

**OPTICAL AND THERMAL CHARACTERISTICS OF THIN
POLYMER AND POLYHEDRAL OLIGOMERIC
SILSESQUIOXANE (POSS) FILLED POLYMER FILMS**

Ufuk Karabiyik

Dissertation submitted to the faculty of the
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of

**Doctor of Philosophy
in
CHEMISTRY**

Alan R. Esker, Chair
Timothy E. Long
John R. Morris
Diego Troya
Thomas C. Ward

April 30, 2008
Blacksburg, Virginia

Keywords: Polymer thin films, Langmuir-Blodgett films, Surface glass transition, Refractive index, Polyhedral oligomeric silsesquioxanes (POSS)

Copyright 2008, Ufuk Karabiyik

OPTICAL AND THERMAL CHARACTERISTICS OF THIN POLYMER AND POLYHEDRAL OLIGOMERIC SILSESQUIOXANE (POSS) FILLED POLYMER FILMS

Ufuk Karabiyik

(ABSTRACT)

Single wavelength ellipsometry measurements at Brewster's angle provide a powerful technique for characterizing ultrathin polymeric films. By conducting the experiments in different ambient media, multiple incident media (MIM) ellipsometry, simultaneous determinations of a film's thickness and refractive index are possible. Poly(tert-butyl acrylate) (PtBA) films serve as a model system for the simultaneous determination of thickness and refractive index (1.45 ± 0.01 at 632 nm). Thickness measurements on films of variable thickness agree with X-ray reflectivity results ± 0.8 nm. The method is also applicable to spincoated films where refractive indices of PtBA, polystyrene and poly(methyl methacrylate) are found to agree with literature values within experimental error. Likewise, MIM ellipsometry is utilized to simultaneously obtain the refractive indices and thicknesses of thin films of trimethylsilylcellulose (TMSC), regenerated cellulose, and cellulose nanocrystals where Langmuir-Blodgett (LB) films of TMSC serve as a model system.

Ellipsometry measurements not only provide thickness and optical constants of thin films, but can also detect thermally induced structural changes like surface glass transition temperatures (T_g) and layer deformation in LB-films. Understanding the

thermal properties of the polymer thin films is crucial for designing nanoscale coatings, where thermal properties are expected to differ from their corresponding bulk properties because of greater fractional free volume in thin films and residual stresses that remain from film preparation. Polyhedral oligomeric silsesquioxane (POSS) derivatives may be useful as a nanofiller in nanocomposite formulations to enhance thermal properties. As a model system, thin films of trisilanolphenyl-POSS (TPP) and two different molar mass PtBA were prepared as blends by Y-type Langmuir-Blodgett film deposition. For comparison, bulk blends were prepared by solution casting and the samples were characterized via differential scanning calorimetry (DSC). Our observations show that surface T_g is depressed relative to bulk T_g and that magnitude of depression is molar mass dependent for pure PtBA films (surface T_g changes for 5 and 23.6 kg·mol⁻¹ PtBA samples are different). By adding TPP as a nanofiller both bulk and surface T_g increase. Whereas, bulk T_g shows comparable increases for both molar masses (~10 °C), the increase in surface T_g for 23.6 kg·mol⁻¹ PtBA is greater than for 5 kg·mol⁻¹ PtBA (~21 °C vs. ~13 °C, respectively). These studies show that POSS can serve as a model nanofiller for controlling T_g in nanoscale coatings.

ACKNOWLEDGEMENTS

I would like to thank my advisor, Prof. Alan R. Esker for his guidance and tremendous support during the course of my doctoral studies at Virginia Tech. I appreciate his patience and confidence in me from the first day. I would like to thank my committee members, Profs. Timothy E. Long, John R. Morris, Diego Troya, and Thomas C. Ward for their valuable time and guidance during my graduate career.

I would like to recognize all my past and present research group members: Bingbing Li, Suolong Ni, Woojin Lee, Abdulaziz Kaya, Wen Yin, Qiongdan Xie, Jae Hyun Sim, Zelin Liu, Yang Liu, Jonathan Conyers, Jianjun Deng, Sheila Gradwell, Hyong-Jun Kim, Sarah Huffer, Michael Swift, John Hottle, Ben Vastine, Xiaosong Du, Yang Liu, Chuanzi OuYang, Heejun Choi, Jonathan Conyers, Samanta Farris, and Aaron Holley. Thanks to all of you for your help and support over the years. A special thank you goes to Ritu for being a great friend and being patient about my complaints when experiments did not work.

I would also like to thank to my colleagues in Blacksburg. Special thanks go to Gozde I. Ozturk for being in my life and her constant support and to Serkan Unal for his unlimited support and friendship at all times. Last but not least, a big thank you to all of my friends, though I did not list you individually here, you know who you are.

I cannot end without thanking my parents, Hasibe and Murat Karabiyik, and my brother I. Safak Karabiyik, who have always been there for me and trusted in me. I would have never made it without their love and support.

Table of Contents

ACKNOWLEDGEMENTS	iv
Table of Contents	v
List of Figures	ix
List of Tables	xvii
CHAPTER 1	1
Overview	1
CHAPTER 2: Introduction and Review	5
2.1 Introduction	5
2.2 Optical Properties: Refractive Indices and Extinction Coefficients	6
2.2.1 Dispersion Functions for Refractive Index	9
2.2.2 Interference of Light with Matter	10
2.2.3 Polarization of Light	13
2.2.4 Angle of Incidence Effects: Snell's Law and Brewster's Angle	15
2.2.5 Optical Properties of Polymers	18
2.3 Glass Transition Behavior in Polymers	20
2.3.1 Simple Mechanical Relationship	21
2.3.2 Regions of Viscoelastic Behavior	22
2.3.3 Theories for explaining the Glass Transition	25
2.3.3.1 Free-Volume Theory	25
2.3.3.2 The Thermodynamic Theory	29
2.3.4 Factors Affecting the Glass Transition Temperature	33
2.3.4.1 Effect of Molecular Weight on T_g	33
2.3.4.2 Effect of Plasticizers	34
2.3.4.2 Effects of Chain Stiffness, Chemical Structure, and Cross-linking	35
2.3.4.4 T_g of Multicomponent Systems	36
2.3.5 The Glass Transition in Thin Films	38
2.3.6 Methods for Studying the Glass Transition Temperature	43

2.4 Experimental Techniques	45
2.4.1 Langmuir-Blodgett (LB) Technique	45
2.4.1.1 Monolayer Systems and Subphase Materials	45
2.4.1.2 Monolayer Phases in a Langmuir Film	47
2.4.1.3 Langmuir and Langmuir-Blodgett (LB) Film Preparation	53
2.4.1.4 Langmuir-Blodgett (LB) Film Transfer	56
2.4.2 X-Ray Reflectivity	59
2.4.2.1 Basic Principles	60
2.4.2.2 Specular XR Experiments	64
2.4.2.3 XR Profile Analyses	66
2.4.3 Ellipsometry	68
2.4.3.1 Basic Principles of Ellipsometry	69
2.4.3.2 Interpretation of Ellipsometry Data	75
2.5 Polyhedral Oligomeric Silsesquioxanes (POSS) Model Nanoparticles	77
2.6 References	81
CHAPTER 3: Materials and Experimental Methods	93
3.1 Materials	93
3.2 Cleaning Procedure of Silicon Wafers	95
3.3 Thin Film Preparation	95
3.4 Experimental Techniques	96
3.4.1 Ellipsometry	96
3.4.1.1 Multiple Incidence Media (MIM) Ellipsometry	96
3.4.1.2 Multiple Angle of Incidence (MAOI) Measurements	99
3.4.1.3 Spectroscopic Ellipsometry (SE) Measurements	99
3.4.1.4 Anisotropy Measurements	100
3.4.1.5 Temperature Dependent Ellipsometry Scans	100
3.4.2 X-ray Reflectivity (XR)	102
3.4.3 Bulk Characterization via Differential Scanning Calorimetry (DSC)	103

3.5 References	104
CHAPTER 4: Determination of Thicknesses and Refractive Indices of Polymer Thin Films by Multiple Incident Media Ellipsometry	105
4.1 Abstract	105
4.2 Introduction	105
4.3 Results and Discussion	108
4.3.1 XR Characterization of PtBA LB-Films	108
4.3.2 MIM Ellipsometry for PtBA LB-Films	110
4.3.3 MIM Ellipsometry Studies for Spincoated PtBA Films	114
4.3.4 MIM Ellipsometry Studies for PtBA Films in Different Ambient Media	116
4.3.5 Application of MIM Ellipsometry to PS and PMMA in Different Ambient Media	120
4.3.6 Spectroscopic Ellipsometry (SE) and Multiple Angle of Incidence (MAOI) Ellipsometry Measurements	128
4.4 Conclusions	139
4.5 References	141
CHAPTER 5: Optical Characterization of Cellulose Derivatives via Multiple Incident Media Ellipsometry	143
5.1 Abstract	143
5.2 Introduction	143
5.3 Results and Discussion	146
5.3.1 Multiple Incidence Media (MIM) Ellipsometry for TMSC LB-Films	146
5.3.2 MIM Ellipsometry Studies for Spincoated TMSC Films	149
5.3.3 MIM Ellipsometry Studies of Cellulose Films Regenerated from TMSC Films	151
5.3.4 MIM Ellipsometry Studies of Cellulose Nanocrystal Films	154
5.3.5 MIM Ellipsometry versus SE and MAOI Ellipsometry Measurements	156
5.4 Conclusions	159

5.5 References	160
CHAPTER 6: Nanofiller Effects on Glass Transition Temperatures of Ultrathin Polymer Films and Bulk Systems	162
6.1 Abstract	163
6.2 Introduction	163
6.3 Results and Discussion	166
6.3.1 PtBA, TPP, and PtBA/TPP Blend LB-Films: First vs. Second Heating Scans	167
6.3.2 LB vs. Spincoated Films of PtBA	175
6.3.3 LB-films vs. Bulk PtBA/TPP Blends	179
6.4 Conclusions	185
6.5 References	187
CHAPTER 7: Conclusions and Suggestions for Future Work	189
7.1 Overall Conclusions	189
7.1.1 Applications of Multiple Incident Media (MIM) Ellipsometry	189
7.1.2 Effect of Nanofillers on Surface Glass Transition Temperatures	191
7.2 Suggestions for Future Work	192
7.2.1 Applications of Multiple Incident Media (MIM) Ellipsometry	192
7.2.2 Temperature Dependent Ellipsometry Experiments	196
7.3 References	201
APPENDIX	202

List of Figures

Chapter 2

Figure 2.1	(a) Destructive and (b) constructive interference of light waves. Two waves with equal amplitudes and the same frequency or wavelength cancel if they are out of phase by 180° and will add if they are in phase. Other types of interactions such as unequal amplitudes or arbitrary phase differences result in a wave that is a combination of the two interfering light waves.	11
Figure 2.2	A thin film stack structure with different refractive indices for each layer. The index of refraction is indicated by n_i , and layers are numbered starting from the incident medium ($i=0$). Reflection and refraction occurs at each interface.	12
Figure 2.3	A schematic representation of a (a) linear (b) circular (c) elliptically polarized light wave propagating along Z direction.	14
Figure 2.4	The refractive index of a material can be determined from the angle of refraction for a beam incident from a medium with a known refractive index and incident angle.	16
Figure 2.5	Nonpolarized light incident upon an interface. (a) $\theta_i \neq \theta_B$ (Brewster's angle) (b) $\theta_i = \theta_B$, which is constant with the Equation 2.19, $n_2 = \tan\theta_B$. The arrows and dots represent parallel and perpendicular components of the light with respect to the plane of incidence, respectively.	17
Figure 2.6	Contribution of different types of atoms to a polymer's refractive index.	19
Figure 2.7	The regions of viscoelastic behavior for linear amorphous polymer (solid line) along with the effects of crystallinity (dashed line) and cross-linking (dotted line). The numbers on the graph correspond to (1) the glassy state, (2) the glass to rubber transition, (3) the rubbery state, (4) the end of the rubbery state, and (5) viscous flow, for an amorphous polymer. For a crystalline polymer melting starts at (7). For permanently crosslinked materials (3) to (6) there is no viscous flow regime.	23
Figure 2.8	Plot of specific volume versus temperature to illustrate the concept of free volume.	26
Figure 2.9	Schematic representation of variations in (a) volume, (V) (b) enthalpy, (H) (c) thermal expansion coefficient, (α) and (d) isobaric heat capacity (C_p) as a function of temperature for a second order phase transition described by Ehrenfest.	30
Figure 2.10	Schematic plot of conformational entropy versus temperature of a glass forming substance. The temperature where the entropy reaches zero is the T_2 of Gibbs and DiMarzio. The dotted line is the original extrapolation of Kauzmann.	32

