

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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7/5/2019

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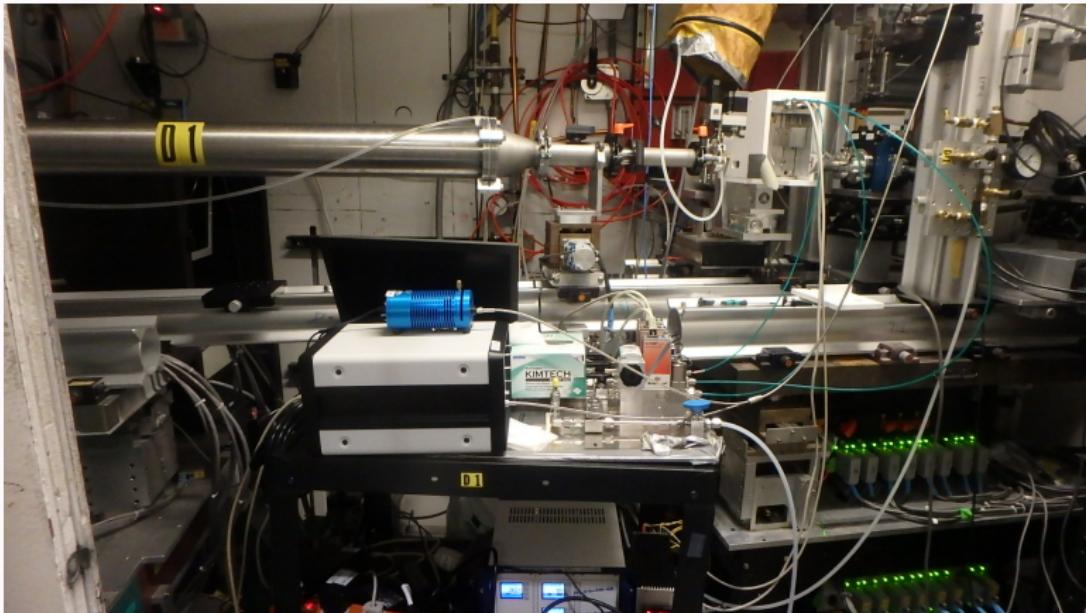
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- 10. Results - 2 polymer layers
- 11. Perspective

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

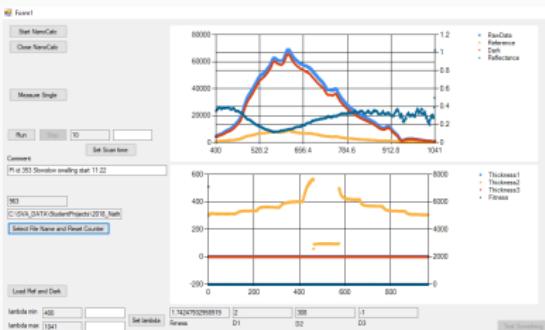


Figure 2: Polyisoprene - SVA run used in Master Thesis

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

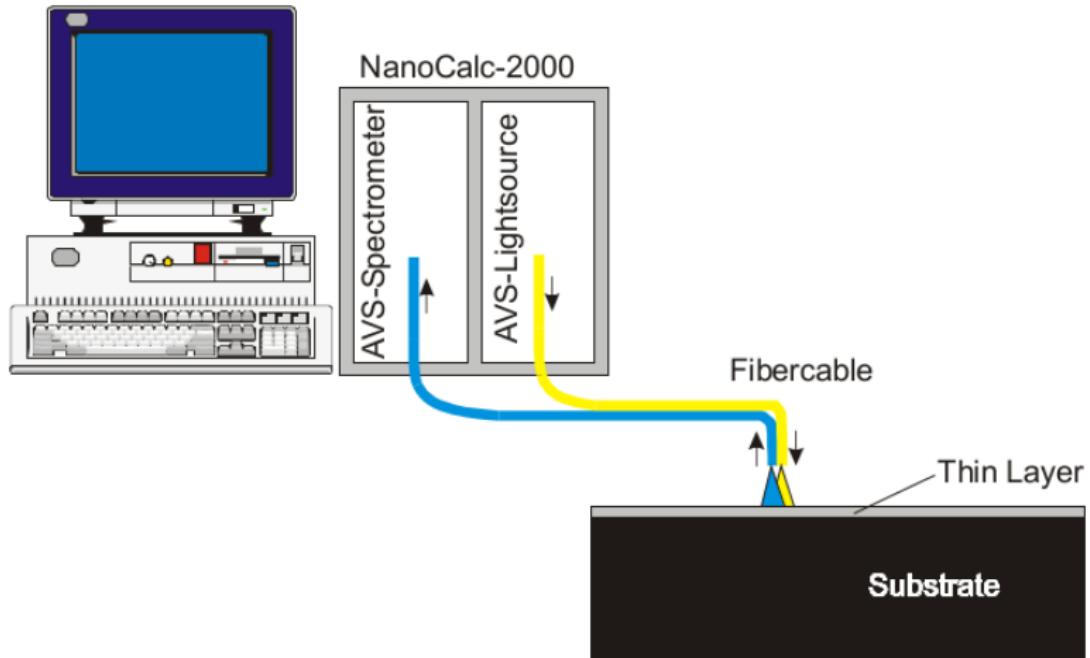
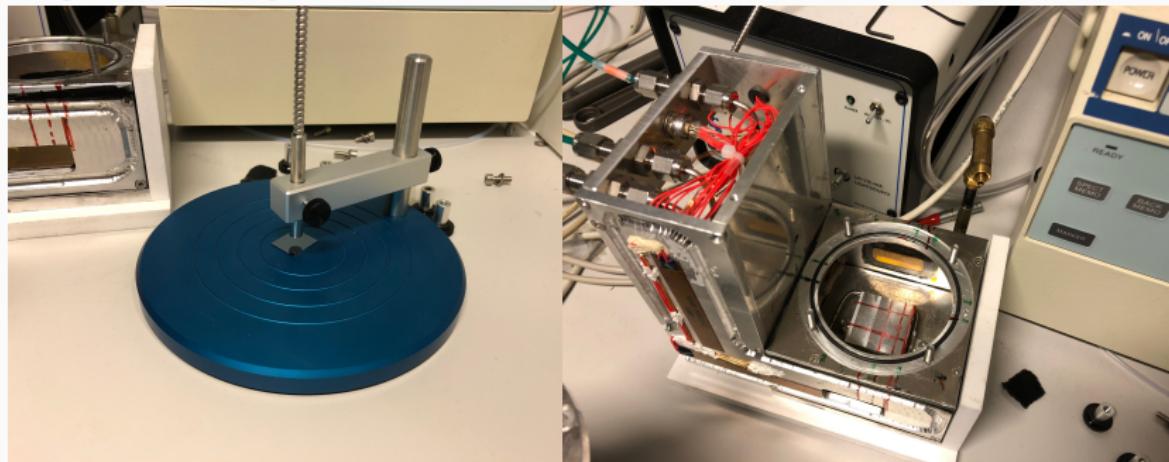


