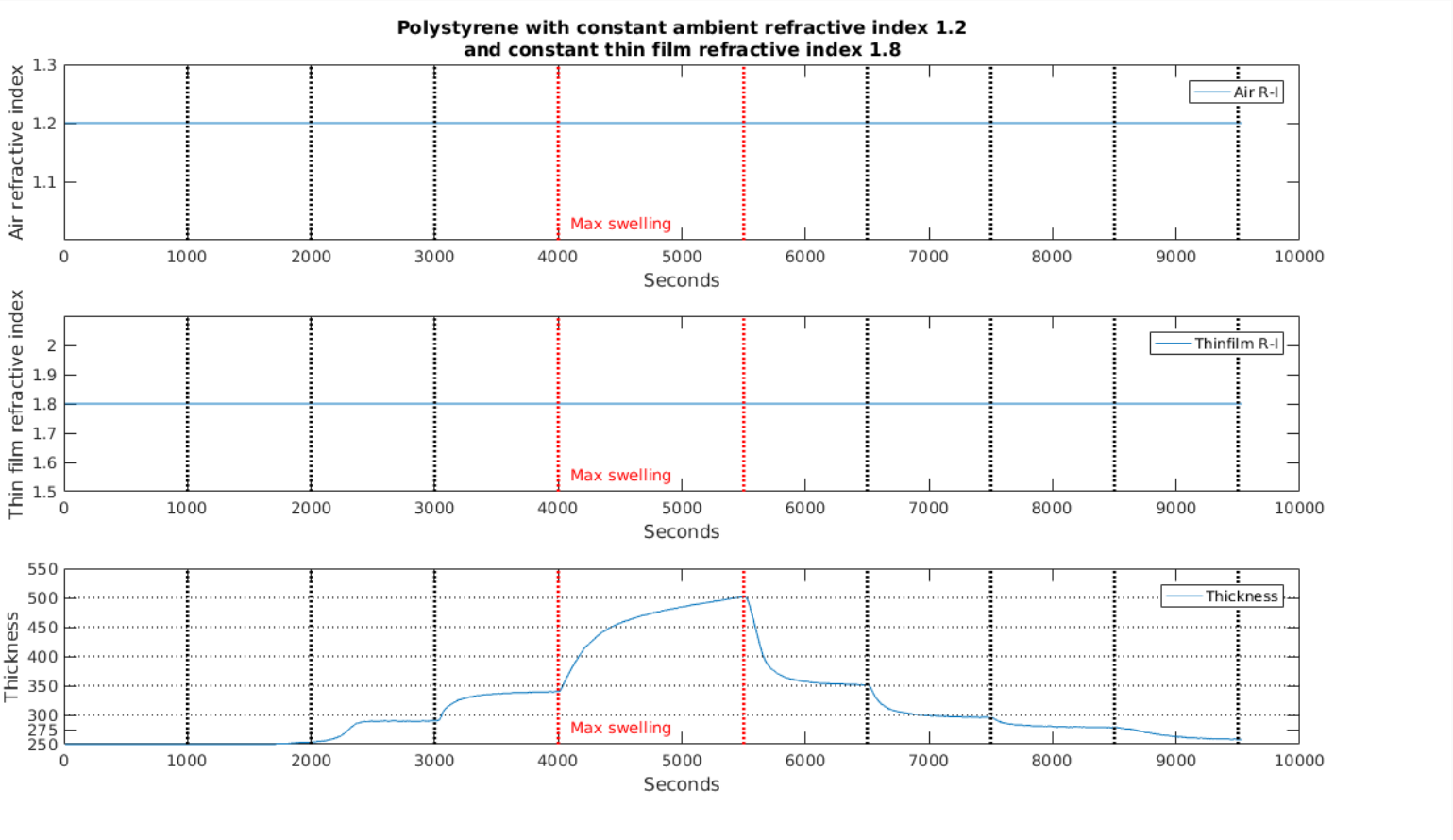
Polystyrene Results



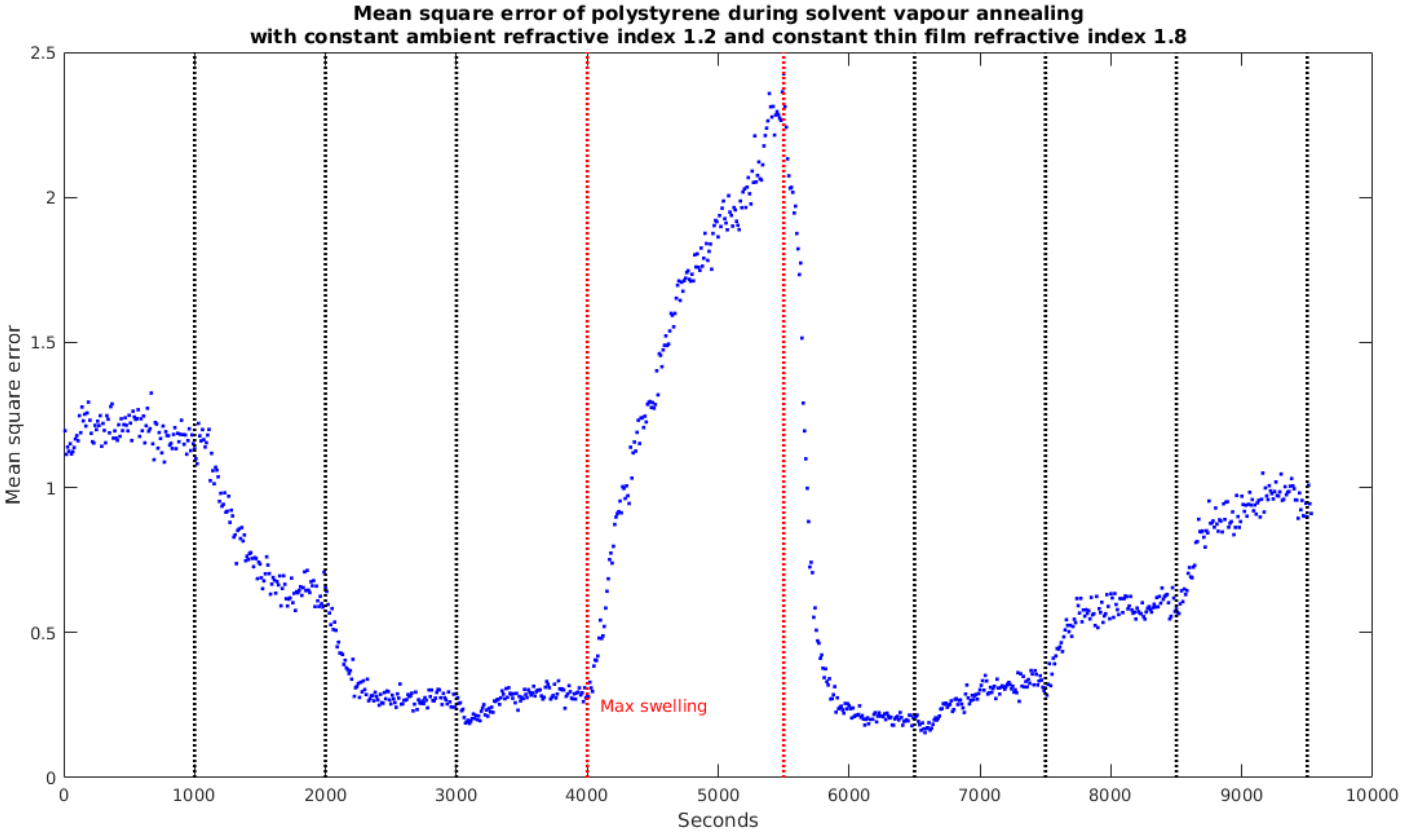
Polystyrene MSE



Polystyrene comparison



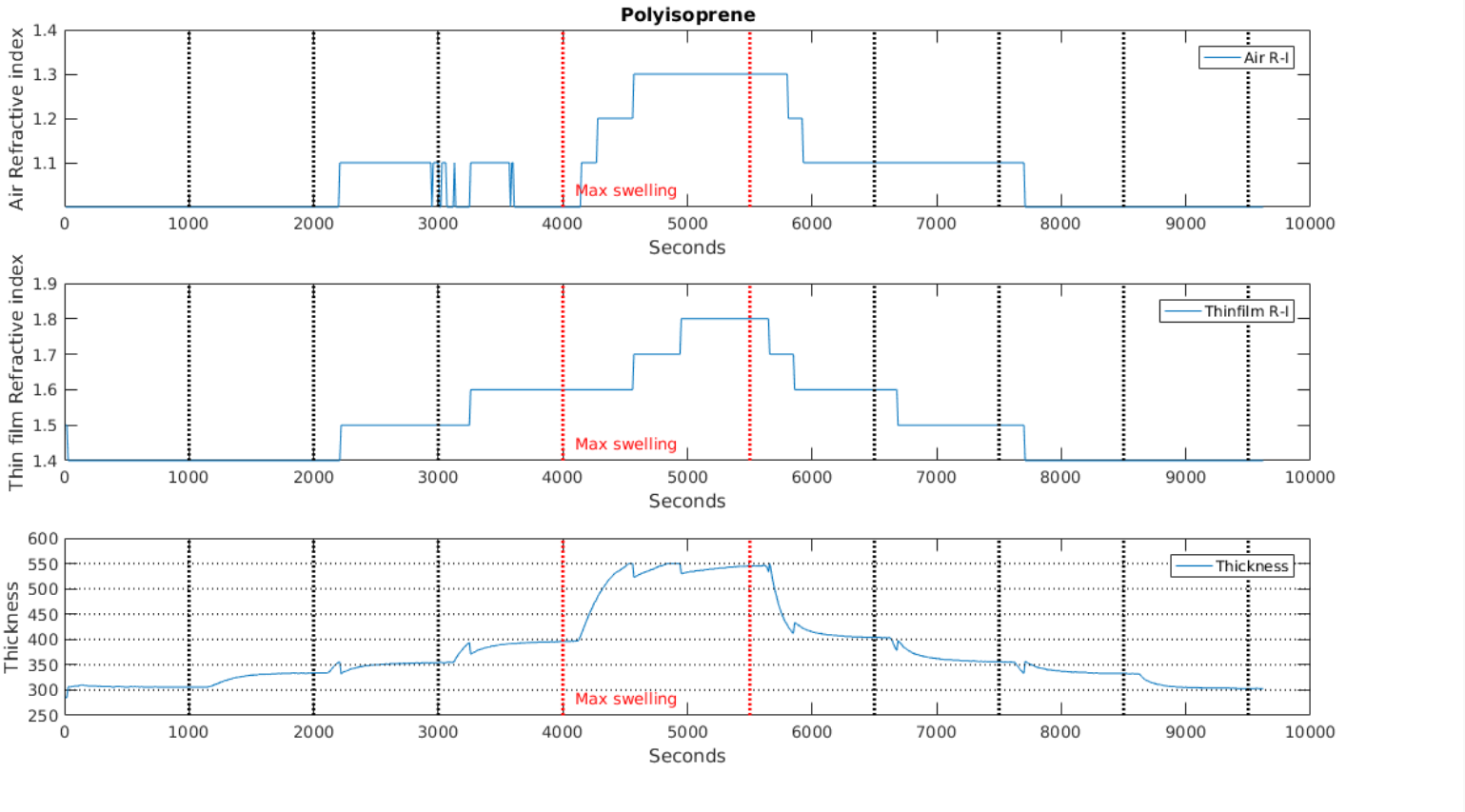
Polystyrene comparison