Figure 2.11	Schematic representation of different glass transition temperatures observed for different cooling rates, (a) fast cooling rate (T_{g1}) and (b) a slower cooling rate (T_{g2} .)	33
Figure 2.12	Schematic representation of a generalized Π -A isotherms of Langmuir monolayers showing (a) G to LE, (b) G to LC, and (c) LE to LC phase transitions.	52
Figure 2.13	A schematic representation of a Wilhelmy plate (a) front view and (b) side view attached to the LB Trough.	55
Figure 2.14	Schematic representations of three different LB-deposition methods (a) Y-type, (b) X-type, and (c) Z-type.	58
Figure 2.15	Schematic representations of reflection and refraction at an interface with medium ₁ and medium ₂ . θ_{i1} is the angle between the incident ray and the surface, θ_{r1} is the angle between the reflected ray and the surface, and θ_{t2} is the angle between the refracted ray and the surface. The refracted beam reflects the assumption that $n_2 < n_1$.	63
Figure 2.16	Schematic diagram of the x-ray beam path in a thin film with a thickness of d on a supported solid substrate.	66
Figure 2.17	An X-ray reflectivity profile for a multilayer LB-film deposited on a H terminated silicon substrate. The oscillations (Kiessig fringes) occur because of the total thickness of the sample. Δq can be used to determine the film thickness from Equation 2.75. The Bragg peak at $q = 0.37 \text{ \AA}^{-1}$ provides the double layer spacing through Bragg's Law.	67
Figure 2.18	Optical interference of light reflected from a thin film on solid substrate.	71
Figure 2.19	Optical interference of light in a thin film on a solid substrate. Optical model for an ambient/thin film/substrate structure is drawn. In this figure, r_{jk} and t_{jk} represents the amplitude coefficients for reflection and transmission from different interfaces.	73
Figure 2.20	A representative data analysis flow chart for ellipsometry measurements.	76
Figure 2.21	Chemical structures for (a) an open cage heptasubstituted trisilanol-POSS, and (b) a closed cage fully functional octasubstituted-POSS. R is most commonly an alkyl, aryl, or arylene substituent.	78
Scheme 2.1	Hydrolytic condensation of XSiY_3 monomers.	79

Chapter 3

Figure 3.1	Chemical structures of (a) PtBA, (b) PS, (c) PMMA, (d) TPP, and (e) TMSC and regenerated cellulose.	94
Figure 3.2	Schematic depiction of the multiple incident media (MIM) ellipsometry sample cell.	97

Chapter 4

- Figure 4.1** A representative XR profile for a 10 layer PtBA LB-film. The open circles are the experimental data and the solid line corresponds to the fit obtained through a multilayer algorithm. The inset shows $Q_m(q)$ vs. m which is used to obtain D according to the method of Thomson *et al.* 109
- Figure 4.2** D determined by X-ray reflectivity ($\circ$, left-hand axis), and ρ obtained from ellipsometry at Brewster's angle in air ($\square$, right-hand axis) as a function of the number of LB layers. One standard deviation error bars on the XR and ellipsometry data are smaller than the size of the data points. 110
- Figure 4.3** MIM ellipsometry data for PtBA LB-films in air ($\square$) and in water ($\circ$) at a wavelength of 632 nm. One standard deviation error bars for the ellipsometry data are smaller than the size of the data points. 112
- Figure 4.4** (a) ρ vs. the wt% PtBA in the spincoating solution. (b) ρ vs. D deduced from MIM ellipsometry data for spincoated systems of PtBA in air ($\square$) and in water ($\circ$) at a wavelength of 632 nm. One standard deviation errorbars on ρ are smaller than the size of the data points. The thickness values in (b) are obtained by analyzing the air and water measurements for a given film from (a) via Approach 1. 115
- Figure 4.5** MIM ellipsometry data for of PtBA LB-films (a) air ($\square$) and ethylene glycol (EG) ($\circ$), (b) air ($\square$) and triethylene glycol (TEG) ($\circ$), and (c) air ($\square$) and glycerol ($\circ$). One standard deviation errorbars on ρ are smaller than the size of the data points. 117
- Figure 4.6** MIM ellipsometry data for spincoated PtBA films. ρ obtained for measurements made in (a) air ($\square$) and ethylene glycol (EG) ($\circ$), (b) air ($\square$) and triethylene glycol TEG ($\circ$), and (c) air ($\square$) and glycerol ($\circ$) are plotted vs. wt% PtBA of spincoating solution. d, e, and f contain the same data in a, b, and c, respectively plotted as a function of the thickness obtained via Approach 1 for each film. One standard deviation error bars on ρ are smaller than the size of the symbols for the data points. 118
- Figure 4.7** MIM ellipsometry data for spincoated 23 kg·mol⁻¹ PS films. ρ obtained for measurements made in (a) air ($\square$) and water ($\circ$), (b) air ($\square$) and ethylene glycol (EG) ($\circ$), (c) air ($\square$) and triethylene glycol (TEG) ($\circ$), and (d) air ($\square$) and glycerol ($\circ$) are plotted vs. wt% PS of spincoating solution. e, f, g, and h contain the same ρ data as a, b, c, and d, respectively, plotted as a function of the thickness obtained via Approach 1 for each film. One standard deviation error bars on ρ are smaller than the size of the symbols for the data points. 121

- Figure 4.8** MIM ellipsometry data for spincoated 76 kg·mol⁻¹ PS films. ρ obtained for measurements in (a) air ($\square$) and water ($\circ$), (b) air ($\square$) and ethylene glycol (EG) ($\circ$), (c) air ($\square$) and triethylene glycol TEG ($\circ$), and (d) air ($\square$) and glycerol ($\circ$) are plotted vs. wt% PS of the spincoating solution. e, f, g, and h contain same ρ data as a, b, c, and d, respectively, plotted as a function of the thickness obtained via Approach 1 for each film. One standard deviation error bars on ρ are smaller than the size of the symbols for data points. 123
- Figure 4.9** MIM ellipsometry data for spincoated 604 kg·mol⁻¹ PS films. ρ obtained for measurements in (a) air ($\square$) and water ($\circ$), (b) air ($\square$) and ethylene glycol (EG) ($\circ$), (c) air ($\square$) and triethylene glycol (TEG) ($\circ$), and (d) air ($\square$) and glycerol ($\circ$) are plotted vs. wt% PS of the spincoating solution. e, f, g, and h, contain the same ρ data as a, b, c, and d, respectively plotted as a function of the thickness obtained via Approach 1 for each film. One standard deviation error bars on ρ are smaller than the sizes of the symbols for the data points. 125
- Figure 4.10** MIM ellipsometry data for spincoated PMMA films. ρ obtained for measurements in (a) air ($\square$) and water ($\circ$), (b) air ($\square$) and ethylene glycol (EG) ($\circ$), (c) air ($\square$) and triethylene glycol (TEG) ($\circ$), and (d) air ($\square$) and glycerol ($\circ$) are plotted vs. the wt% of the spincoating solution. e, f, g, and h contain the same data as a, b, c, and d, respectively, as a function of the thickness obtained via Approach 1 for each film. One standard deviation error bars on ρ are smaller than the size of the symbols for the data points. 127
- Figure 4.11** Refractive index values for a 100 layer PtBA LB-Film (93.2 ± 1.3 nm) as a function of wavelength. Empirical relationships for n as a function of wavelength via the Cauchy equations (solid lines) are provided for the PtBA LB-film with $n_{\text{PtBA}}(\lambda) = 1.4403 + 4938.9/\lambda^2 + 7.6420 \cdot 10^6/\lambda^4 + 2.5070 \cdot 10^{12}/\lambda^6$. Deviations between the empirical Cauchy equations and the n values obtained from SE ellipsometry are < 0.001 for $230 \text{ nm} < \lambda < 800 \text{ nm}$. The inset shows the experimental data and model fits of the X($\circ$) and Y($\square$) data at a wavelength range of 250-800 nm. 130
- Figure 4.12** Refractive index values of a spincoated PtBA film (128.3 ± 3.5 nm) as a function of wavelength. Empirical relationships for n as a function of wavelength via the Cauchy equations (solid lines) are provided for the PtBA spincoated system with $n_{\text{PtBA}}(\lambda) = 1.4553 + 4635.6/\lambda^2 + 6.8655 \cdot 10^6/\lambda^4 + 2.3816 \cdot 10^{12}/\lambda^6$. Deviations between the empirical Cauchy equations and the n values obtained from SE ellipsometry are < 0.001 for $230 \text{ nm} < \lambda < 800 \text{ nm}$. The inset shows the experimental data and model fits of the X($\circ$) and Y($\square$) data at a wavelength range of 250-800 nm. 131

- Figure 4.13** Refractive index values of a spincoated $M_n = 23 \text{ kg}\cdot\text{mol}^{-1}$ PS film ($202.1 \pm 4.0 \text{ nm}$) as a function of wavelength. Empirical relationships for n as a function of wavelength via the Cauchy equations (solid lines) are provided for the $23 \text{ kg}\cdot\text{mol}^{-1}$ PS with $n_{\text{PS}}(\lambda) = 1.57908 + 12383.2/\lambda^2 - 6.8002\cdot 10^8/\lambda^4 + 5.9001\cdot 10^{13}/\lambda^6$. Deviations between the empirical Cauchy equations and the n values obtained from SE ellipsometry are < 0.001 for $230 \text{ nm} < \lambda < 800 \text{ nm}$. The inset shows the experimental data and model fits of the $X(\circ)$ and $Y(\square)$ data at a wavelength range of 250-800 nm. 132
- Figure 4.14** Refractive index values of a spincoated $M_n = 76 \text{ kg}\cdot\text{mol}^{-1}$ PS film ($197.2 \pm 3.5 \text{ nm}$) as a function of wavelength. Empirical relationships for n as a function of wavelength via the Cauchy equations (solid lines) are provided for the $76 \text{ kg}\cdot\text{mol}^{-1}$ PS with $n_{\text{PS}}(\lambda) = 1.5633 + 11599/\lambda^2 - 7.6826\cdot 10^8/\lambda^4 + 6.45056\cdot 10^{13}/\lambda^6$. Deviations between the empirical Cauchy equations and the n values obtained from SE ellipsometry are < 0.001 for $230 \text{ nm} < \lambda < 800 \text{ nm}$. The inset shows the experimental data and model fits of the $X(\circ)$ and $Y(\square)$ data at a wavelength range of 250-800 nm. 133
- Figure 4.15** Refractive index values of a spincoated $M_n = 604 \text{ kg}\cdot\text{mol}^{-1}$ PS ($195.4 \pm 4.3 \text{ nm}$) as a function of wavelength. Empirical relationships for n as a function of wavelength via the Cauchy equations (solid lines) are provided for the $604 \text{ kg}\cdot\text{mol}^{-1}$ PS with $n_{\text{PS}}(\lambda) = 1.5894 + 11739/\lambda^2 - 7.3434\cdot 10^8/\lambda^4 + 6.25005\cdot 10^{13}/\lambda^6$. Deviations between the empirical Cauchy equations and the n values obtained from SE ellipsometry are < 0.001 for $230 \text{ nm} < \lambda < 800 \text{ nm}$. The inset shows the experimental data and model fits of the $X(\circ)$ and $Y(\square)$ at a wavelength range of 250-800 nm. 134
- Figure 4.16** Refractive index values of a spincoated PMMA film ($145.5 \pm 5.6 \text{ nm}$) as a function of wavelength. Empirical relationships for n as a function of wavelength via the Cauchy equations (solid lines) are provided for the PMMA with $n_{\text{PMMA}}(\lambda) = 1.4752 + 4626.4/\lambda^2 - 1.06194\cdot 10^8/\lambda^4 + 8.6036\cdot 10^{12}/\lambda^6$. Deviations between the empirical Cauchy equations and the n values obtained from SE ellipsometry are < 0.001 for $230 \text{ nm} < \lambda < 800 \text{ nm}$. The inset shows the experimental data and model fits of the $X(\circ)$ and $Y(\square)$ data at a wavelength range of 250-800 nm. 135