Figure 3: Taken from NanoCalc Software Manual v.4

Experimental Components

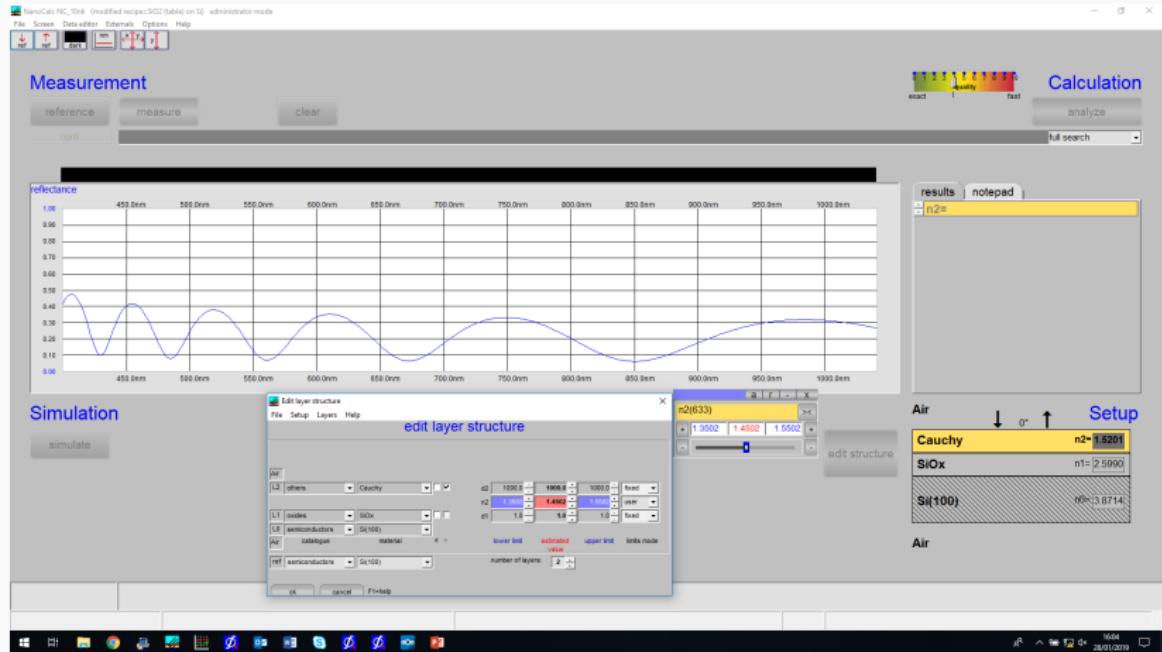
Single Point Stage and SVA test chamber.



Step Wafer



NanoCalc Software



Taking Measurements

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

- Dark Measurement - *Dark*
 - Measuring stray light.
- Reference Measurement - *Ref*
 - Measuring light from blank wafer - SiO_x/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 6: Source:wbcisd.org

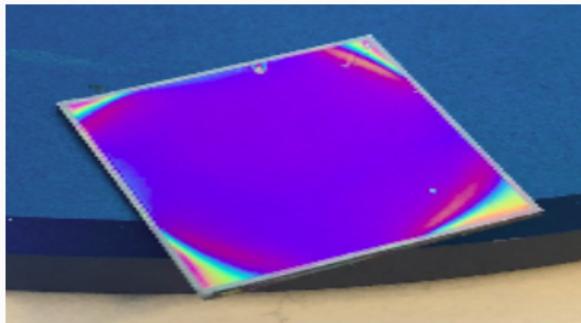


Figure 5: Polystyrene wafer

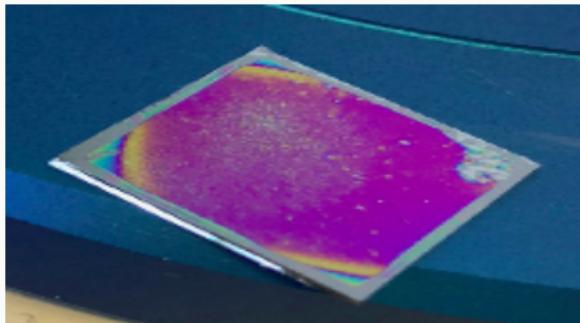


Figure 7: Polyisoprene wafer

Polymers used in Master Thesis

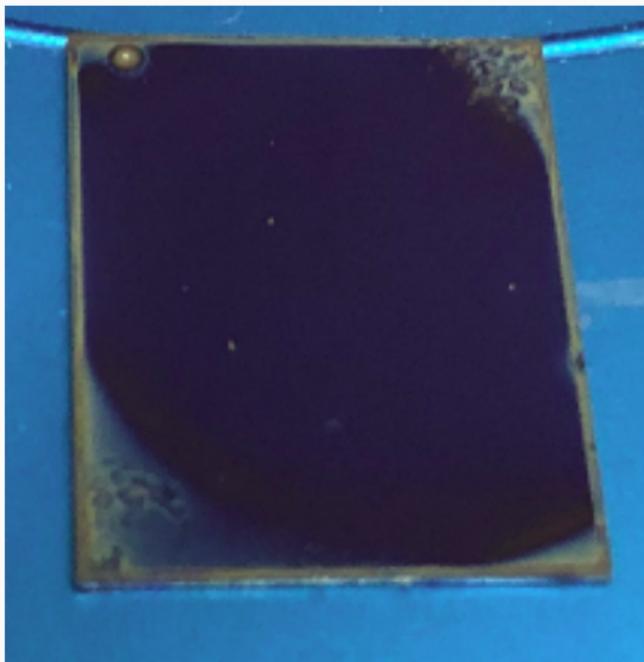
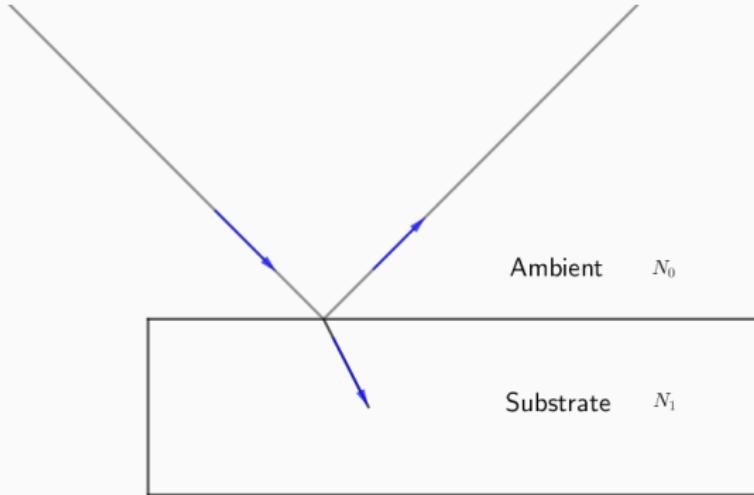