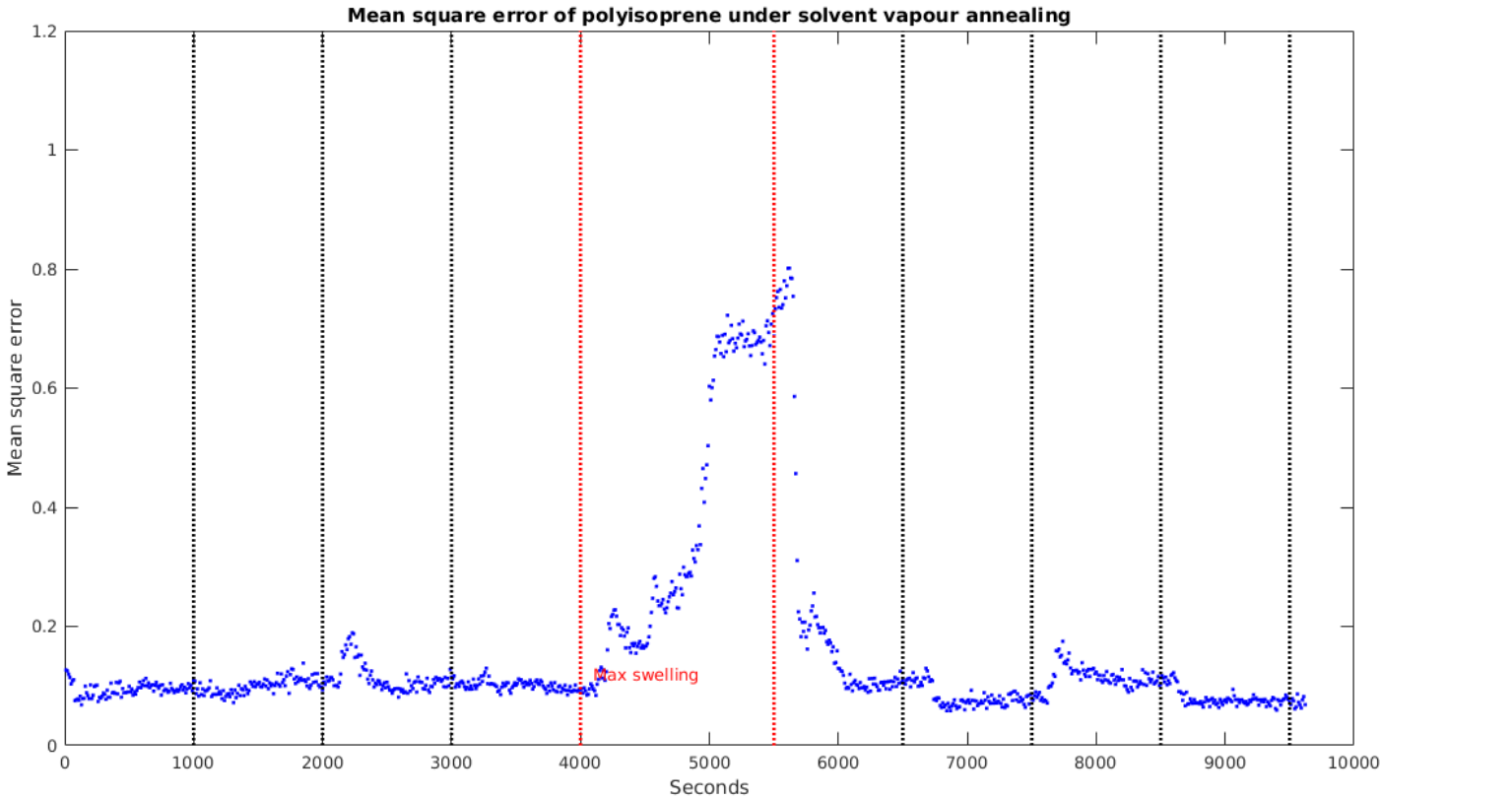
Polyisoprene

Movie:PIsvaframevalue2.avi

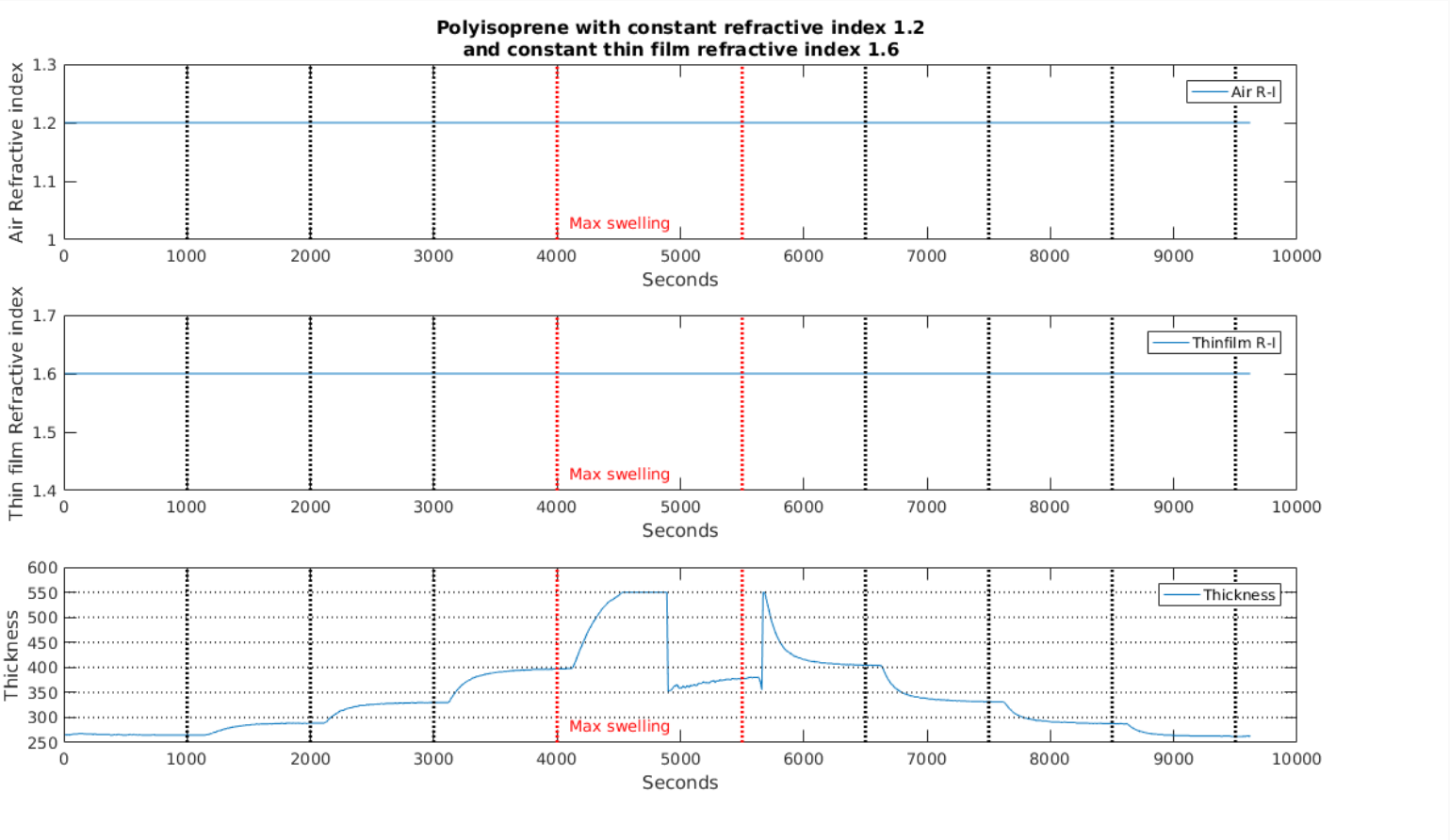
Polyisoprene Results



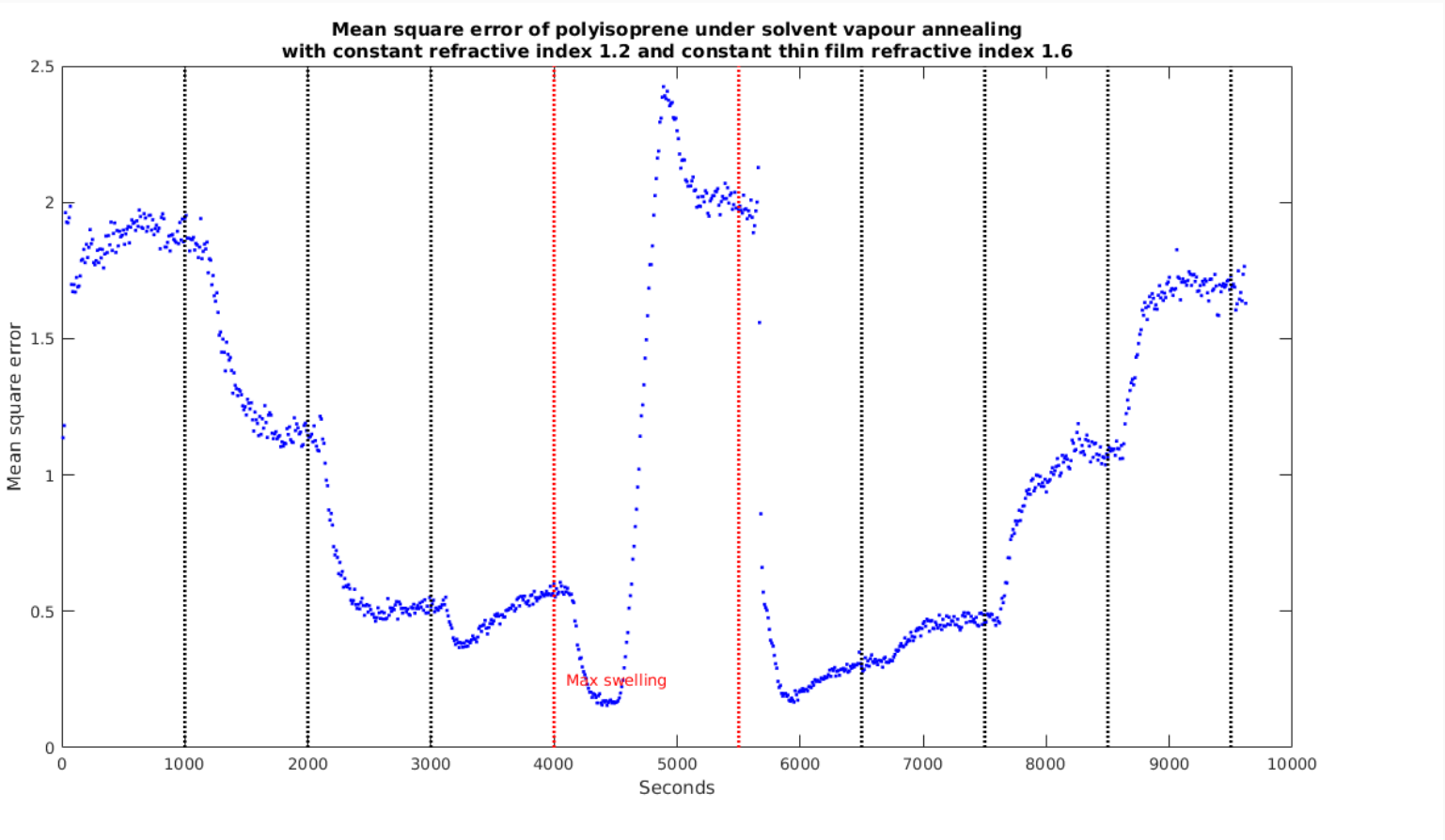
Polyisoprene MSE



Polyisoprene comparison