Chapter 5

- Figure 5.1** ρ vs. the number of layers in TMSC LB-films measured in air ($\square$) and water ($\circ$) at Brewster's angle and a wavelength of 632 nm. One standard deviation error bars for ρ are smaller than the size of the symbols used to represent the data. 147
- Figure 5.2** (a) ρ vs. the wt% TMSC of the spincoating solution. (b) ρ vs. D obtained from MIM ellipsometry data utilizing Approach 1 for spincoated TMSC films in (a). Symbols correspond to measurements in air ($\square$) and water ($\circ$) at a wavelength of 632 nm. One standard deviation error bars for ρ are smaller than the size of the symbol used to represent the data. 150
- Figure 5.3** (a) ρ vs. the number of LB-layers in the precursor TMSC film and (b) ellipticity vs. film thicknesses obtained from MIM ellipsometry data utilizing Approach 1 for cellulose films regenerated from TMSC LB-films. (c) Ellipticity vs. wt % concentration of TMSC in the spincoating solution and (d) ellipticity vs. film thicknesses obtained from MIM ellipsometry data utilizing Approach 1 for cellulose films regenerated from spincoated TMSC films. Symbols correspond to measurements in air ($\square$) and hexane ($\circ$) at a wavelength of 632 nm. One standard deviation error bars on ρ are smaller than the size of the symbols used to represent the data. 152
- Figure 5.4** (a) ρ vs. wt% concentration of cellulose nanocrystals in the spincoating dispersions and (b) ρ vs. D obtained from MIM ellipsometry data utilizing Approach 1 for spincoated cellulose nanocrystal films. Symbols correspond to measurements in air ($\square$) and hexane ($\circ$) at a wavelength of 632 nm. One standard deviation errorbars on ρ are smaller than the size of the symbols used to represent the data. 155
- Figure 5.5** n of regenerated cellulose and TMSC films as a function of wavelength obtained via SE ellipsometry. CPE fitting parameters are summarized in Table 7. Solid lines represent empirical fits (according to the Cauchy equations) for $n_{\text{Cellulose}}(\lambda) = 1.4953 + 7628.8/\lambda^2 - 3.5445 \cdot 10^8/\lambda^4 + 8.3012 \cdot 10^{12}/\lambda^6$ and $n_{\text{TMSC}}(\lambda) = 1.436 + 4155.3/\lambda^2 - 1.1466 \cdot 10^8/\lambda^4 + 9.712 \cdot 10^{12}/\lambda^6$. Deviations between the empirical Cauchy equations and the n values obtained from SE ellipsometry are < 0.001 for the wavelength range of $230 \text{ nm} < \lambda < 800 \text{ nm}$. 157

Chapter 6

- Figure 6.1** Representative first heating scans showing double layer transitions for 30 layer LB-films of (a) $M_n=23.6 \text{ kg}\cdot\text{mol}^{-1}$ PtBA, (b) $M_n = 5.0 \text{ kg}\cdot\text{mol}^{-1}$ PtBA and (c) TPP. Insets show the absence of double layer transitions for second heating cycles. 168

Figure 6.2	(a) A schematic depiction of the double layer structure proposed by Esker <i>et al.</i> (b) A representative X-ray reflectivity profile for a 48 layer LB-film of TPP showing Kiessig fringes and a single Bragg peak. (c) A schematic representation of a double layer structure for TPP molecules on hydrophobic silicon substrates that is consistent with (b).	169
Figure 6.3	Representative first heating scans showing both double layer transitions and surface T_g for 30 layer LB-films of $M_n = 5.0 \text{ kg}\cdot\text{mol}^{-1}$ PtBA filled with (a) 1, (b) 3, (c) 5, and (d) 20 wt% TPP nanofiller. Insets show the absence of a double layer transition for the second heating cycles.	172
Figure 6.4	Representative first heating scans showing both double layer transitions and surface T_g for 30 layer LB-films of $M_n = 5.0 \text{ kg}\cdot\text{mol}^{-1}$ PtBA filled with (a) 40, (b) 60, and (c) 90 wt% TPP nanofiller. Insets show the absence of a double layer transition for the second heating cycles.	173
Figure 6.5	Representative first heating scans showing both double layer transitions and surface T_g for 30 layer LB-films of $M_n = 23.6 \text{ kg}\cdot\text{mol}^{-1}$ PtBA filled with (a) 1, (b) 3, (c) 5, and (d) 20 wt% TPP nanofiller. Insets show the absence of a double layer transition for the second heating cycles.	174
Figure 6.6	Representative first heating scans showing both double layer transitions and surface T_g for 30 layer LB-films of $M_n = 23.6 \text{ kg}\cdot\text{mol}^{-1}$ PtBA filled with (a) 40, (b) 60, and (c) 90 wt% TPP nanofiller. Insets show the absence of a double layer transition for the second heating cycles.	175
Figure 6.7	Thermal expansion curves for $M_n = 23.6 \text{ kg}\cdot\text{mol}^{-1}$ PtBA films. (a) and (b) contain second heating scans for (a) $\sim 30 \text{ nm}$ spincoated and (b) $\sim 28 \text{ nm}$ LB films without first subjecting the films to overnight annealing. (c) and (d) contain first heating scans for (c) $\sim 30 \text{ nm}$ spincoated and (d) $\sim 28 \text{ nm}$ LB films after annealing at 90°C for 16 h. The insets show the entire heating scan range in (c) and (d).	177
Figure 6.8	Thermal expansion curves for $M_n = 5.0 \text{ kg}\cdot\text{mol}^{-1}$ PtBA films after first annealing the films for 16h at 90°C under vacuum. First heating scans for (a) an $\sim 30 \text{ nm}$ thick spincoated film and (b) an $\sim 28 \text{ nm}$ thick LB-film.	179
Figure 6.9	Thermal expansion curves (second heating scans) for $\sim 28 \text{ nm}$ thick films of $M_n = 23.6 \text{ kg}\cdot\text{mol}^{-1}$ PtBA LB-films (a) without (b) with 5 wt% TPP.	180
Figure 6.10	Thermal expansion curves for second heating scans of $\sim 28 \text{ nm}$ $M_n = 23.6 \text{ kg}\cdot\text{mol}^{-1}$ PtBA LB-films containing (a) 1, (b) 3, (c) 20, (d) 40, (e) 60, and (f) 90 wt% TPP.	181
Figure 6.11	Thermal expansion curves for second heating scans of $\sim 28 \text{ nm}$ $M_n = 5.0 \text{ kg}\cdot\text{mol}^{-1}$ PtBA LB-films containing (a) 1, (b) 3, (c) 5, and (d) 20 wt% TPP.	182

Figure 6.12	Thermal expansion curves for second heating scans of ~28 nm, $M_n = 5.0 \text{ kg}\cdot\text{mol}^{-1}$ PtBA LB-films containing (a) 40, (b) 60, and (c) 90 wt% TPP.	183
Figure 6.13	Plots of surface and bulk T_g as a function of TPP content for ~28 nm LB-films of $M_n = 23.6 \text{ kg}\cdot\text{mol}^{-1}$ and $M_n = 5.0 \text{ kg}\cdot\text{mol}^{-1}$ PtBA. Surface and bulk T_g values are obtained from second heating scans by ellipsometry and DSC, respectively.	185
Chapter 7		
Figure 7.1	Representative XR profiles for TPP LB-films. The inset shows D vs. the number of LB-layers (layer #) for each film. The slope of the inset yields the thickness per layer, $d = 0.84 \pm 0.01 \text{ nm}$.	193
Figure 7.2	MIM ellipsometry data for TPP LB-films in air ($\square$) and in water ($\circ$) at a wavelength of 632 nm.	195
Figure 7.3	α for ~28 nm LB-films of $M_n = 5$ and $23.6 \text{ kg}\cdot\text{mol}^{-1}$ PtBA/TPP blends obtained from second heating scans.	198

List of Tables

Chapter 4

Table 4.1	X-Ray reflectivity data for PtBA LB-films.	109
Table 4.2	Ellipsometry data for PtBA LB-films obtained from MIM ellipsometry experiments.	114
Table 4.3	Thickness and refractive index values for spincoated PtBA films deduced from MIM ellipsometry data.	116
Table 4.4	Thickness and refractive index values for PtBA LB-films deduced from MIM ellipsometry experiments in different media.	119
Table 4.5	Thickness and refractive index values for spincoated PtBA films deduced from MIM ellipsometry experiments in different media.	119
Table 4.6	Refractive index values for PS and PMMA spincoated films calculated from MIM ellipsometry measurements made in different ambient media.	120
Table 4.7	Thickness and refractive index values for $M_n = 23 \text{ kg}\cdot\text{mol}^{-1}$ PS spincoated films obtained from MIM ellipsometry measurements made in different ambient media.	122
Table 4.8	Thickness and refractive index values for $M_n = 76 \text{ kg}\cdot\text{mol}^{-1}$ PS spincoated films obtained from MIM ellipsometry measurements made in different ambient media.	124
Table 4.9	Thickness and refractive index values for $M_n = 604 \text{ kg}\cdot\text{mol}^{-1}$ PS spincoated films obtained from MIM ellipsometry measurements made in different ambient media.	126
Table 4.10	Thickness and refractive index values for PMMA spincoated films obtained from MIM ellipsometry measurements made in different ambient media.	128
Table 4.11	Thickness and refractive index values ($\lambda = 632.8 \text{ nm}$) for thick spincoated films obtained from SE and MAOI ellipsometry measurements.	129
Table 4.12	Thicknesses of PtBA LB-films obtained from XR and MIM ellipsometry, and from SE and MAOI ellipsometry measurements utilizing the optical constants deduced from thick films.	136
Table 4.13	Thicknesses of spincoated PtBA films obtained from MIM ellipsometry, and SE and MAOI ellipsometry measurements utilizing the optical constants deduced from thick films.	136
Table 4.14	Thicknesses of spincoated $M_n = 23 \text{ kg}\cdot\text{mol}^{-1}$ PS films obtained from MIM ellipsometry and SE and MAOI ellipsometry measurements utilizing the optical constants deduced from thick films.	137
Table 4.15	Thicknesses of spincoated $M_n = 76 \text{ kg}\cdot\text{mol}^{-1}$ PS films obtained from MIM ellipsometry and SE and MAOI ellipsometry measurements utilizing the optical constants deduced from thick films.	137
Table 4.16	Thicknesses of spincoated $M_n = 604 \text{ kg}\cdot\text{mol}^{-1}$ PS films obtained from MIM ellipsometry and SE and MAOI ellipsometry measurements utilizing the optical constants deduced from thick films.	138