Figure 8: Polystyrene-b-polyisoprene

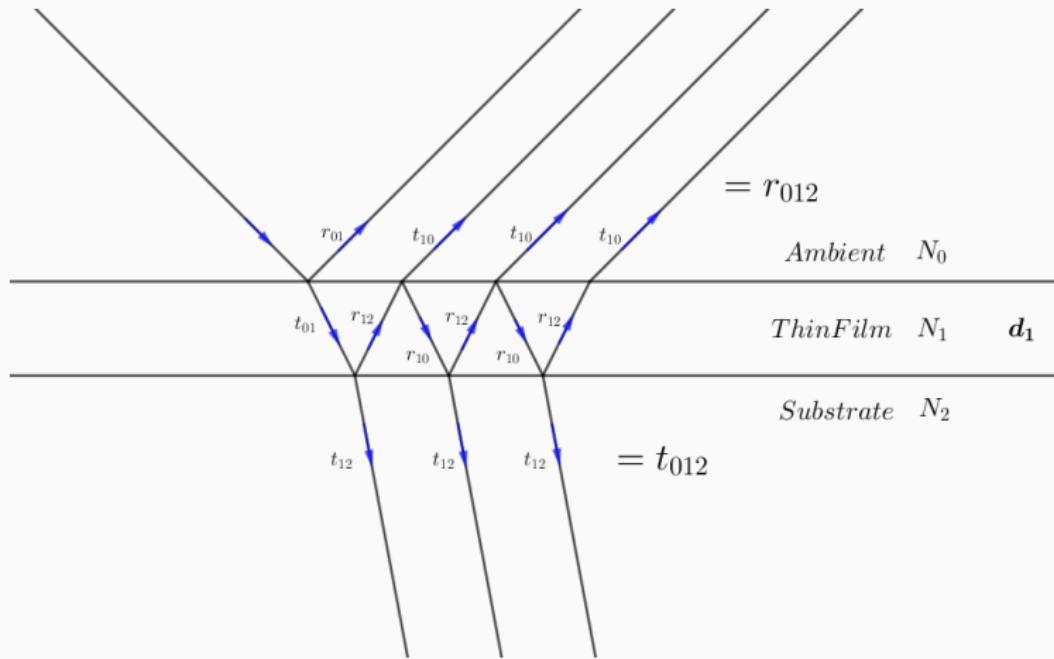
Fresnel Models

Fresnel Equations - Substrate



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

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

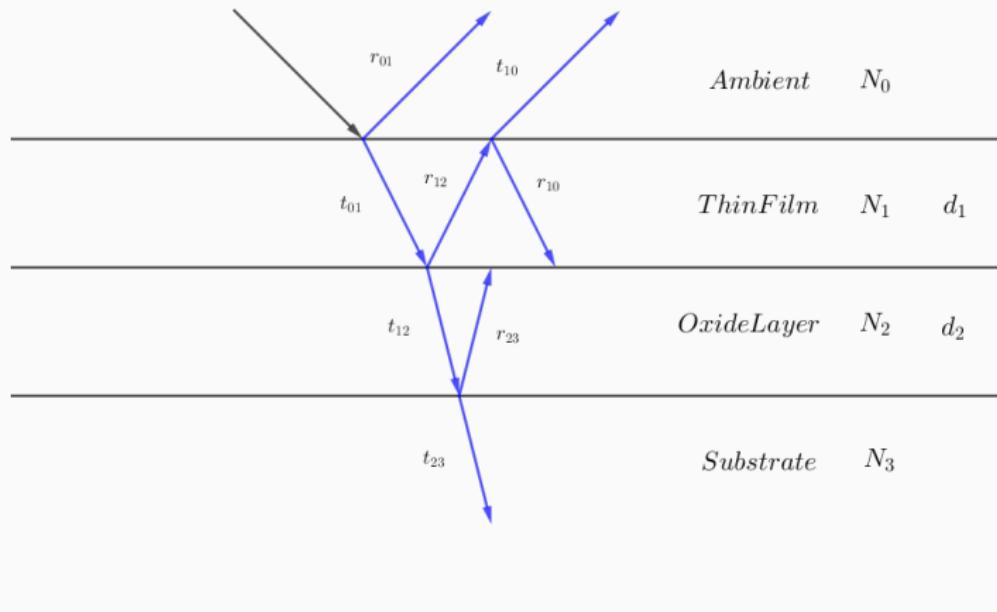
$$r_{012} = \frac{r_{01} + r_{12} \exp(-i2\beta)}{1 + r_{01}r_{12} \exp(-i2\beta)}$$

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

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

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

Homopolymer Fresnel Model



Homopolymer Fresnel equations

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

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

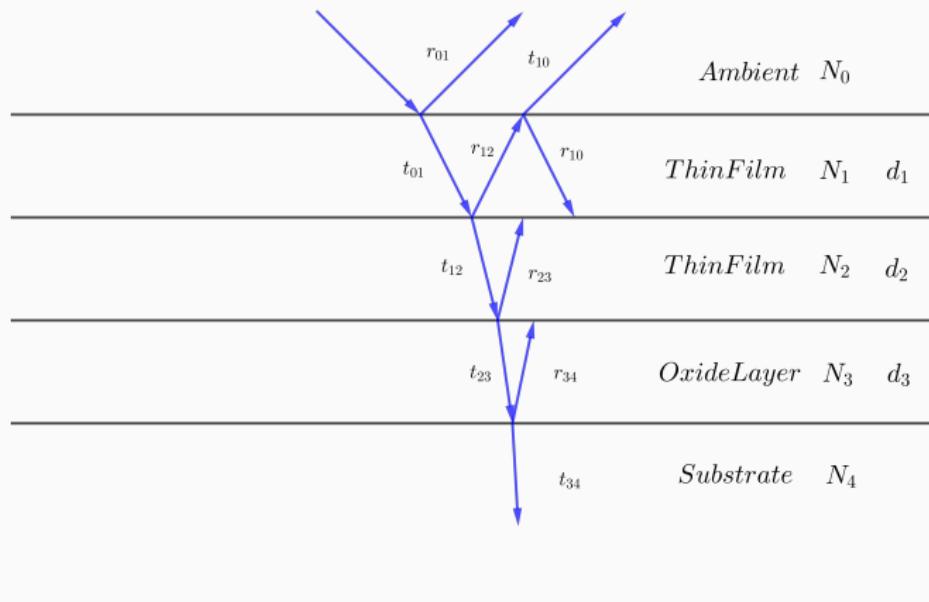
$$r_j k = \frac{N_k - N_j}{N_j + N_k}$$

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

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

N_0, N_1 and d_1 fitted during solvent vapour annealing.

Diblock copolymer Fresnel model



Diblock copolymer Fresnel Equations

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

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

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

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

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

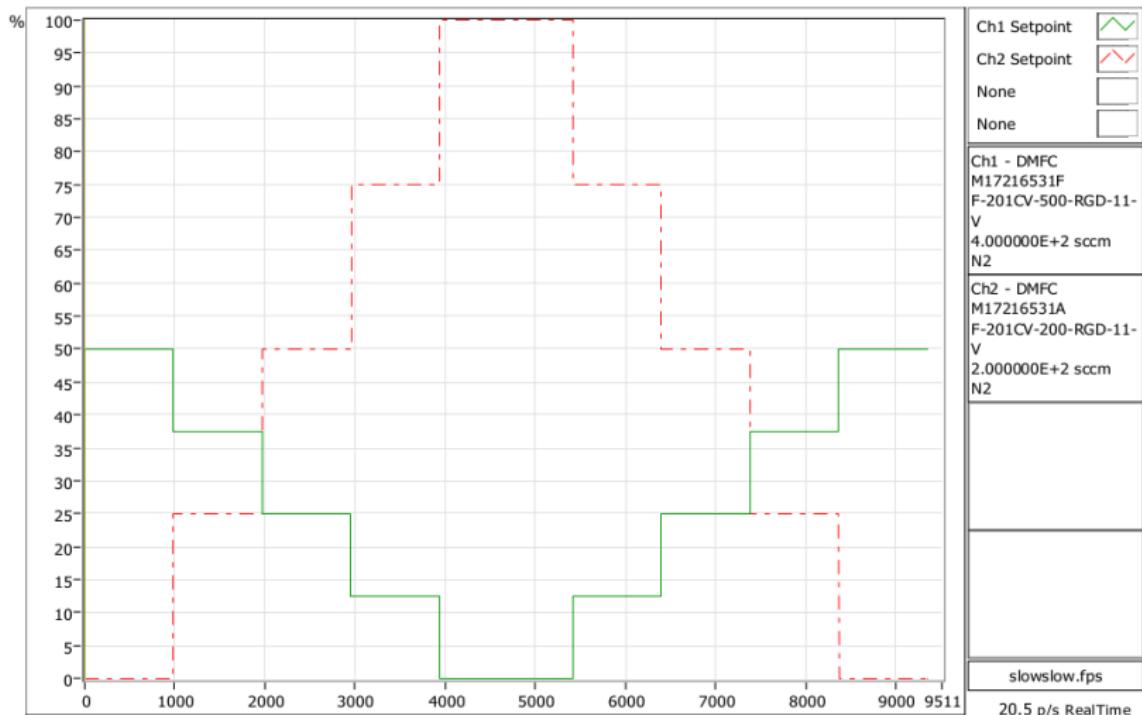
N_0, N_1, N_2, d_1 and d_2 fitted during solvent vapour annealing.