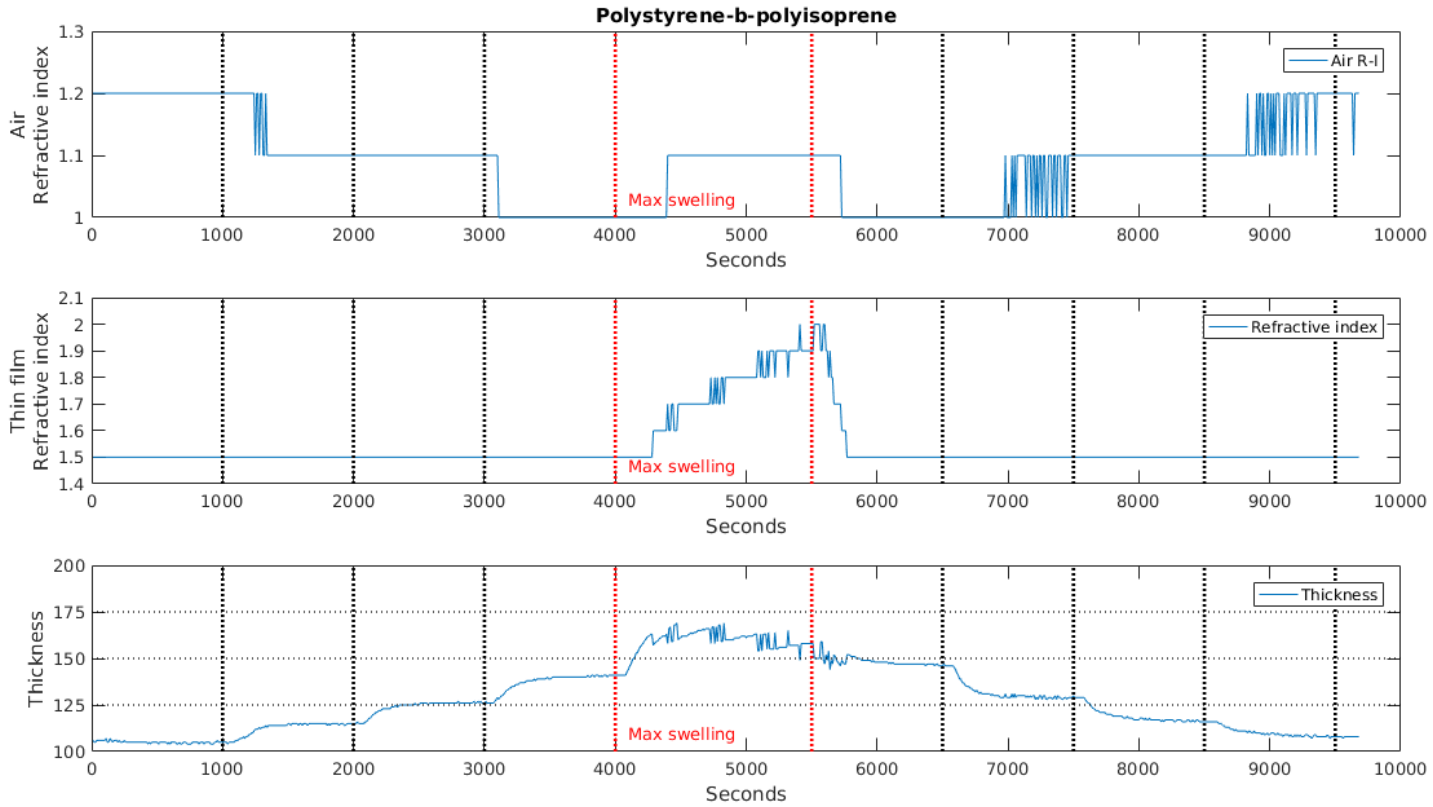
Polyisoprene comparison



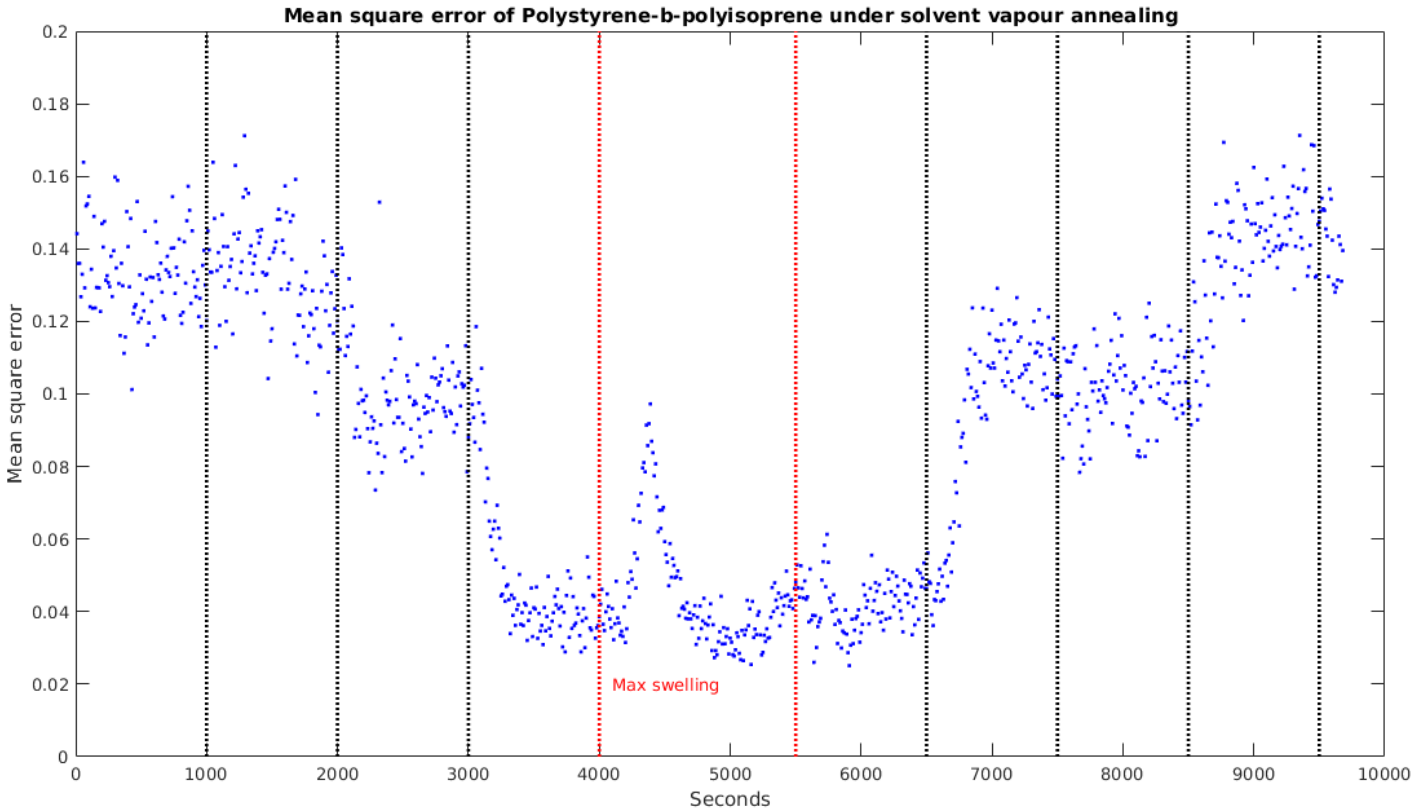
Polystyrene-b-polyisoprene

Movie: PSbPIsinglemodel.avi

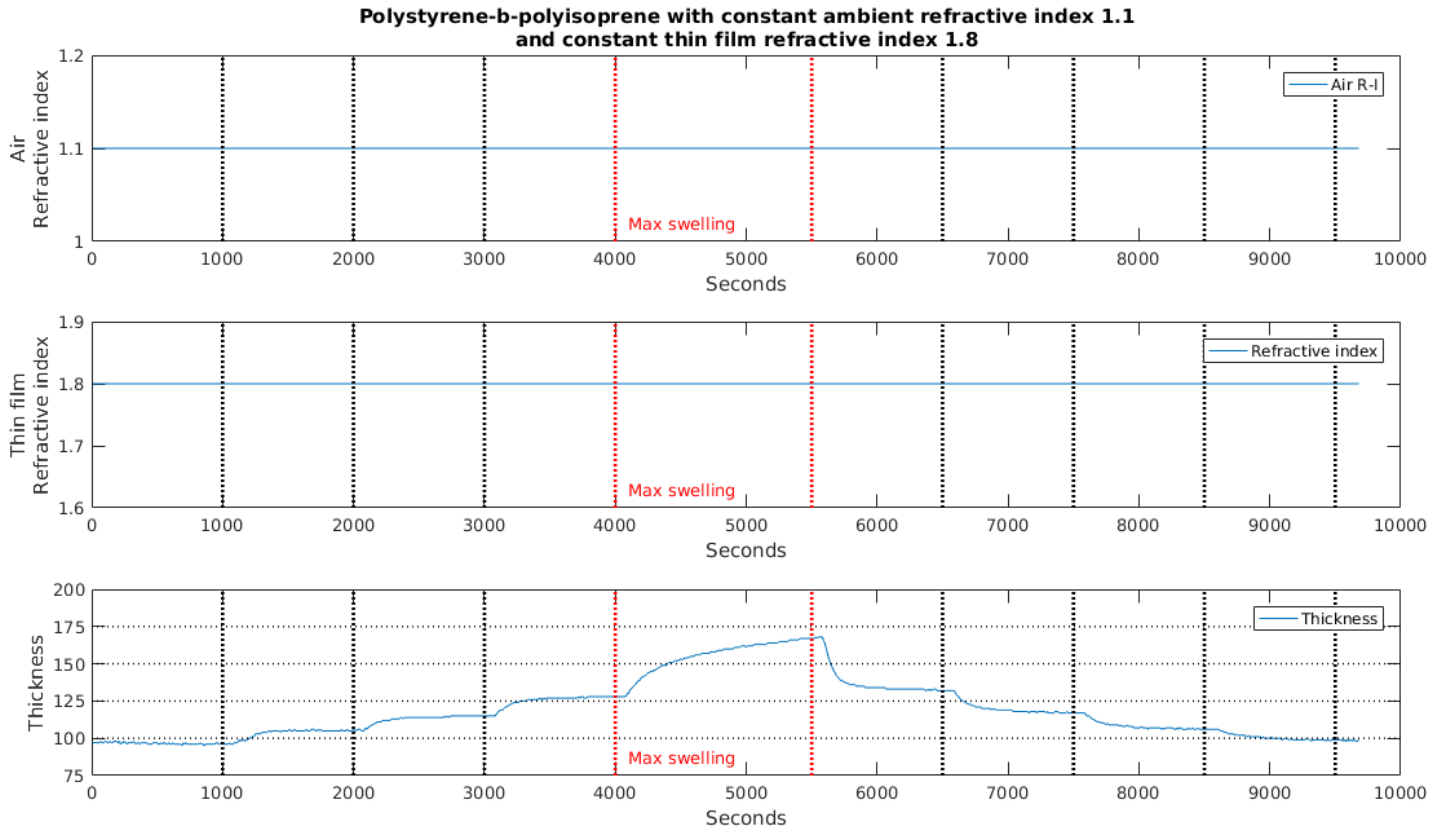
Polystyrene-b-polyisoprene Results