Table 4.17	Thicknesses of spincoated PMMA films obtained from MIM ellipsometry and SE and MAOI ellipsometry measurements utilizing the optical constants deduced from thick films.	138
Table 4.18	CPE parameters for PtBA, PS, and PMMA.	139
Chapter 5		
Table 5.1	MIM ellipsometry results of TMSC LB-films.	148
Table 5.2	Thickness and refractive index values for spincoated TMSC films deduced from MIM ellipsometry data.	150
Table 5.3	Thickness and refractive index values obtained by MIM ellipsometry for cellulose films regenerated from TMSC LB-films.	153
Table 5.4	Thickness and refractive index values obtained by MIM ellipsometry for cellulose films regenerated from spincoated TMSC films.	153
Table 5.5	Thickness and refractive index values for spincoated films of cellulose nanocrystals deduced from MIM ellipsometry data.	155
Table 5.6	Thickness and refractive index values for representative thin TMSC LB-films from SE and MAOI ellipsometry without any constraints on their values.	157
Table 5.7	CPE parameters for TMSC and regenerated cellulose.	158
Table 5.8	Thickness and refractive index values for a thick spincoated film of TMSC and the corresponding regenerated cellulose film.	158
Table 5.9	Thicknesses of TMSC LB-films obtained from SE and MAOI ellipsometry measurements utilizing the optical constants in Table 5.8 compared to MIM ellipsometry results.	158
Chapter 6		
Table 6.1	Double layer transition temperatures for 30 layer TPP filled PtBA LB-films.	171
Chapter 7		
Table 7.1	X-Ray reflectivity and ellipsometry data for TPP LB-films.	194

CHAPTER 1

Overview

Precise film thickness and refractive index determinations are often a critical challenge parameters in thin film metrology of polymer systems. Furthermore, rapid and non-destructive measurements are desired prior to additional surface characterization. Moreover, the refractive index is a parameter of considerable interest for any optical system that utilizes reflection or refraction. On the other hand, polymer thin films below a certain thickness exhibit physical properties that are substantially different from their corresponding bulk properties due to the confinement effects. Properties such as the glass transition temperature (T_g), phase separation, and viscosity are properties that change upon confinement. T_g is one of the most important thermal parameters for characterizing a polymer as an engineering material, and as a consequence confinement effects on T_g have received considerable attention in recent years. In this dissertation, we investigate the optical and thermal properties of polymers in confined geometries. Simultaneous determinations of film thickness and refractive index of polymeric thin films are provided. These measurements provided the ground work for the subsequent study of how surface T_g changes in the presence of a model nanofiller.

Chapter 2 includes an overall introduction and review. A general introduction to the importance of polymer thin films supported on solid substrates is presented. Then, a fundamental understanding of optical properties of materials and light-matter interactions is established. Next, the refractive index properties of polymeric materials, chemical group contributions to refractive index and the importance of refractive index in optical applications are provided. Afterwards, the nature of glass transition, factors effecting T_g ,

and surface T_g behavior are reviewed with examples from the literature. After establishing the problems, techniques for preparing samples and for characterizing thin films are covered. The Langmuir-Blodgett (LB) technique, a method for depositing monolayers of amphiphilic molecules onto solid substrates from the surface of a liquid, has been used to prepare films of controlled thicknesses. A detailed description of the LB-technique including the various thermodynamic phase transitions of Langmuir monolayers, the apparatus for the preparation of Langmuir monolayers and LB-films, and LB-deposition patterns are provided. Since X-ray reflectivity and ellipsometry measurements were the main characterization techniques for the pure polymers and polymer/nanofiller systems in this thesis, the background for these methods is also provided in Chapter 2. Finally, the general synthesis scheme and applications of polyhedral oligomeric silsesquioxanes (POSS) as model, monodisperse nanofillers are reviewed.

Chapter 3 introduces the materials and experimental techniques that are used in this dissertation. The description of materials and experimental methods will not be repeated in subsequent chapters.

Simultaneous determinations of film thickness and refractive index for a polymer thin film via multiple incidence medium (MIM) ellipsometry are introduced in Chapter 4. LB-films of poly(*tert*-butyl acrylate) (PtBA) serve as a model system for the MIM method. The agreement between film thicknesses deduced by MIM ellipsometry and X-ray reflectivity is demonstrated. Next, MIM ellipsometry was applied to spincoated films of PtBA. These results are consistent with PtBA LB-films. Hence, MIM ellipsometry was also applied to polystyrene (PS) and poly (methyl methacrylate) (PMMA). All

results were consistent with the literature. As a further check, different inert, non-swelling, nonsolvent liquid media show MIM ellipsometry yields consistent results in all cases. Finally, MIM results are compared to traditional ellipsometry measurements to demonstrate the results are consistent.

In Chapter 5, optical characterization of trimethylsilylcellulose (TMSC), regenerated cellulose, and cellulose nanocrystals are presented. First, MIM ellipsometry is utilized to investigate LB-films of TMSC. After obtaining a reasonable value of refractive index from MIM ellipsometry measurements on LB-films of TMSC, the data analysis procedure is applied to spincoated systems of TMSC, regenerated cellulose derived from the TMSC films, and cellulose nanocrystals. Comparisons between MIM ellipsometry results and spectroscopic ellipsometry (SE) and multiple angle of incidence (MAOI) ellipsometry are also included.

One of the main goals of this dissertation is to explore the surface glass transition temperature of thin polymer and polymer/nanofiller films. Chapter 6 provides a detailed investigation of surface T_g . First, heating scans were used to track thermal expansion from changes in ellipticity in order to illustrate the difference between first and second heating cycles for LB-films of PtBA and TPP. Next, the thermal expansion coefficients of spincoated systems are compared to LB-films having similar thicknesses. Finally the effect a polyhedral oligomeric silsesquioxane (POSS) [i.e. trisilanolphenyl-POSS (TPP)] has on surface T_g is provided and compared to bulk T_g values.

Chapter 7 summarizes the overall conclusions and provides suggestions for future work on pure polymer and polymer/POSS blend systems confined to thin films that naturally follow from this dissertation. The manipulation of variables such as film

thickness, polymer molar mass, and choice of nanofiller are suggested for controlled studies of both refractive index and surface glass transition temperatures.

CHAPTER 2

Introduction and Review

2.1 Introduction

Polymer thin films are important for technological applications such as electromechanics,¹⁻⁵ biocompatible coatings,⁶ novel drug delivery systems,⁷ chemical and biochemical sensors,⁸⁻¹² lenses,¹³ waveguides,^{14,15} and other optical devices.¹⁶⁻¹⁸ In the optical applications refractive index (n) must be matched or carefully controlled during fabrication. Therefore, the determination of refractive indices for ultrathin polymer films is crucial for understanding the interaction of light with matter. In addition, polymer thin films can also be used in high temperature and space survivable coatings applications.¹⁹ These applications often require a reduction in the film thicknesses to nanoscale regimes, while maintaining or improving the stability of the material. The glass transition temperature is one of the most important factors that influences the film stability and helps to define the temperature window where a polymeric material can be used. In spite of the general importance of T_g , surface T_g remains poorly understood. Near a surface or interface, T_g of both pure polymers and nanofilled polymeric systems must be better understood in order to take advantage of unique and enhanced properties that can be obtained in polymer films upon the addition of nanoparticles.

2.2 Optical Properties: Refractive Indices and Extinction Coefficients

Investigations of optical properties and experimental determinations of optical properties of materials are ubiquitous throughout the history of materials research. The characteristics of light passing through a material can change. The changes are in either the direction of the propagation vector of the incident light or the intensity of light traveling through the material. The refractive index (n) and the extinction coefficient (K) are the two most important optical constants for materials. These optical constants for various materials can be found in journals, books, and handbooks.²⁰⁻²⁸ These properties could be measured through experimental techniques such as ellipsometry which will be discussed in detail in the experimental techniques section of this chapter and in Chapter 3.

The refractive index of a material is the ratio of the velocity of the light, c , in a vacuum to the velocity of light in a medium, v . Utilizing this ratio and Maxwell's equations it is possible to obtain Maxwell's formula for the refractive index of a substance.²⁹⁻³²

$$n = \sqrt{\epsilon_r \mu_r} \quad (2.1)$$

where ϵ_r is the dielectric constant, also known as the relative permittivity, and μ_r is the relative permeability. μ_r reduces to 1 for nonmagnetic materials and therefore Equation 2.1 has the form:

$$n = \sqrt{\epsilon_r} \quad (2.2)$$

Equation 2.2 is a very useful relationship as it relates the refractive index of a nonmagnetic material to its dielectric constant at any particular frequency of interest. Refractive index depends on the wavelength of the electromagnetic wave (light). As an

electromagnetic wave travels through the material, energy can be dissipated. Therefore, the refractive index is expressed as a complex number, $n^* = n + Ki$ ²⁹⁻³². As the complex refractive index is usually denoted as n^* and this convention will be followed throughout this thesis. The complex relative permittivity is given as,

$$\epsilon_r = \epsilon'_r - i\epsilon''_r \quad (2.3)$$

where ϵ'_r is the real and ϵ''_r is imaginary part of ϵ_r . As a consequence, n^* can also be expressed as

$$n^* = n - iK = \sqrt{\epsilon_r} = \sqrt{\epsilon'_r - i\epsilon''_r} \quad (2.4)$$

The optical constants n and K are also related to the reflection coefficient, r , the reflectance, R through Equations 2.5 and 2.6, respectively:²⁹

$$r = \frac{1 - n^*}{1 + n^*} = \frac{1 - n + iK}{1 + n - iK} \quad (2.5)$$

$$R = |r|^2 = \left| \frac{1 - n + iK}{1 + n - iK} \right|^2 = \frac{(1 - n)^2 + K^2}{(1 + n)^2 + K^2} \quad (2.6)$$

The optical properties of materials are frequency dependent therefore, n , K , ϵ'_r , and ϵ''_r can be represented in terms of the vacuum permittivity, ϵ_0 , and frequency dependent real and imaginary polarizabilities, α' and α'' , respectively,

$$\epsilon'_r = 1 + \frac{N_{at}}{\epsilon_0} \alpha'_e \quad (2.7)$$

$$\epsilon''_r = 1 + \frac{N_{at}}{\epsilon_0} \alpha''_e \quad (2.8)$$

where N_{at} is the number of atoms per unit volume, and the α' and α'' are defined as

$$\alpha_e' = \alpha_{e0} \frac{1 - (\omega/\omega_0)^2}{\left[1 - (\omega/\omega_0)^2\right]^2 + (\gamma/\omega_0)^2 (\omega/\omega_0)^2} \quad (2.9)$$

$$\alpha_e' = \alpha_{e0} \frac{(\gamma/\omega_0)^2 (\omega/\omega_0)^2}{\left[1 - (\omega/\omega_0)^2\right]^2 + (\gamma/\omega_0)^2 (\omega/\omega_0)^2} \quad (2.10)$$

In Equations 2.9 and 2.10, α_{e0} is the polarizability corresponding to an angular frequency, $\omega = 0$, and γ is the loss coefficient which characterizes the electromagnetic wave damping within the material. It is clear from the Equations 2.7 through 2.10 that n and K are frequency dependent.^{29,30} In general optical properties of materials are expressed as a function of frequency, wavelength, or photon energy. Additionally, it is seen that the relative permittivity of a material is larger for molecules having polar interactions or molecules that are highly polarizable. A quantitative description for the relationship between relative permittivity and polarizability of the material is provided through the Debye equation:^{33,34}

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{\rho}{M} \frac{N_A}{3\epsilon_0} \left(\alpha + \frac{\mu^2}{3kT} \right) \quad (2.11)$$

where ρ is the mass density of the sample, M is the molar mass of the molecules, μ is the thermally averaged electric dipole moment at a given temperature, T , and k is Boltzmann's constant. This expression could be further reduced to the Clausius-Mossotti equation³⁵ for systems lacking a permanent dipole moment ($\mu=0$). This condition is satisfied for nonpolar molecules or high frequency experiments where molecules do not have sufficient time to orient along the direction of the applied field.