Plotted Fresnel models

Movie:varyRI.avi

Solvent vapour Annealing

SVA protocol



Preliminary Studies

Light Fluctuation

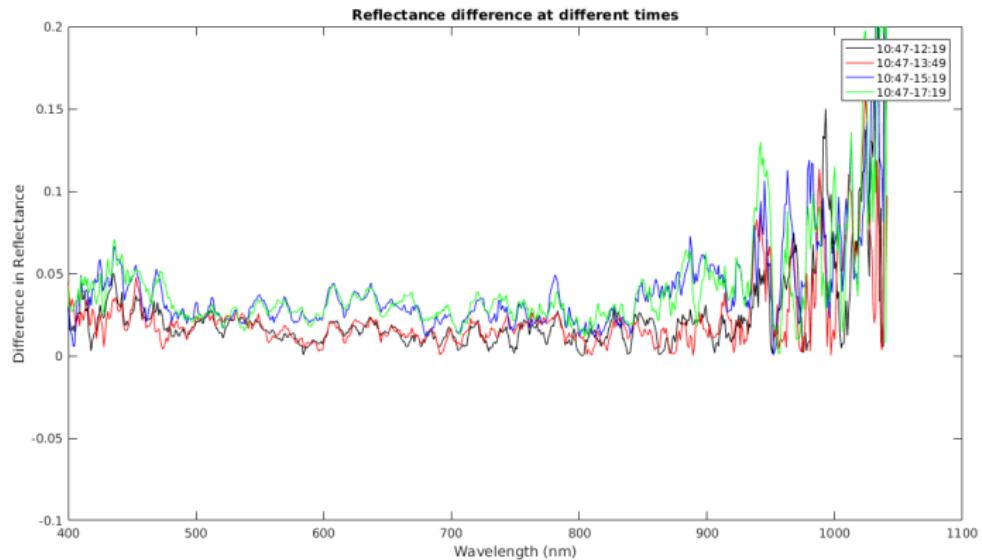


Figure 9: Light Fluction study 1

Light Fluctuation continued

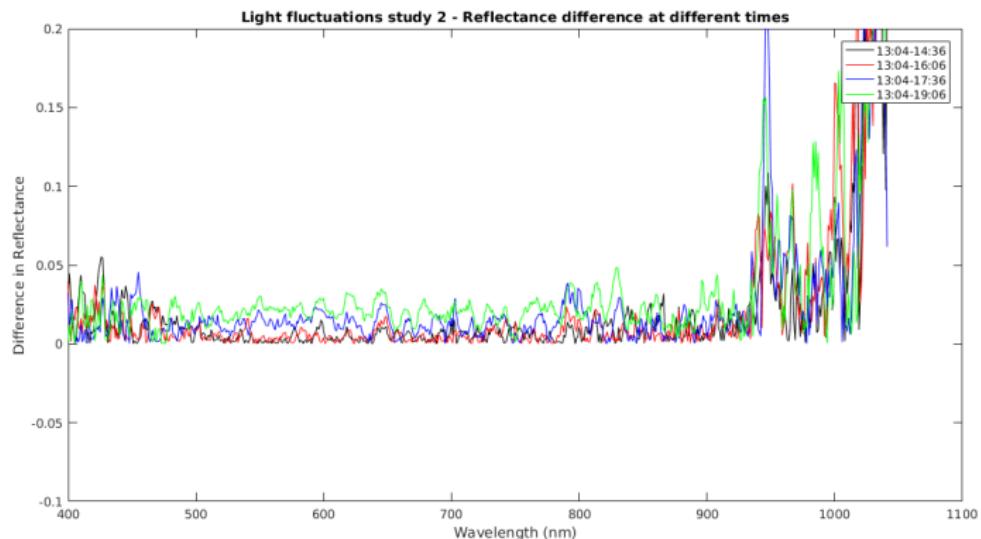


Figure 10: Light Fluction study 2

Solvent vapour annealing ambient study

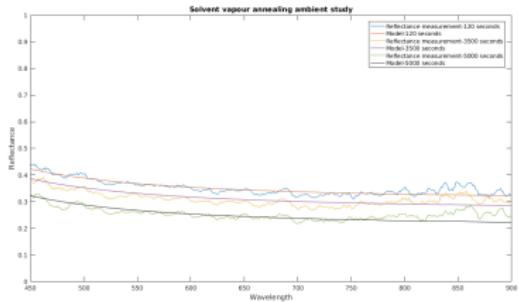


Figure 11: Reflectance curves at different times during SVA