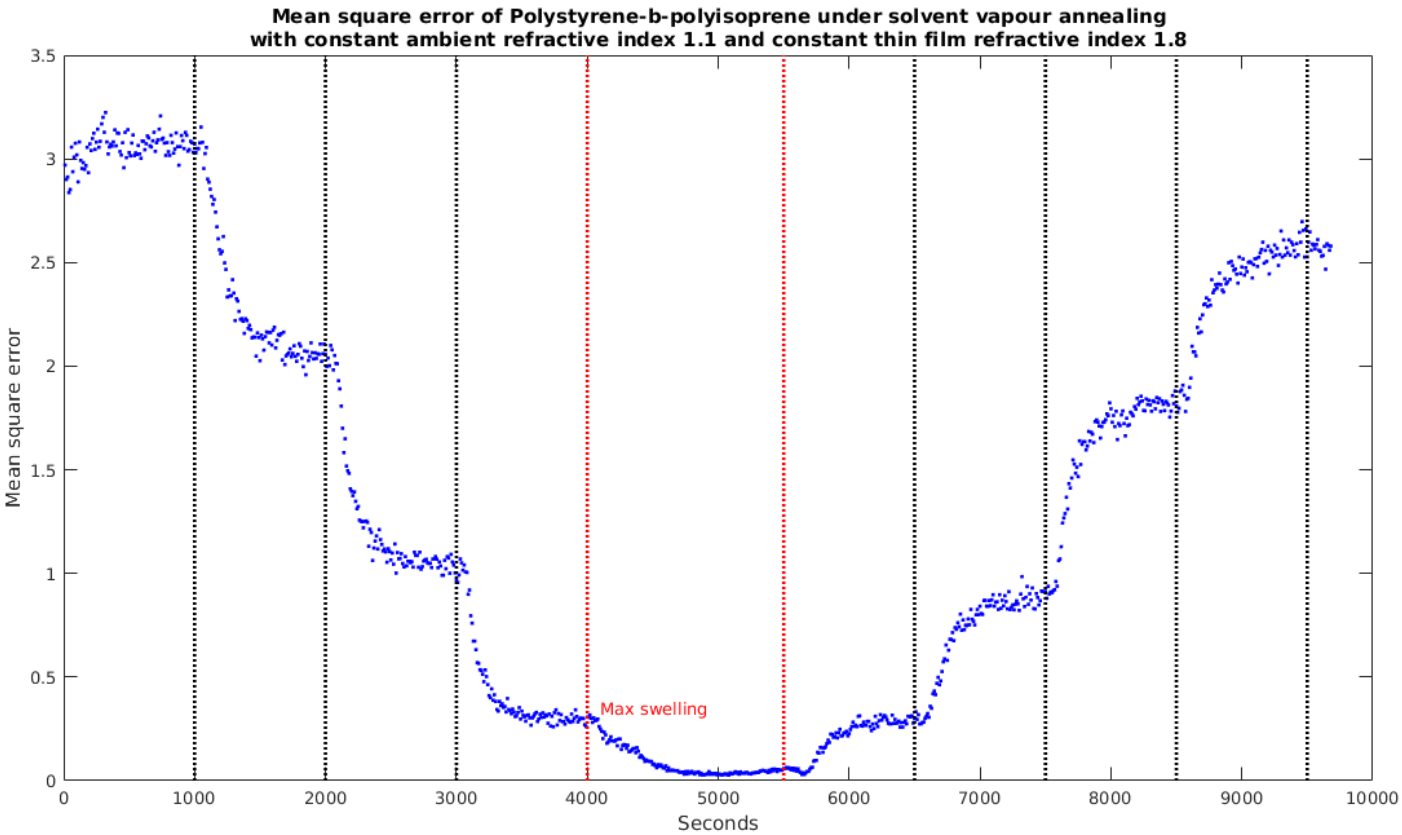
Polystyrene-b-polyisoprene MSE



Polystyrene-b-polyisoprene comparison



Polystyrene-b-polyisoprene comparison



Conclusion/Perspective

Conclusion/Perspective

Conclusion:

- Fresnel equations - easily calculated
- Care needed when taking dark measurements
- Light intensity decreases
- Homopolymer Fresnel model seems optimal for Polystyrene and Polyisoprene but not Polystyrene-b-polyisoprene

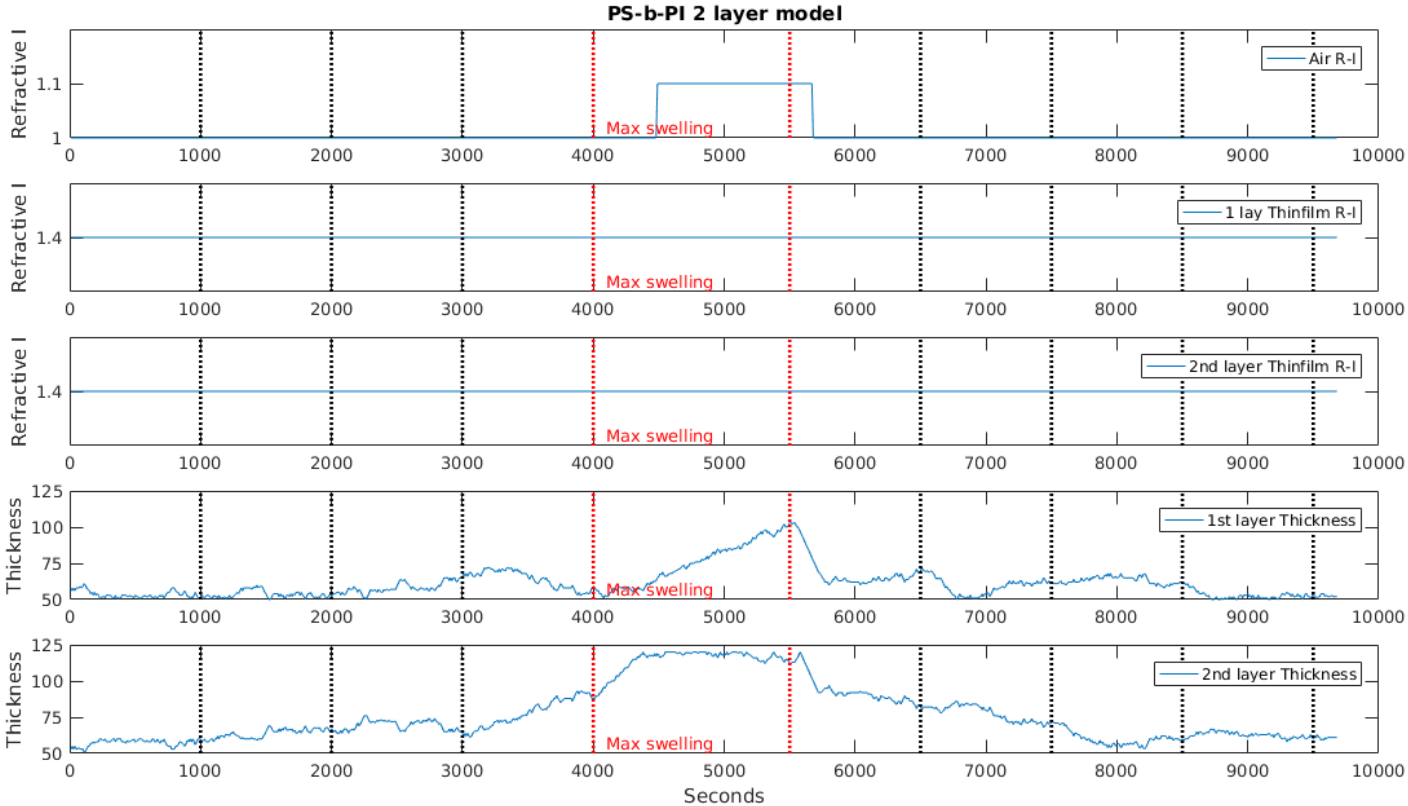
Perspective:

- Refractive index during SVA - Dispersion
- Polymer - absorption of light
- Modelling vapour pressure inside solvent vapour annealing test chamber
- Implementing fitting for multiple layer systems