2.2.1 Dispersion Functions for Refractive Index

Optical properties are commonly expressed in terms of their wavelength dependence. Various models exist to describe the wavelength dependence of n . Models such as the Cauchy and Sellmeier dispersion relations can be considered as reasonable dispersion functions of the refractive index over a limited spectral range.³⁶⁻⁴⁰ In the Cauchy relationship the dispersion of refractive index as a function of wavelength is given as

$$n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \quad (2.12)$$

In Equation 2.12, A , B , and C are material specific constants. This equation is also known as the Cauchy formula. The Cauchy formula is widely used in the visible spectrum^{41,42} and has a normal dispersion indicating that refractive index decreases with increasing wavelength.^{43,44} The third term can be eliminated or a fourth term can be added for a simpler or more complicated dispersion relationship respectively, since Equation 2.12 is only a part of the complete series expansion.^{43,44} –

$$n = a_0 + \frac{a_2}{\lambda^2} + \frac{a_4}{\lambda^4} + \frac{a_6}{\lambda^6} + \dots \quad (2.13)$$

In Equation 2.13, a_2 , a_4 , a_6 are material constants.⁴⁵ On the other hand, another commonly used empirical relation is called the Sellmeier equation. The Sellmeier equation provides an empirical relationship between the refractive index of the material and the wavelength of the light interacting with the material,

$$n^2 = 1 + \frac{A_1 \lambda^2}{\lambda^2 - \lambda_1^2} + \frac{A_2 \lambda^2}{\lambda^2 - \lambda_2^2} + \frac{A_3 \lambda^2}{\lambda^2 - \lambda_3^2} + \dots \quad (2.14)$$

where A_1 , A_2 , A_3 , λ_1 , λ_2 and λ_3 are called Sellmeier coefficients.⁴⁶⁻⁴⁸

There are other Sellmeier and Cauchy-like dispersion relationships such as the critical point exciton (CPE) material approximation^{49,50} that is commonly used to analyze amorphous polymer systems. The generalized expression for the line shape in the CPE model is

$$n^2(E) = \varepsilon(E) = UV_{\text{term}} - \sum_1^N A_j e^{i\phi_j} (Ec_j - E + \Gamma_j)^{-1} \quad (2.15)$$

where, $\varepsilon(E)$ is the dielectric constant as a function of the energy of the electromagnetic radiation, and the UV_{term} is a constant that represents the UV absorption peaks, A_j is the amplitude, E_c is the critical point energy, Γ_j is the broadening, and ϕ_j is the phase of the j^{th} transition. Furthermore, N is the number of critical points and determines the number of parameters. In general $N=1$ is sufficient to obtain a realistic optical dispersion for most polymers.

In this thesis it will be seen that the index of refraction varies as a function of wavelength. However, n may be relatively constant for restricted wavelength ranges.

2.2.2 Interference of Light with Matter

The interference of light arises from its wave characteristics. Overlapping light waves undergo interference phenomena. Therefore, the incident light wave could interfere with another wave that is reflecting from the surface of a thin film or substrate. The phases and amplitude of the light undergo a constructive or destructive interference as shown in Figure 2.1.⁵¹⁻⁵⁵ This interference can also cause a decrease or increase in the reflectance or the transmittance of the incident light.

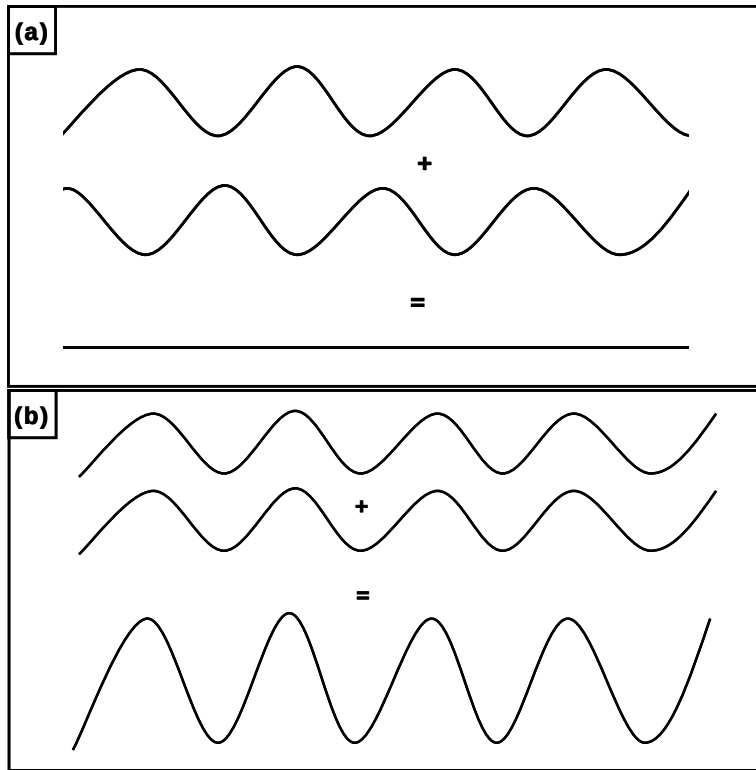


Figure 2.1. (a) Destructive and (b) constructive interference of light waves. Two waves with equal amplitudes and the same frequency or wavelength cancel if they are out of phase by 180° and will add if they are in phase. Other types of interactions such as unequal amplitudes or arbitrary phase differences result in a wave that is a combination of the two interfering light waves.

Figure 2.2 shows a layered film structure supported on a solid substrate. In Figure 2.2, each layer has a different refractive index than the neighboring layers. Light is reflected from and also transmitted through the interfaces. The transmitted and reflected light undergo interference. This interference can be destructive or constructive.

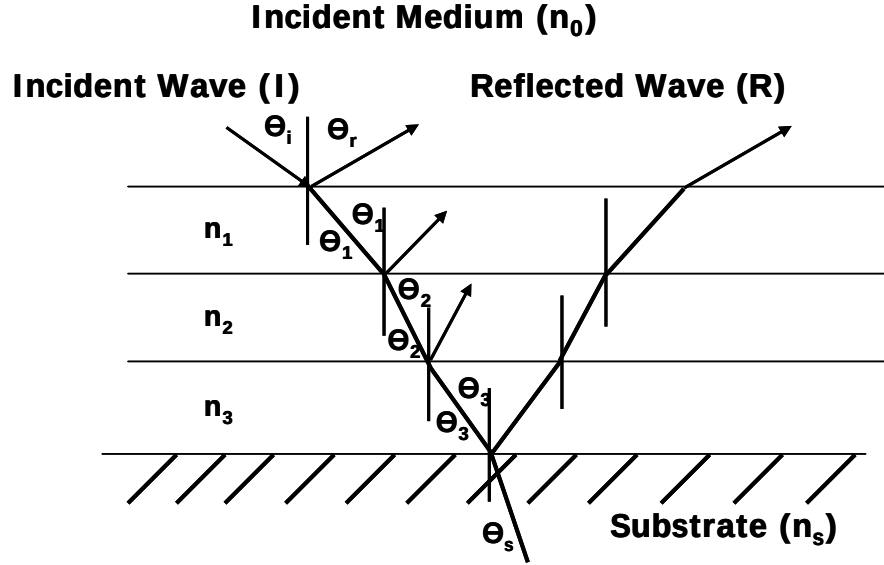


Figure 2.2. A thin film stack structure with different refractive indices for each layer. The index of refraction is indicated by n_i , and layers are numbered starting from the incident medium ($i=0$). Reflection and refraction occurs at each interface.

The reflection of incident light from an interface between materials with different refractive indices can be theoretically calculated and explained via the Fresnel equations.⁵²⁻⁵⁶ The simplest version of the equation for a two layer system, an infinite incident medium and an infinite substrate (air/substrate), is given as

$$r = (n_0 - n_1) / (n_0 + n_1) \quad (2.16)$$

where r is the amplitude reflection coefficient, n_0 is refractive index of the incident medium, and n_1 is the refractive index of the second medium or the substrate. On the other hand, the transmitted amplitude t is defined as

$$t = 1 - r \quad (2.17)$$

Equations 2.16 and 2.17 are valid for the two simple interfaces. However, these equations could also be applied to more complex interfaces. The Fresnel formula applies to each

interface; however, the phase behavior of each wave reflecting from or transmitting through an interface should be taken into account in these reflectivity coefficient calculations. Utilizing the Fresnel equations, interference information can be related to the thickness or optical properties of the comprising layers. Application of the Fresnel equations on the treatment of the X-ray reflectivity and ellipsometry data will be introduced in Section 2.4.2 and 2.4.3 of this chapter, respectively.

2.2.3 Polarization of Light

Propagating light has amplitude fluctuations that are perpendicular to the direction of propagation. For linear polarized light the oscillations take place in a single plane, the plane of polarization. As shown in Figure 2.3 amplitude fluctuations can be decomposed into two components for all waves. In Figure 2.3, the propagation direction is chosen to coincide with the z-axis. As such, the polarization can be decomposed to the XZ and XY planes. Figure 2.3 (a) shows light propagation for linear polarized light. As seen in Figure 2.3 (a), both the XY and YZ components are completely in phase ($\Phi = 0$). An additional feature for Figure 2.3 is that the electric field amplitudes are depicted as having equal magnitudes. ($E_{XZ} = E_{YZ}$). As such, the corresponding Lissajous figure is a straight line that makes a 45° angle relative to the X or Y axis.⁵⁷

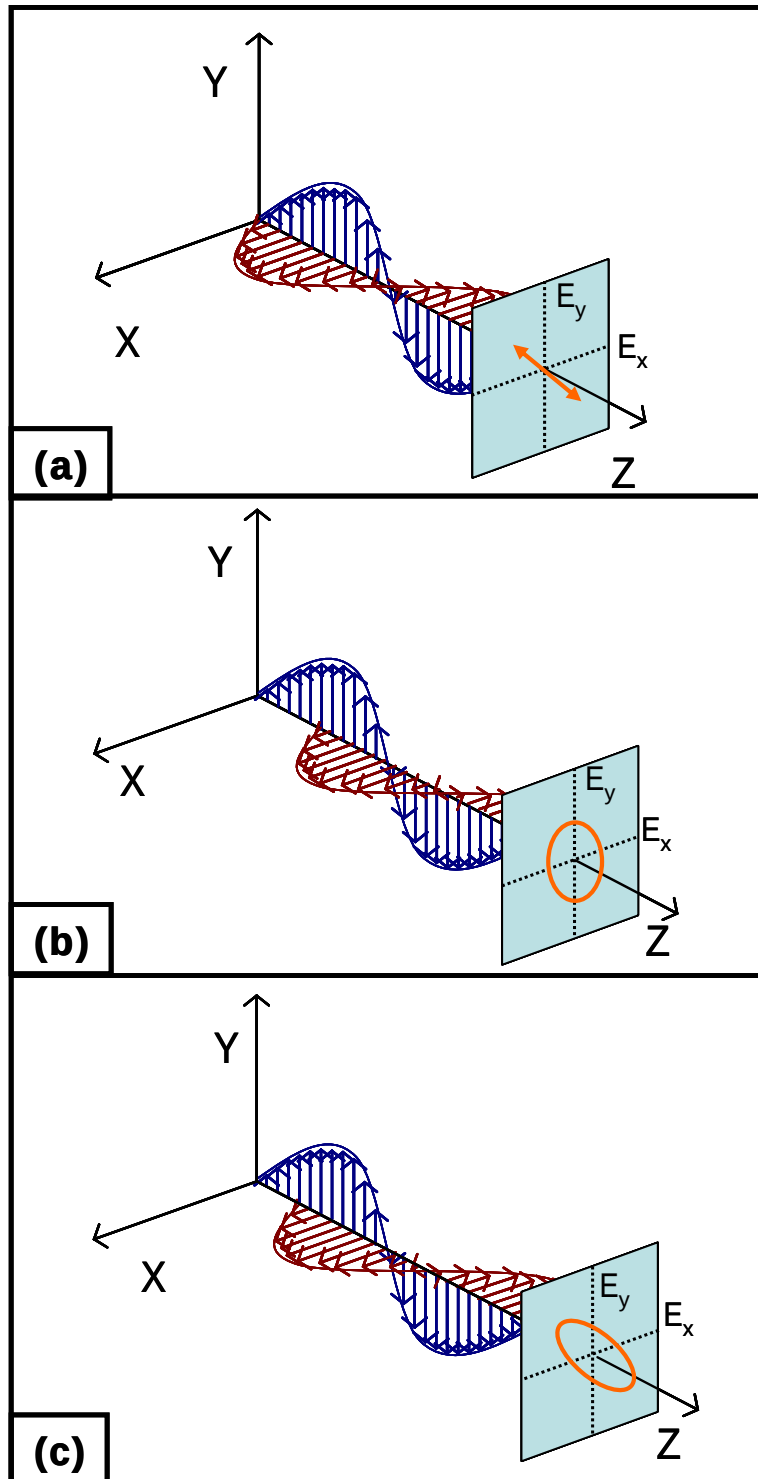


Figure 2.3. A schematic representation of a (a) linear, (b) circular, and (c) elliptically polarized light wave propagating along Z direction.