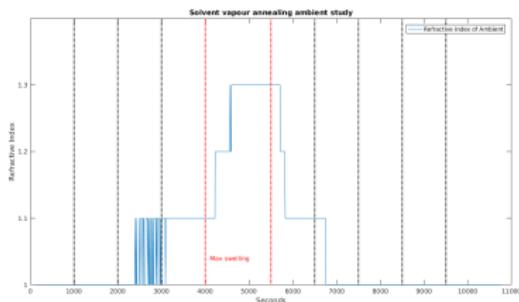


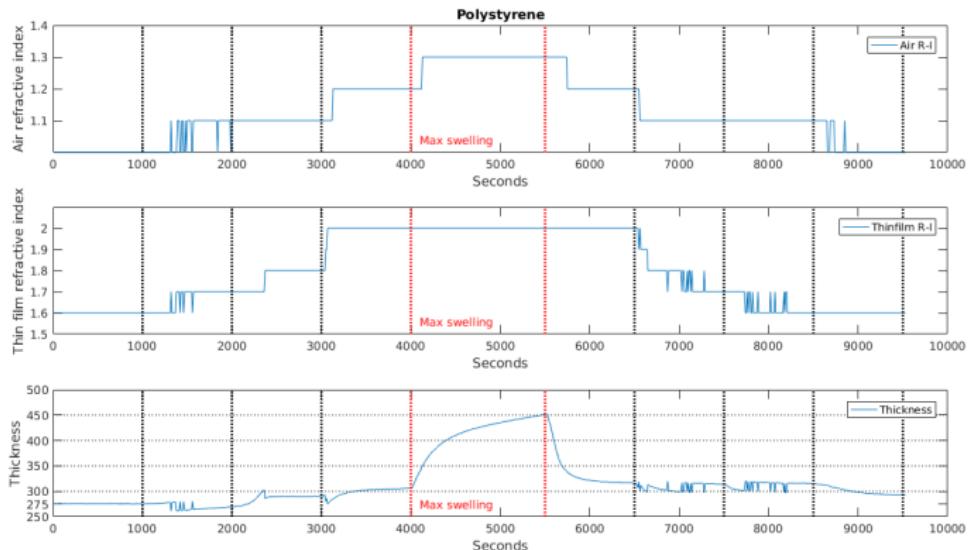
Figure 12: Ambient refractive index

Results - 1 polymer layer

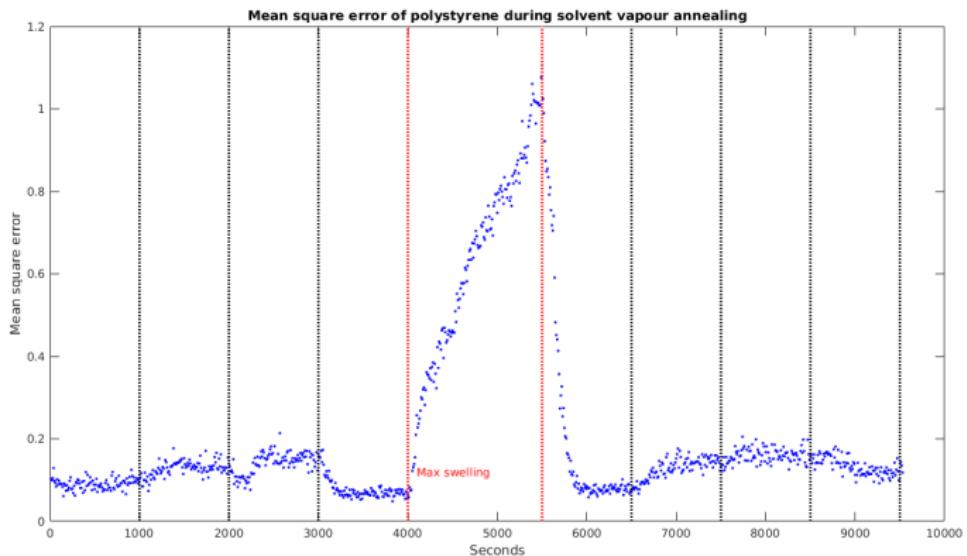
Polystyrene

Movie: PSsva.avi

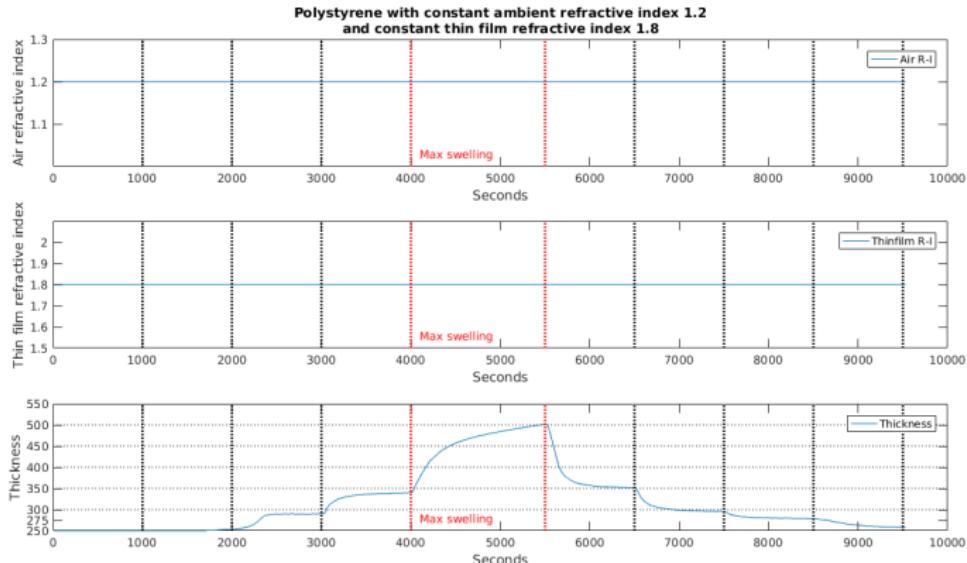
Polystyrene Results



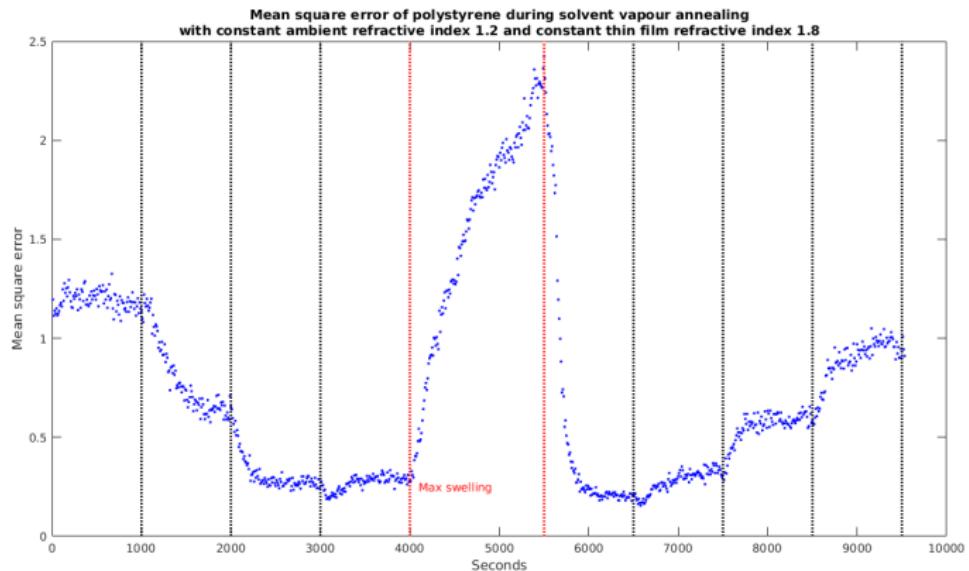
Polystyrene MSE



Polystyrene comparison

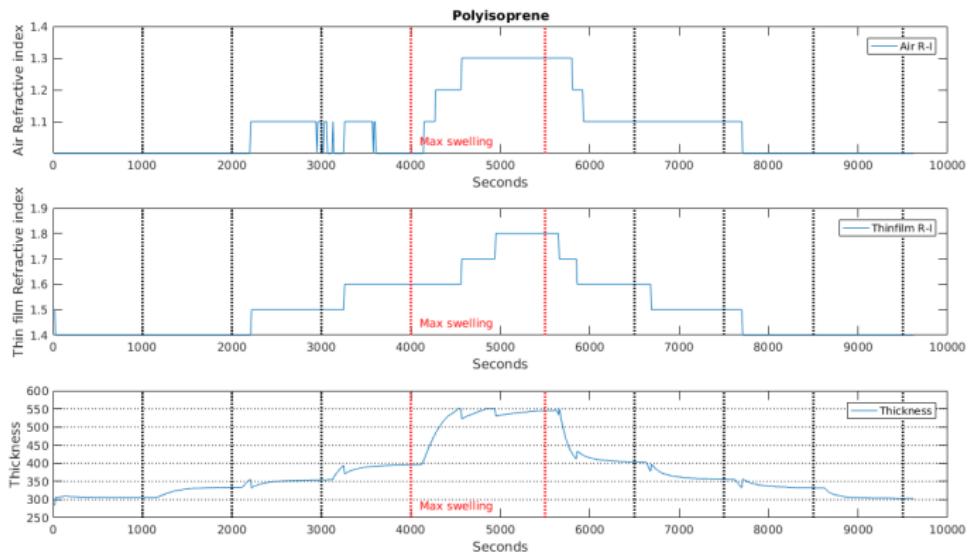


Polystyrene comparison

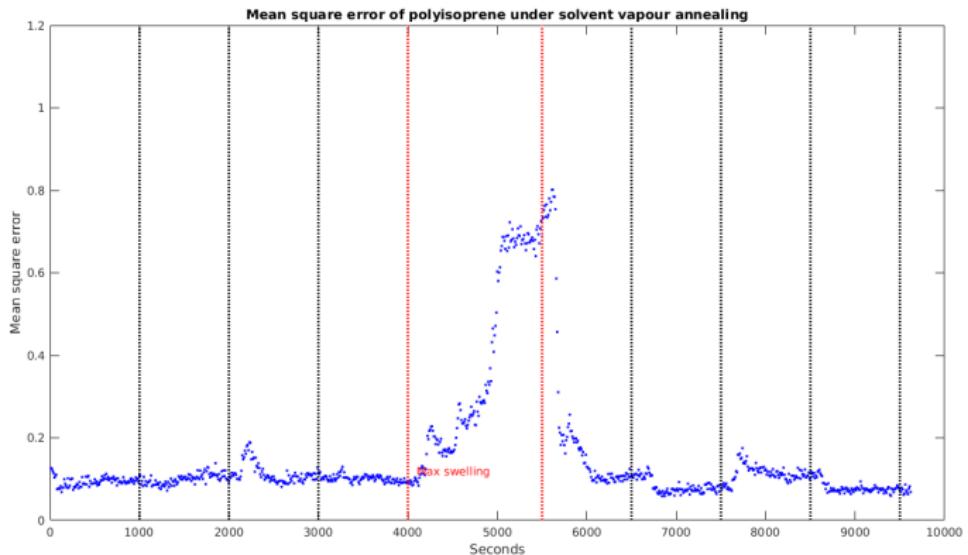