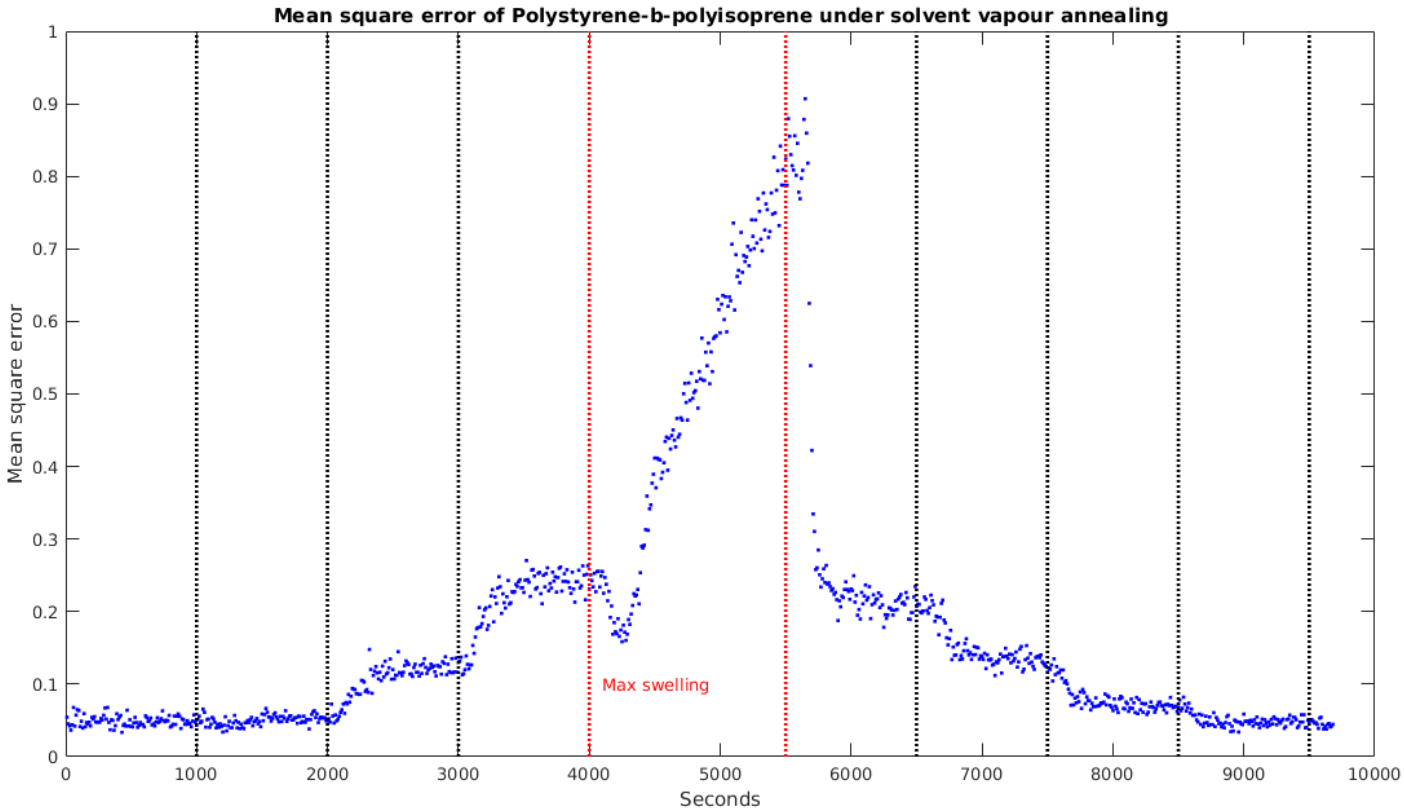
Results - 2 polymer layers

Movie: PSbPIfit2layermodelV2.avi

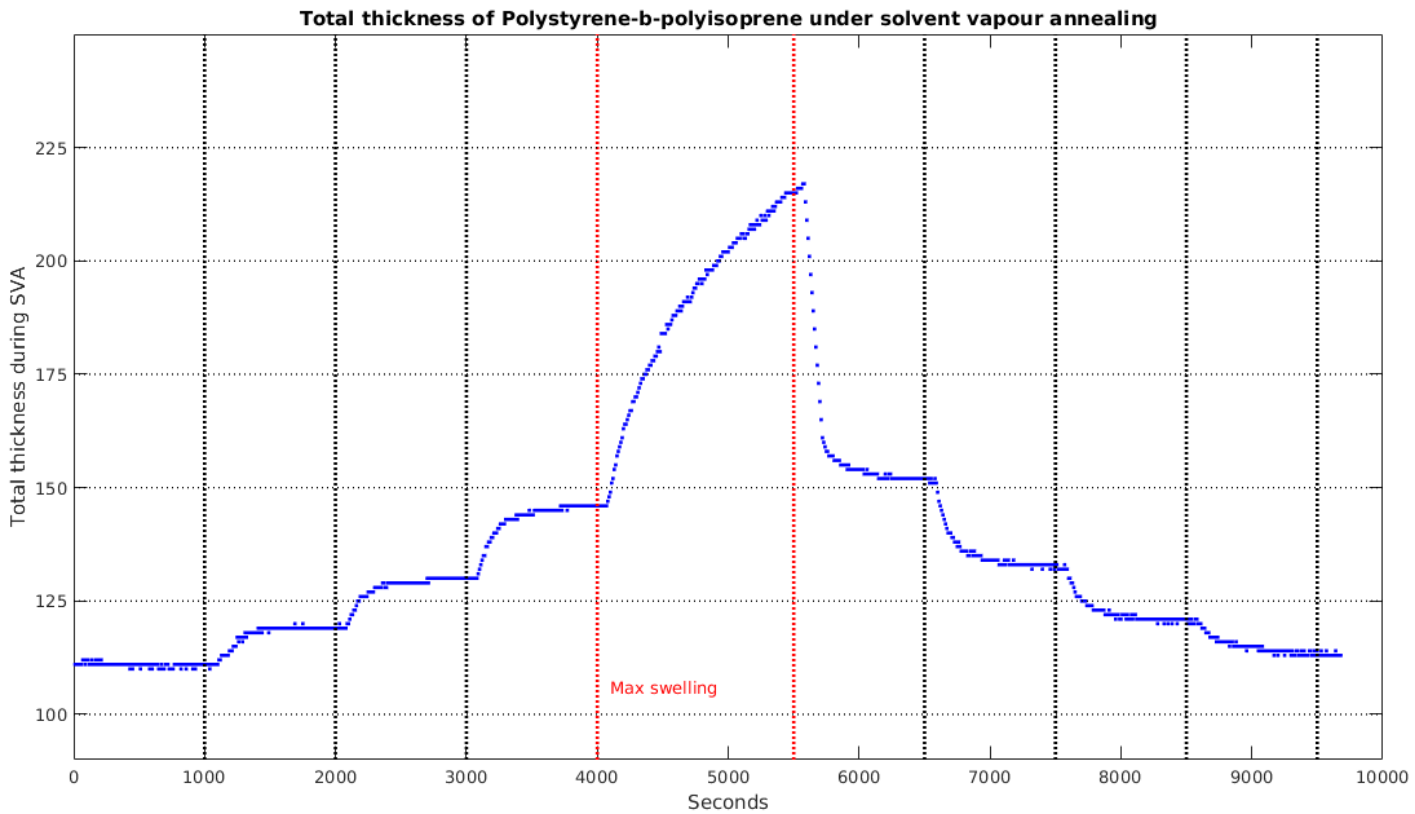
PS-b-PI - 2 layer model Results



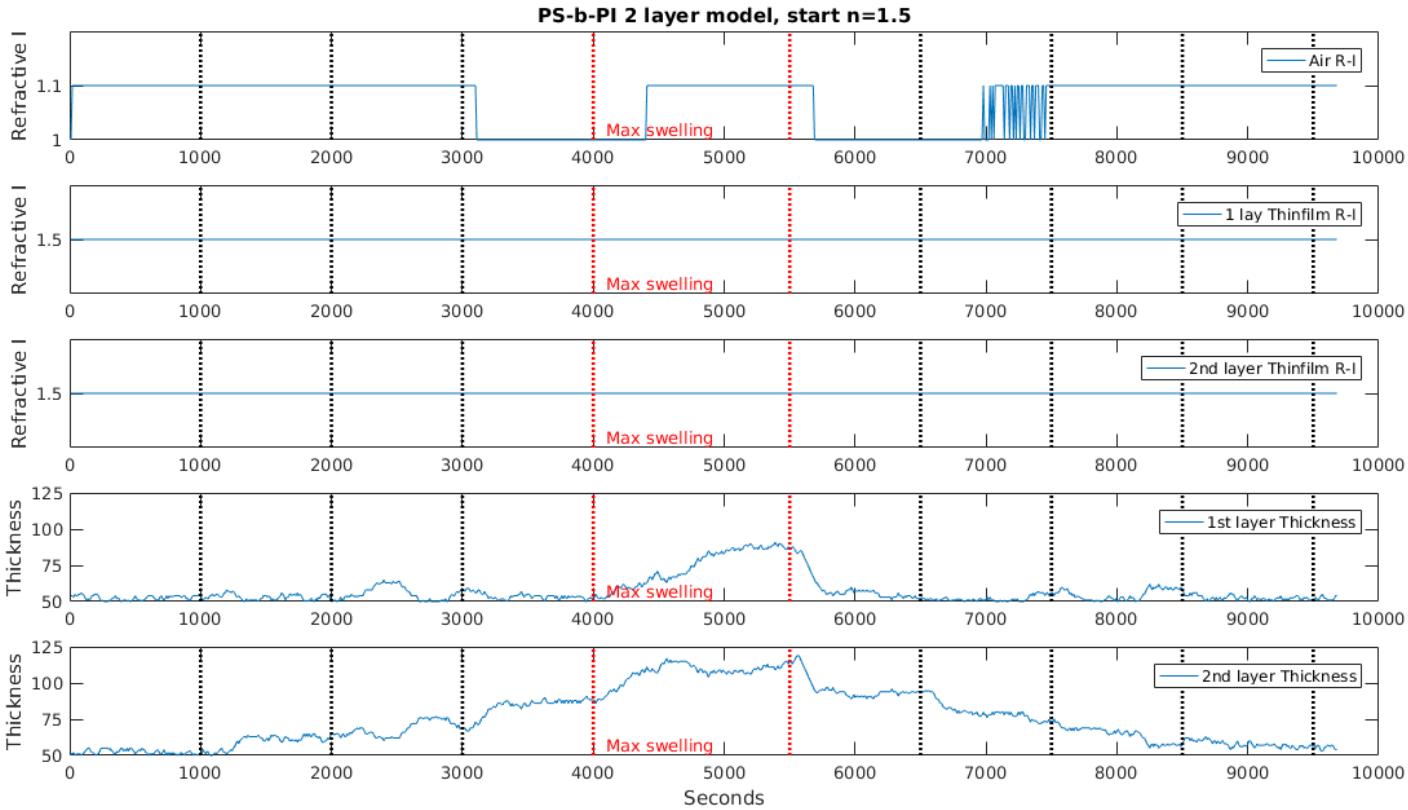