The second form of polarized light is circularly polarized light. Figure 2.3 (b) depicts circularly polarized light for the case where $E_{XZ} = E_{YZ}$. For circularly polarized light the decomposed linearly polarized beams have a phase difference of $\Phi = \pi/2$ between the XZ and YZ components. As a consequence, the Lissajous figure is a circle leading the name circularly polarized light.

Another form of polarized light is elliptically polarized light. Figure 2.3 (c) depicts elliptically polarized light for the case where $E_{XZ} = E_{YZ}$ with a random phase difference Φ . As seen in Figure 2.3 (c) the corresponding Lissajous figure is an ellipse.

2.2.4 Angle of Incidence Effects: Snell's Law and Brewster's Angle

A light beam incident upon an interface between two media having different refractive indices at an angle of incidence other than 90° changes its propagation direction. The change in the direction of propagation of the light wave is given by Snell's Law:⁵⁸⁻⁶⁴

$$n_1 \sin \theta_1 = n_2 \sin \theta_2 \quad (2.18)$$

where n_1 and n_2 are the refractive index of medium 1 and 2, respectively, θ_1 is the angle of incidence defined relative to the surface normal, and θ_2 is the angle of refraction, also defined relative to the surface normal as seen in Figure 2.4.

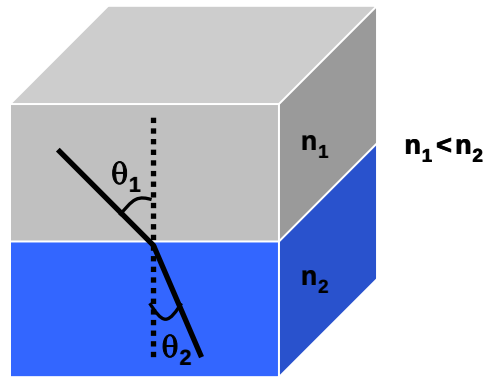


Figure 2.4. The refractive index of a material can be determined from the angle of refraction for a beam incident from a medium with a known refractive index and incident angle.

The reflected and refracted beams lie in the same plane defined by the incident beam and the surface normal (the plane of incidence). When a nonpolarized light beam propagates through an interface, the light will be transmitted, reflected, or refracted. The refractive index of the incident and the second media where light wave is transmitted or refracted determines the light wave's behavior upon interaction with an interface.

Upon reflection from a surface the nonpolarized light can be completely polarized, partially polarized, or nonpolarized depending on the angle of incidence. It should be noted that the reflected light will be fairly polarized provided that the angle of incidence is not normal (0°) or at grazing incidence (90°) relative to the surface normal. At a specific incident angle, which is dependent on the refractive index of the media and the material, the light beam arriving at an interface will be completely polarized. The nonpolarized light arriving at a surface can be decomposed into two components as shown in Figure 2.5. One component is parallel to the plane of incidence shown with the arrows and is called p-polarized light. The other component is perpendicular to the plane

of incidence shown with dots and is called s-polarized light. Both components are perpendicular to the propagation direction.

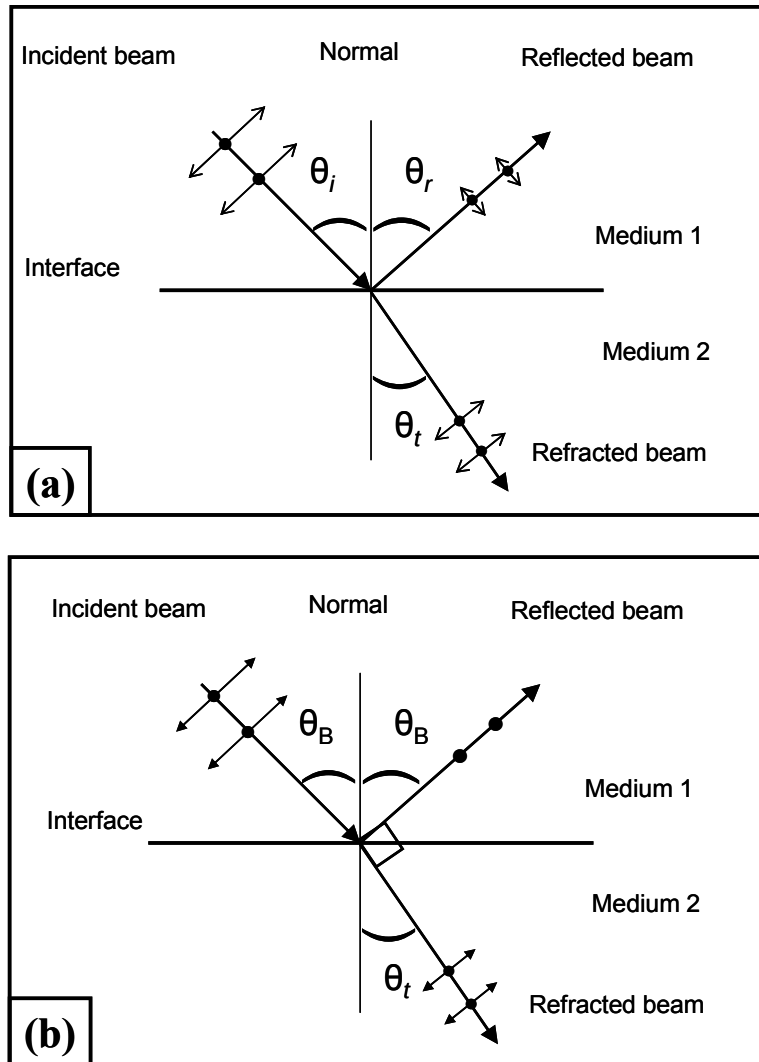


Figure 2.5. Nonpolarized light incident upon an interface. (a) $\theta_i \neq \theta_B$ (Brewster's angle)
 (b) $\theta_i = \theta_B$, which is consistent with Equation 2.19, $n_2 = \tan\theta_B$. The arrows and dots represent parallel and perpendicular components of the light with respect to the plane of incidence, respectively.

In Figure 2.5 (a), it is clear that the reflected and refracted beams contain both p and s polarized light for non normal and non grazing angles of incidence. On the other hand, in Figure 2.5 (b) the reflected beam is s-polarized (only), while the refracted beam contains both s and p polarized light when the incident angle corresponds to Brewster's angle. As depicted in Figure 2.5 (b) at $\theta_i = \theta_B$, $\theta_t = 90 - \theta_B$. Utilizing Snell's Law (Equation 2.18), it can be shown that

$$\theta_B = \tan^{-1}\left(\frac{n_2}{n_1}\right) \quad (2.19)$$

Equation 2.19 is known as Brewster's Law, and θ_B is different for each substance and wavelength of light since materials have material and wavelength dependent n . For instance, $\theta_B = 75.5^\circ$ for silicon ($n = 3.88$, $\lambda=632.8$) and $\theta_B = 53.1^\circ$ for water ($n = 1.33$, $\lambda=632.8$) is 53.1° .^{65,66}

2.2.5 Optical Properties of Polymers

Polymers provide remarkable advantages in optical applications over common inorganic glasses, especially with respect to their light weight, and impact and shatter resistance. For example, polymeric materials give rise to useful optical designs such as, filters,⁶⁷⁻⁷⁰ antireflective coatings⁷¹⁻⁷³ waveguides,⁷⁴⁻⁷⁶ and Bragg reflectors (i.e. high quality mirrors).⁷⁷ Most polymers are isotropic due to their amorphous structures. Therefore, most polymers do not show angle dependent refractive indices. However, there are a few polymers which are crystalline and show birefringent properties such as poly(ethylene), poly(vinylidene chloride), poly(amide)s, cellulose and some of its derivatives, crystalline rubber and poly(tetrafluoroethylene).⁷⁸⁻⁸⁵

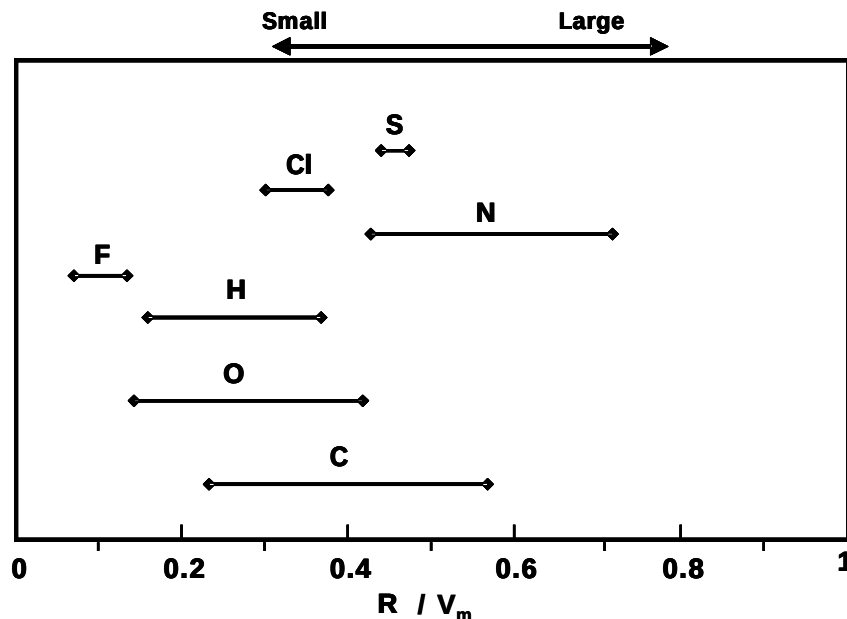


Figure 2.6. Contribution of different types of atoms to a polymer's refractive index.⁸¹

As one can imagine refractive indices of polymers are highly dependent on a substance's polarizability, which is related to the chemical composition of the macromolecule. Individual atom contributions to the refractive index are summarized in Figure 2.6. A polymer with a small refractive index must have a small polarizability (i.e. the dipole moment per unit volume induced by the electromagnetic field needs to be relatively small). In contrast, high refractive index materials require large polarizabilities (i.e. the dipole moment per unit volume induced by the electromagnetic field is relatively large). In Figure 2.6, the ratio of molar refraction, R , which is proportional to the induced dipole moment to molar volume, V_m , for different atoms present in polymers is schematically drawn. R in air is a function of the refractive index of the material, n_2 :

$$R = V_m \frac{n_2 - 1}{n_2 + 2} \quad (2.20)$$

where V_m is the molar volume. As demonstrated in Figure 2.6, there is a broad range of values for each type of atom that arises from their participation in chemically different bonding and the local chemical environment in different polymer compounds. However, some general trends exist: fluorine lowers the refractive index of a polymer, while nitrogen, sulfur, and the heavier halogens have higher molar refraction ratios, thereby increasing the refractive index.⁸⁶⁻⁸⁸ As such, it is possible to control the polarizability and refractive index of a polymer by changing the substituent groups. While efforts to obtain high refractive indices focus on incorporating oxygen, sulfur, or sulfoxide containing groups to aromatic polymethacrylates,⁸⁹ fluorinated core polymers^{90,91} are used to produce low refractive index materials. In general, most polymers have refractive index values near 1.5. For example, the refractive index for poly(methyl methacrylate) is 1.49, and the refractive index for poly(ethylene) is 1.51. Polymers with strongly electronegative substituent groups have lower refractive indices such as poly(tetrafluoroethylene) which has a $n = 1.37$. On the other hand, polymers having bulky aromatic or conjugated substituents have higher refractive indices such as polystyrene and poly(vinylcarbazole), $n = 1.59$ and 1.69 , respectively. According to the current literature most polymers have refractive indices between 1.33 and 1.73 .^{89,92}

2.3 Glass Transition Behavior in Polymers

The thermal properties of polymers depend on the temperature and time scale of an experiment. Of these properties, the glass transition temperature is the most important parameter for amorphous polymers and semicrystalline polymers in the amorphous state. At low temperatures amorphous materials are stiff and glassy, whereas upon warming the polymer softens at a characteristic temperature range known as glass to rubber transition.