Movie:PIsvalframevalue2.avi

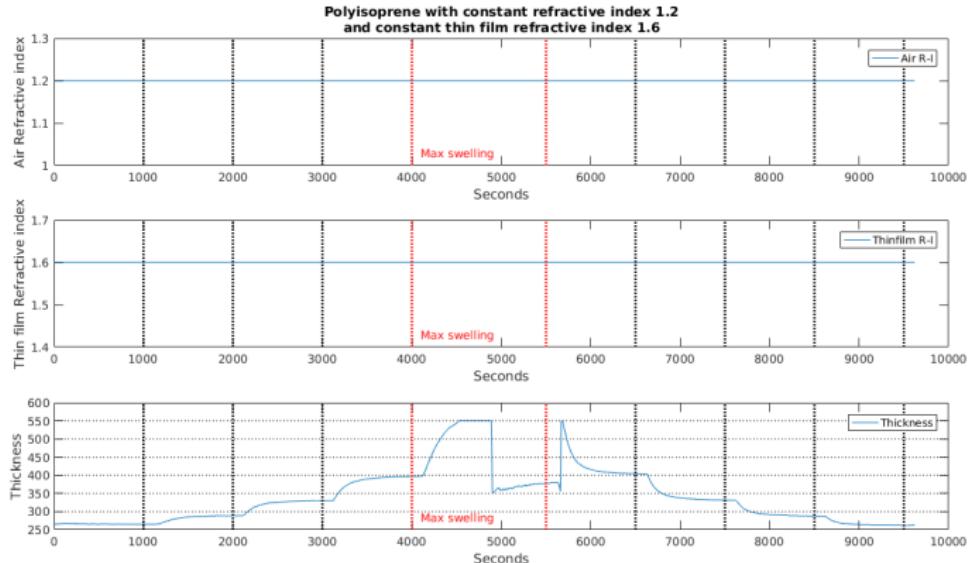
Polyisoprene Results



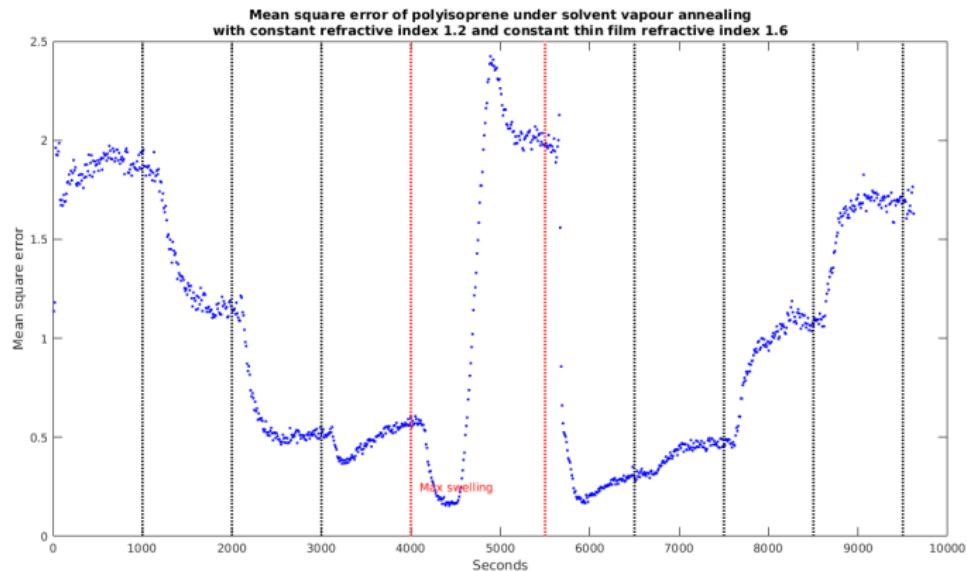
Polyisoprene MSE



Polyisoprene comparison



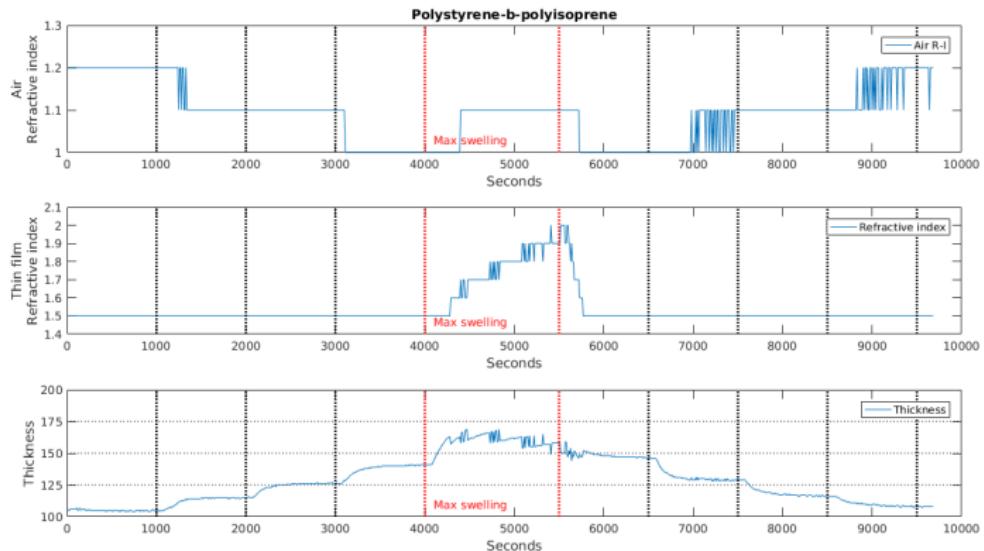
Polyisoprene comparison



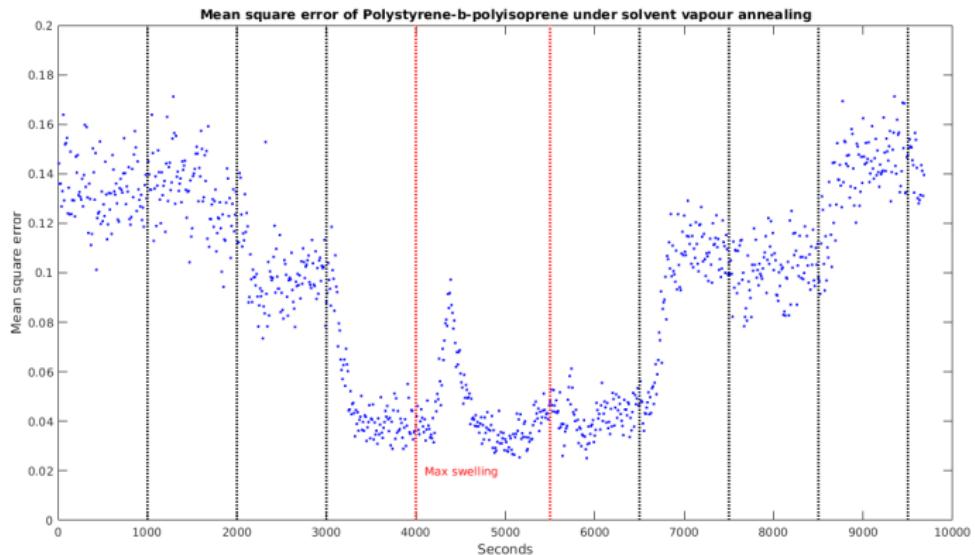
Polystyrene-*b*-polyisoprene

Movie: PSbPIsinglemodel.avi

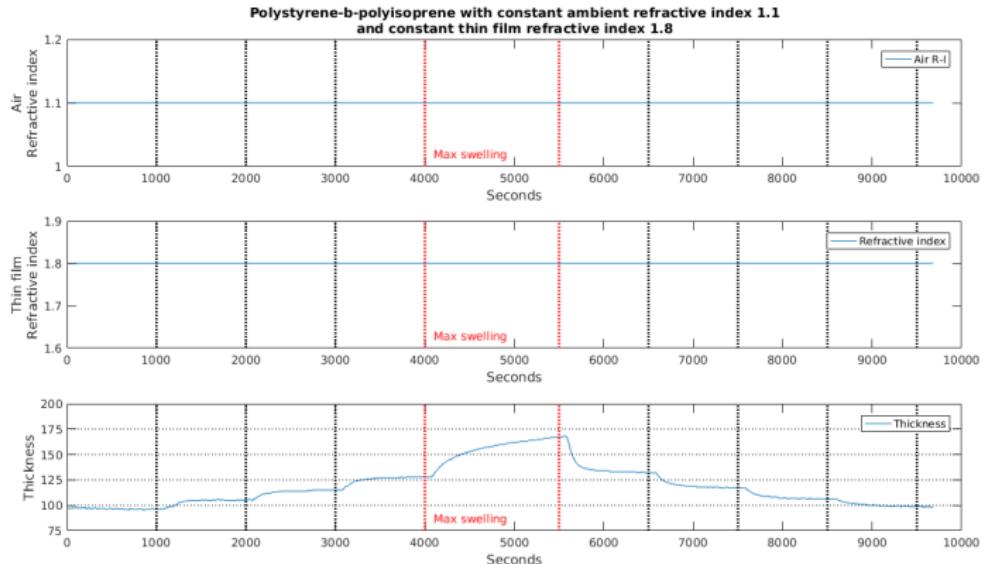
Polystyrene-b-polyisoprene Results



Polystyrene-b-polyisoprene MSE