PS-b-PI - 2 layer model MSE



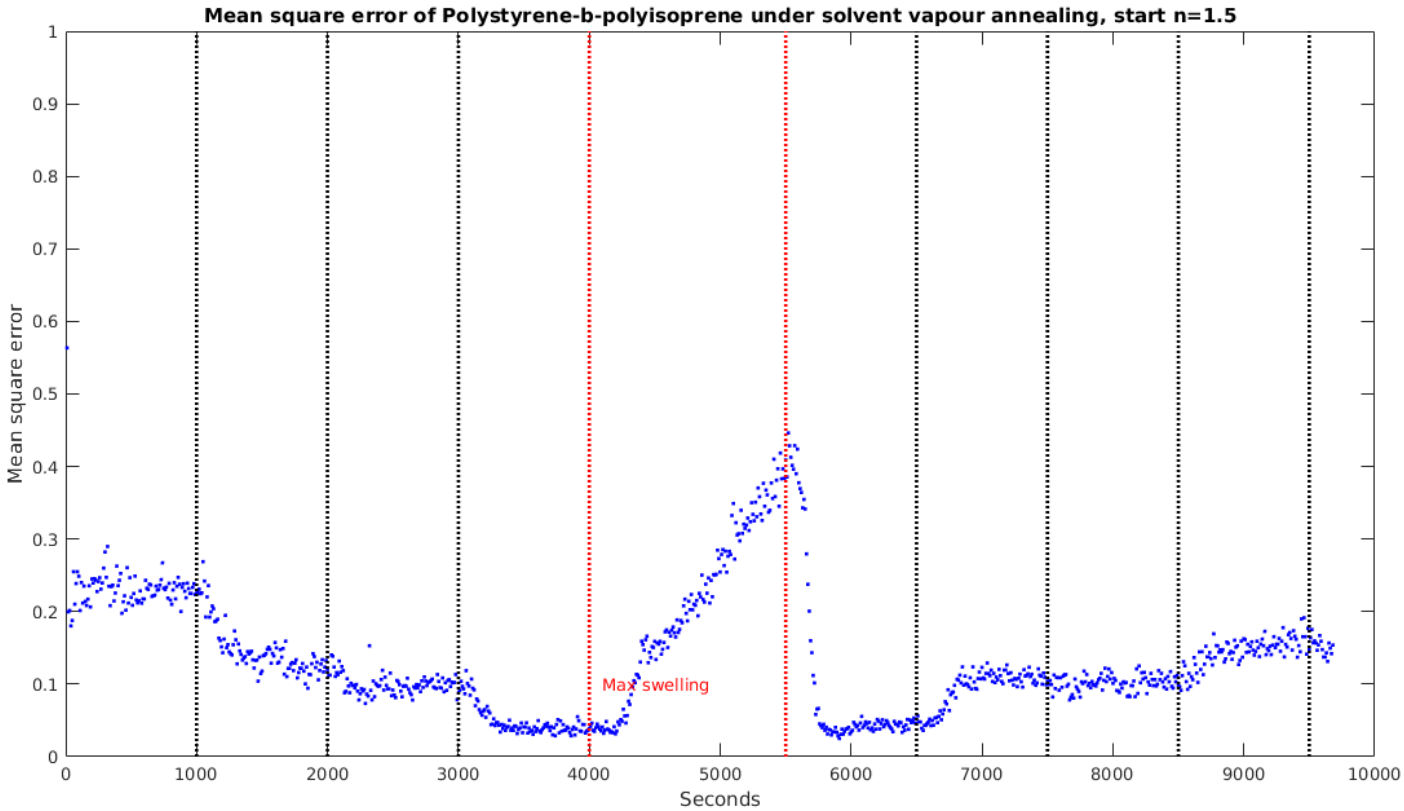
PS-b-PI - 2 layer model total thickness



PS-b-PI - 2 layer model Results



PS-b-PI - 2 layer model MSE



PS-b-PI - 2 layer model total thickness