On a molecular basis, the glass transition involves the onset of long-range cooperative motion, referred to as the onset of reptation. The glass transition is a second order phase transition where the enthalpy and volume are continuous as a function of temperature, however the derivative of these properties with respect to temperature are discontinuous. (i.e. heat capacity and thermal expansion coefficients are discontinuous). In contrast, melting or boiling (i.e first order phase transitions) exhibit discontinuous enthalpy and volume values as a function of temperature with the observation of a latent heat at these transition temperatures. The glass transition has important consequences on the systems mechanical properties. The behavior of amorphous polymers in the glass transition range will be discussed, however, a few simple, yet important relationships for the mechanical properties of materials will be provided to aid the subsequent discussion of glassy, rubbery and viscous states of polymers.

2.3.1 Simple Mechanical Relationships

Hook's law describes the perfect elasticity of an isotropic material through Young's modulus, E , as

$$E = \sigma / \varepsilon \quad (2.21)$$

where σ and ε are tensile stress and strain, respectively. Young's modulus can be perceived as a fundamental measure of stiffness. A higher value of Young's modulus represents a higher resistance of a material to stretching. Rather than deformation through elongation a material can undergo deformation by shearing or twisting motions. The ratio of the shear stress, f , to the shear strain, s , describes the shear modulus, G as

$$G = f / s \quad (2.22)$$

Likewise, a material can also undergo deformation through compression (or dilation).

The associated modulus is the bulk modulus, B:

$$B = -V \left(\frac{\partial P}{\partial V} \right)_T \quad (2.23)$$

where P is the pressure and V is volume. The inverse of the bulk modulus is the thermodynamically defined isothermal compressibility, β :

$$\beta = 1/B \quad (2.24)$$

which is true for materials where there is no time dependent response, since bulk compression does not involve long range conformational changes.

In general, a modulus is a measure of materials stiffness or hardness, conversely compliance is a measure of its softness and is defined as the inverse of a modulus for regions far from transitions. At this stage it is useful to provide some numerical values of E, for polystyrene representing a typical glassy polymer at room temperature. For polystyrene, $E = 3 \times 10^{10}$ dyne/cm² (3×10^9 Pa) where it is about 40 times softer than copper having $E = 1.2 \times 10^{12}$ dyne/cm² (1.2×10^{11} Pa). As another contrast, soft rubber has a modulus $E = 2 \times 10^7$ dyne/cm² (2×10^6 Pa) which is ~1000 times softer than glassy polystyrene.⁹³

2.3.2 Regions of Viscoelastic Behavior

High molecular weight polymers do not achieve totally crystalline structures and many polymers do not even exhibit semicrystalline behavior. As such, most polymers form glasses at low temperatures and viscous liquids at higher temperatures. The transition where the glassy state turns to a viscous state is known as the glass to rubber transition. The five main regions of viscoelastic behavior⁹³⁻⁹⁶ for linear amorphous

polymers (Figure 2.7) will be discussed to better understand the temperature dependence of polymer properties.

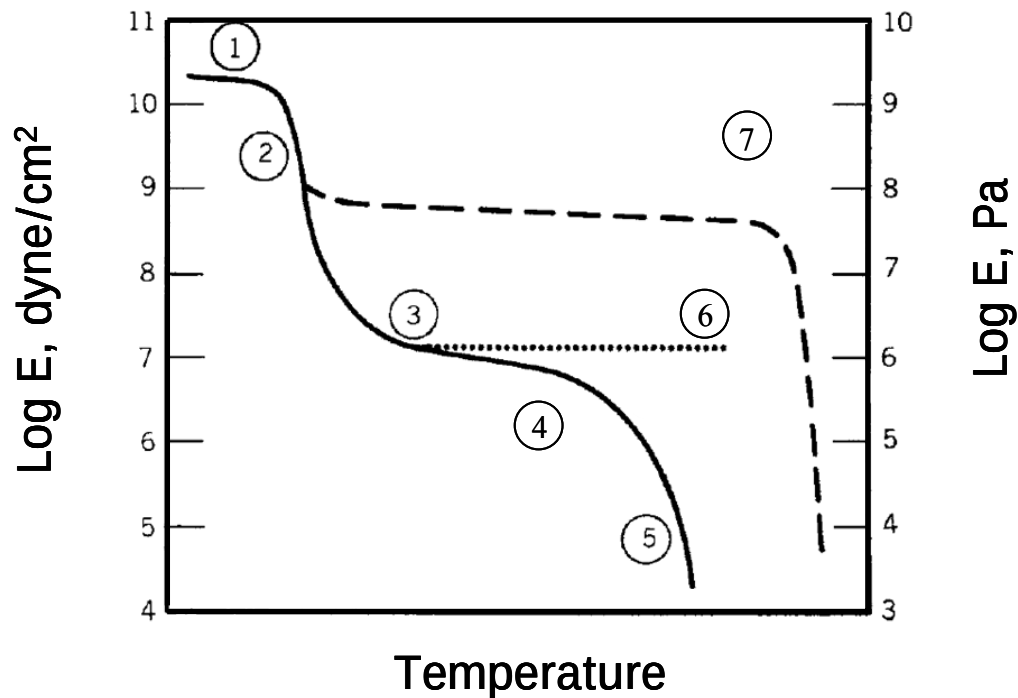


Figure 2.7 The regions of viscoelastic behavior for linear amorphous polymer (solid line) along with the effects of crystallinity (dashed line) and cross-linking (dotted line). The numbers on the graph correspond to (1) the glassy state, (2) the glass to rubber transition, (3) the rubbery state, (4) the end of the rubbery state, and (5) viscous flow, for an amorphous polymer. For a crystalline polymer melting starts at (7). For permanently crosslinked materials (3) to (6) there is no viscous flow regime.

In Region 1 of Figure 2.7 the polymer is in the glassy state and is hard and brittle. Young's modulus for glassy polymers below the glass transition temperature is constant and in the order of 3×10^{10} dyne/cm² (3×10^9 Pa). In the glassy state molecular motion is largely restricted to vibrations and short-range rotational motion. Region 2 of Figure 2.7

is the glass transition region. Typically the modulus decreases by ~ 3 orders of magnitude over a 20 to 30 °C temperature range. The glass transition temperature, T_g , is often taken as the point where the modulus starts to drop, or where $E \cong 10^9$ Pa. The enthalpic and dynamic definitions will be established for glass transition behavior later in this chapter. Qualitatively, the glass transition region can be perceived as the onset of long range cooperative molecular motion. While only 1 to 4 chain atoms are involved in typical motion below T_g , 10 to 50 chain atoms are involved in cooperative motion around T_g . The number of atoms involved in the cooperative motion can be deduced from the dependence of T_g on the molecular weight between cross-links, M_c .⁹⁷⁻¹⁰⁰ T_g will become relatively independent of M_c in a plot of T_g versus M_c . Between Region 3 and Region 4 one observes a rubbery plateau with Young's moduli on the order of 2×10^7 dyne/cm² (2×10^6 Pa). In the rubbery plateau region polymers exhibit long-range rubber elasticity because of entanglements. For the case of a linear polymer, the modulus will decrease slowly and the length of the plateau will be a strong function of the polymers molar mass. Higher molar mass samples yield longer plateaus. At the end of the rubbery plateau, viscous flow is observed (region between 4 and 5). For covalently cross-linked polymer systems, viscous flow is not observed and the dotted line in Figure 2.7 is followed. Enhanced rubber elasticity is generally observed in permanently cross-linked systems. The elastic energy for dotted line follows the equation $E=3nRT$, where n is the number of active chain segments in the network and RT is the gas constant times temperature. The quick coordinated molecular motion in this region is consistent with reptation and diffusion principles. If a polymer is semicrystalline, the dashed line in Figure 2.7 is followed. The modulus of the plateau is a function of the degree of crystallinity. The

crystalline plateau extends until the melting point of the polymer. In this region the polymer exhibits both rubber elasticity and viscous flow. The behavior is dependent on the timescale of the experiment. In addition, it must be noted that the region between 4 and 5 in Figure 2.7 is not observed for cross-linked systems. In this case, the modulus for the plateau that starts at 3 remains constant until the decomposition temperature is reached. The increased energy provided to the chains allows them to reptate out the entanglements and flow as individual molecules.⁹³

2.3.3 Theories for Explaining Glass Transition

2.3.3.1 Free-Volume Theory

Eyring *et al.* first described that the molecular motion in the bulk state depends on the presence of the holes and places where there are vacancies and voids.¹⁰¹ When a molecule moves into a hole, the hole exchanges places with the molecule. A similar model can be considered for polymer chains. For a polymer segment to move from its previous location to a neighboring site a void volume must exist. The molecular motion can not proceed without the presence of holes. An important theory that involves the quantitative development of the exact free volume in polymeric system was introduced by Fox and Flory.¹⁰² They studied the glass transition and the free volume of polystyrene as a function of molar mass and relaxation time. For infinite molar mass the specific free volume v_f , can be expressed at a temperature, T , above T_g as

$$v_f = K + (\alpha_R - \alpha_G)T \quad (2.25)$$

where K was related to the free volume at 0 K, and α_R and α_G represent the volume expansion coefficients in the rubbery and glassy states, respectively. Fox and Flory found that below T_g the same specific volume-temperature relationships were valid for all

the polystyrene samples. Simha and Boyer then described the specific free volume at T_g as¹⁰³

$$v_f = v - (v_{0,R} + \alpha_G T_g) \quad (2.26)$$

and when the Equation 2.27 is substituted into Equation 2.26 , it reduces to the Equation 2.28 which is described by the quantity K_1 , an experimental parameter found to be constant for a series of polymers.¹⁰³

$$v = v_{0,R} + \alpha_R T \quad (2.27)$$

$$(\alpha_R - \alpha_G) T_g = K_1 = 0.113 \quad (2.28)$$

In the Equations 2.26 through 2.28 above, v is the specific volume, and $v_{0,G}$ and $v_{0,R}$ are the volumes extrapolated to 0 K using the α_R and α_G thermal expansion coefficients for rubbery and glassy state, respectively (Figure 2.8). Quantity K_1 leads directly to the finding that free volume at the glass transition temperature is a constant, 11.3%, for a several number of polymers studied.¹⁰³

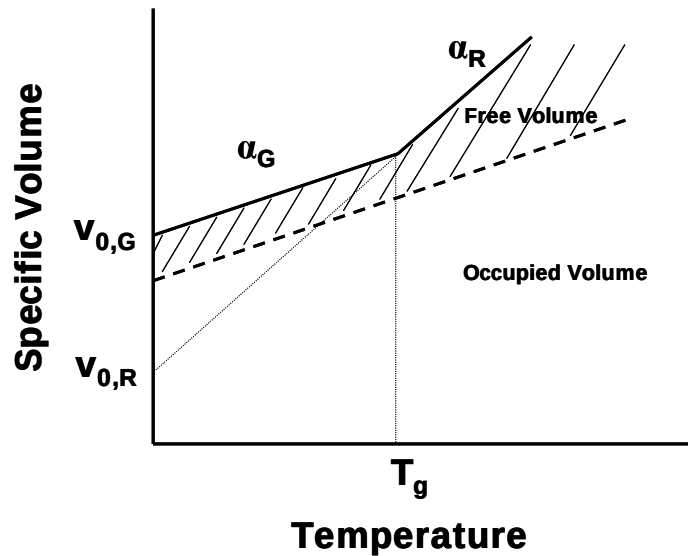


Figure 2.8. Plot of specific volume versus temperature to illustrate the concept of free volume.