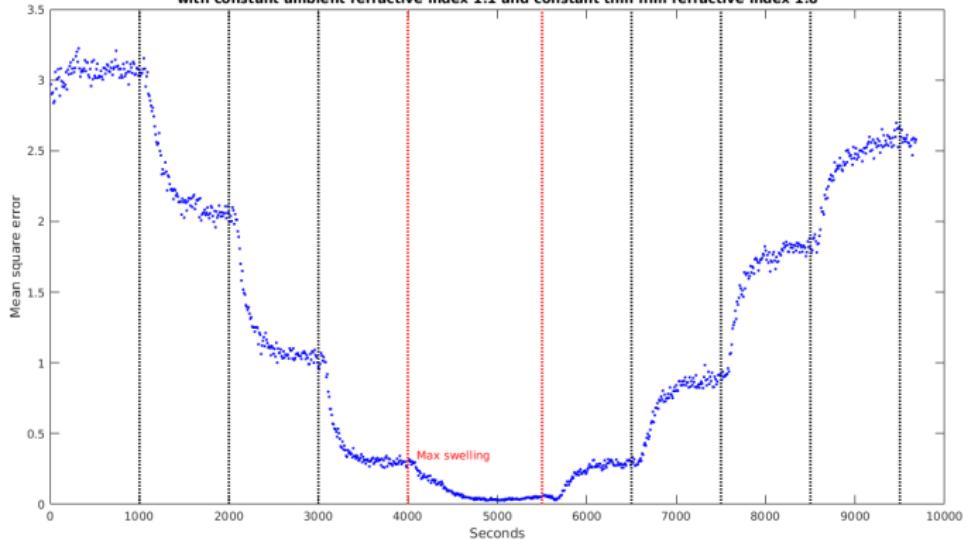


Polystyrene-b-polyisoprene comparison



Polystyrene-b-polyisoprene comparison

Mean square error of Polystyrene-b-polyisoprene under solvent vapour annealing
with constant ambient refractive index 1.1 and constant thin film refractive index 1.8



Conclusion/Perspective

Conclusion/Perspective

Conclusion:

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

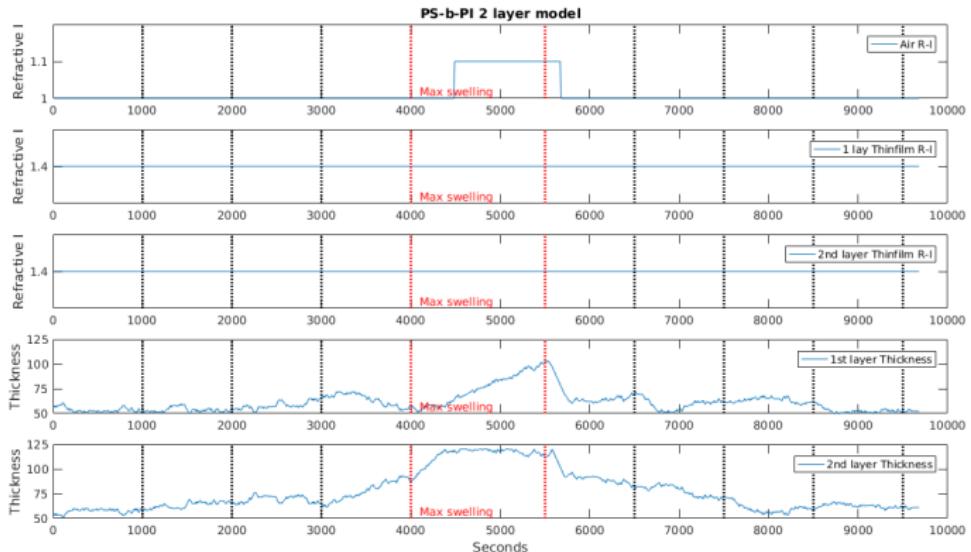
Perspective:

- Refractive index during SVA
- Polymer - absorption of light
- Modelling vapour pressure inside SVA test chamber

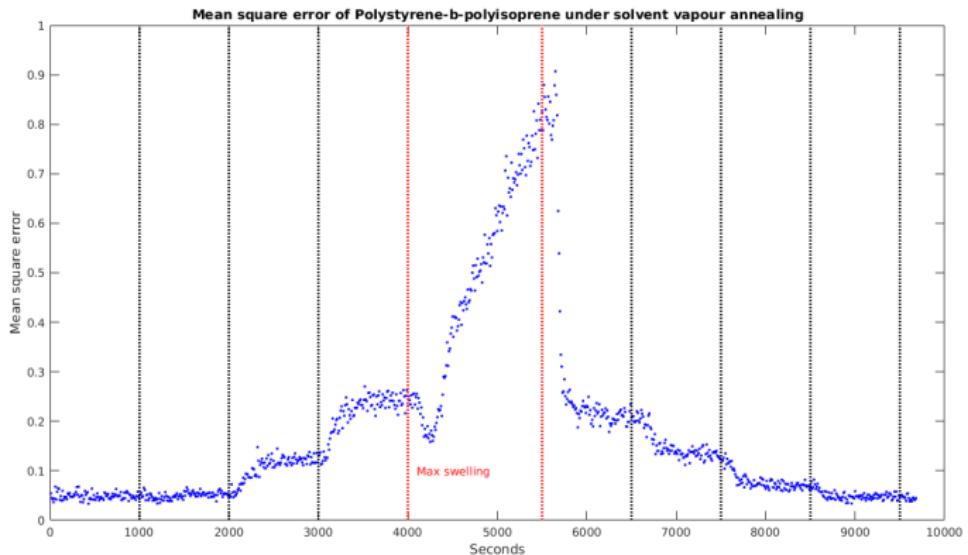
Results - 2 polymer layers

Movie: PSbPIfit2layermodelV2.avi

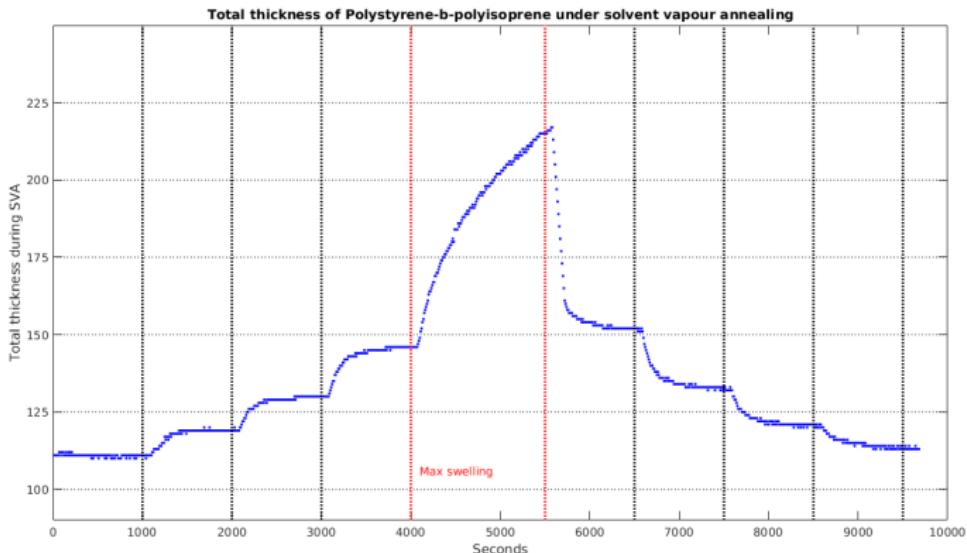
PS-b-PI - 2 layer model Results



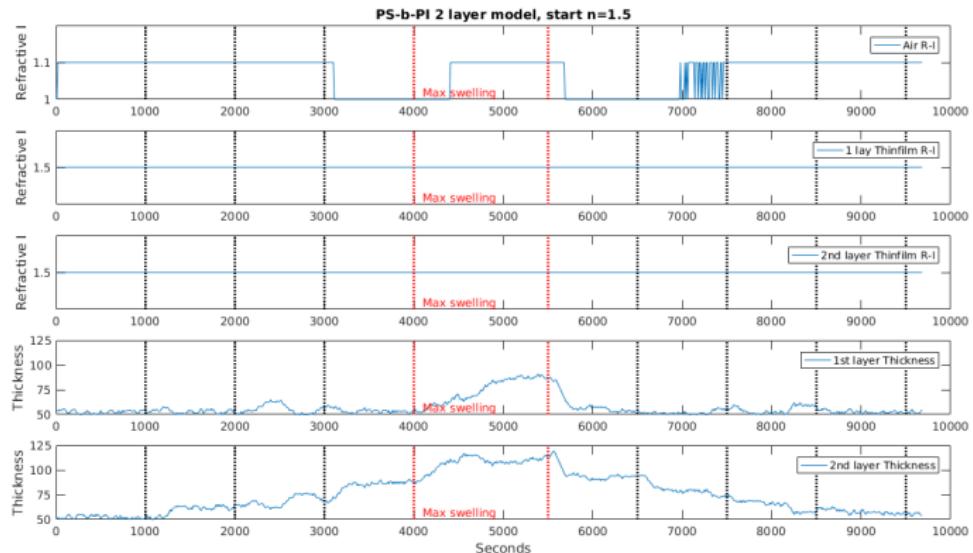
PS-b-PI - 2 layer model MSE



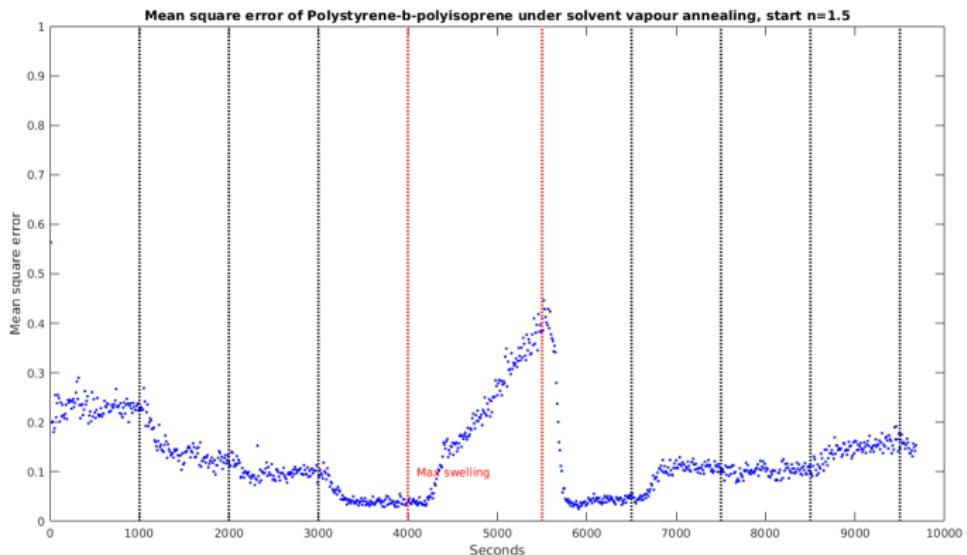
PS-b-PI - 2 layer model total thickness



PS-b-PI - 2 layer model Results



PS-b-PI - 2 layer model MSE



PS-b-PI - 2 layer model total thickness