The flow, which involves a form of molecular motion, also requires an amount of free volume, therefore an analytical relationship between polymer melt viscosity and free volume plays an important role in understanding the free volume theory of glass transition behavior. The viscosity, η , occupied volume, V_o , and free volume, V_f , can be related through the Doolittle equation:¹⁰⁴

$$\eta = A \exp(BV_o / V_f) \quad (2.29)$$

where A and B are constants. The logarithm of Equation 2.29 is expressed as

$$\ln \eta = \ln A + BV_o / V_f \quad (2.30)$$

Once the fractional free volume, f , is defined, as $V_f / (V_o + V_f) \approx V_f / V_o$ ($V_o \gg V_f$), then Equation 2.30 can be written as

$$\ln \eta = \ln A + B / f \quad (2.31)$$

At T_g the fractional free volume is f_g , and f 's increase above T_g is approximately proportional to the difference between the thermal expansion coefficient of the rubbery and glassy states ($\alpha_f = \alpha_R - \alpha_G$). Then the fractional free volume at any temperature T above T_g is given by Equation 2.32:

$$f_T = f_g + \alpha_f (T - T_g) \quad (2.32)$$

By substituting Equation 2.32 into Equation 2.31, the viscosity at any temperature T , η_T , can be related to the viscosity at T_g , η_g , through Equation 2.33:

$$\ln(\eta_T / \eta_{T_g}) = \ln a_T = B(1 / f_T - 1 / f_g) \quad (2.33)$$

In Equation 2.33 a_T is called the shift factor and B is a constant. Once Equation 2.32 is substituted into Equation 2.33, one obtains various forms of Equation 2.34 through appropriate rearrangements:

$$\begin{aligned}
\ln a_T &= B \left[\frac{1}{f_g + \alpha_f (T - T_g)} - \frac{1}{f_g} \right] \\
&= \frac{B}{f_g} \left[\frac{f_g - f_g - \alpha_f (T - T_g)}{f_g + \alpha_f (T - T_g)} \right] \\
&= -\frac{B}{f_g} \left[\frac{T - T_g}{\frac{f_g}{\alpha_f} + T - T_g} \right] \\
\log a_T &= -\frac{B}{2.3 f_g} \left[\frac{T - T_g}{\frac{f_g}{\alpha_f} + T - T_g} \right] \tag{2.34}
\end{aligned}$$

Equation 2.34 is a form of the Williams-Landell-Ferry equation (WLF). The constant B is very close to unity. The WLF equation in terms of universal parameters can be written as Equation 2.35¹⁰⁵

$$\log a_T = \frac{-17.4(T - T_g)}{51.6 + T - T_g} \tag{2.35}$$

The constants 17.4 and 51.6 in Equation 2.35 are nearly universal. The value of the first constant corresponds to $1 / (2.3 f_g) = 17.4$ and $f_g = 0.025$. This value is constant for most polymers. The second universal constant 51.6 means $f_g/\alpha_f = 51.6$. With $f_g = 0.025$ $\alpha_f \sim 4.8 \times 10^{-4}$.

2.3.3.2 The Thermodynamic Theory

Equilibrium phase transitions can be treated utilizing a thermodynamic approach. The chemical potentials two phases at the transition temperature are equal ($\mu_1 = \mu_2$ and $d\mu_1 = d\mu_2$). However, the molar volumes and entropies of the two phases are not equal ($\bar{S}_1 \neq \bar{S}_2$) and $\bar{V}_1 \neq \bar{V}_2$). Ehrenfest^{106,107} describes this type of transition as a first order phase transition since there are discontinuities in the first partial derivatives of the molar Gibbs free energy (chemical potential) at the transition point ($d\mu = -\bar{S}dT + \bar{V}dP$, $\bar{S} = -(\partial\mu/\partial T)_P$ and $\bar{V} = (\partial\mu/\partial P)_T$). This definition can be generalized to higher order transitions. For example second partial derivatives of the chemical potential show discontinuities at the transition point for a second order phase transition. In particular, for a second order phase transition $(\partial\bar{S}/\partial T)_P = \bar{C}_p/T$ and $(\partial\bar{V}/\partial T)_P = \alpha\bar{V}$, therefore a discontinuity for the heat capacity and the thermal expansion coefficient will be observed as in Figure 2.9.

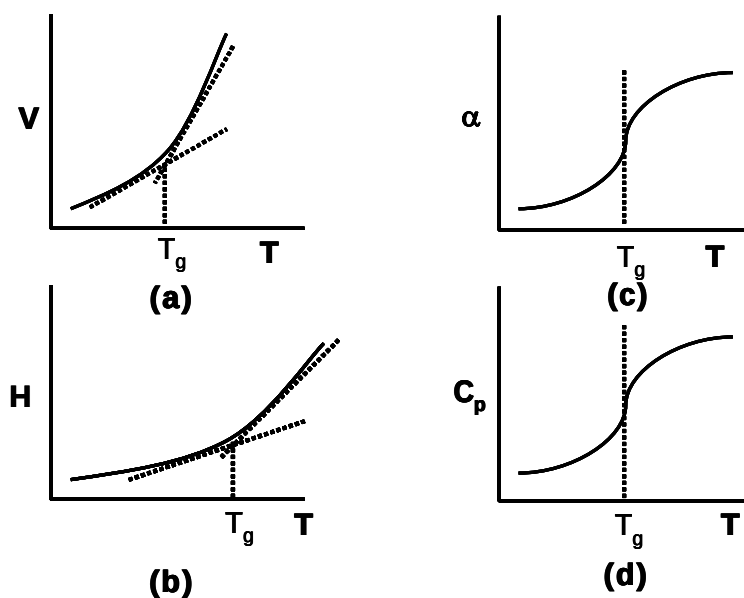


Figure 2.9. Schematic representation of variations in (a) volume (V), (b) enthalpy (H), (c) thermal expansion coefficient (α), and (d) isobaric heat capacity (C_p) as a function of temperature for a second order phase transition described by Ehrenfest.¹⁰⁷

Since these discontinuities occur at T_g , the glass to rubber transition is often referred to as a second order transition. However, it should be kept in mind that the observed T_g is a rate dependent phenomenon. The kinetic nature of the observed T_g means that the glass transition is a pseudo-second order thermodynamic transition. When a polymer is cooled from the rubbery or liquid state, volume contractions occur, indicating conformational rearrangements. At temperatures well above T_g , thermal equilibrium exists during a cooling experiment. However, as the temperature is lowered further, a point is reached where the conformational rearrangements occur at rates that are comparable to the rate of cooling. Below this temperature relaxations and conformational rearrangements will not be observed on the time scale of the experiment and discontinuities of ΔC_p and $\Delta \alpha$ are

observed. These, discontinuities arise from rate dependent phenomena. In order to observe a true thermodynamic second order phase transition infinitesimal cooling rates are required.

Kauzmann stated that once the entropies of simple glass forming materials are extrapolated to low temperatures, they will reach zero long before the absolute zero ($T = 0$) is reached.¹⁰⁸ Such results require negative entropies and are clearly a violation of the Third Law of Thermodynamics. Kauzmann solved this paradox by suggesting that the glassy state is not an equilibrium state and that the glasses could undergo crystallization before $T = 0$ is achieved. However, many polymeric systems never undergo crystallization. Subsequently, Gibbs and DiMarzio suggested that the entropy at equilibrium approaches zero at a finite temperature, T_2 and the material does not undergo further entropic changes between T_2 and absolute zero.¹⁰⁹⁻¹¹¹ This explanation is illustrated in Figure 2.10. The T_2 temperature of Gibbs and DiMarzio is a second order transition temperature. Gibbs and DiMarzio assume that for each chain segment there is one definite lowest energy conformation. Therefore, as the chain is cooled from high to low temperatures fewer high energy conformations will be available until T_2 is reached where only the lowest energy state is allowed. In reality, there are many states available for reorientation at high temperatures where the reorientation might take some time. As the polymer is cooled the molecular motion will slow down, and longer times are required to achieve any particular conformation. To guarantee all the chains reach their lowest energy conformation, the experiment needs to be conducted at infinitesimal cooling rates.

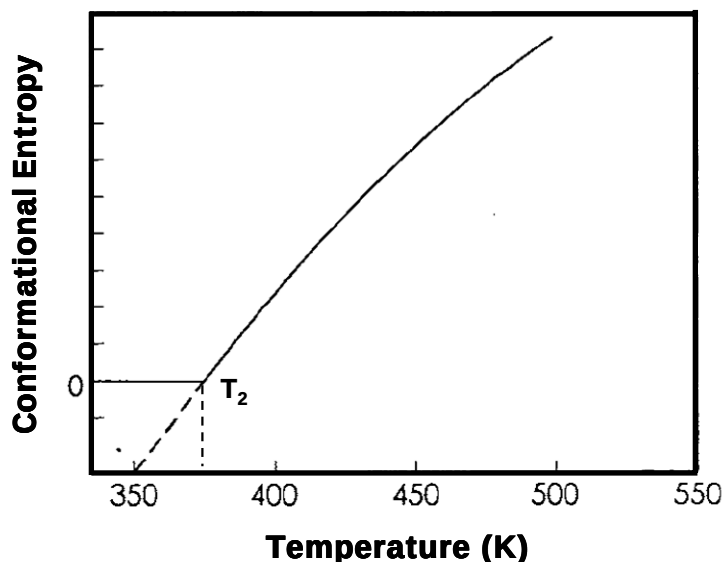


Figure 2.10 Schematic plot of conformational entropy versus temperature of a glass forming substance. The temperature where the entropy reaches zero is the T_2 of Gibbs and DiMarzio.¹⁰⁹ The dotted line is the original extrapolation of Kauzmann.¹⁰⁸

In this treatment, the temperature dependence of the entropy around T_g behaves as a second order phase transition.¹⁰⁹⁻¹¹¹ In a later study by Gibbs and Adam, both equilibrium and rate effects were considered.¹¹² Most publications assume that the glass transition is a kinetically controlled process.¹¹³⁻¹¹⁹ This process is time-dependent since it is related to the time required for molecules to arrange themselves in the new phase.¹²⁰⁻¹²² If volume (or heat capacity) is plotted against temperature for a polymer, heating and cooling rate dependent variations are observed.^{113-115,123,124} When the glass transition is measured via cooling a polymer from the melt, the measured T_g decreases with a decreasing cooling rate as shown in Figure 2.11. Glass₁ corresponds to a fast cooling rate resulting in a higher apparent T_g compared to glass₂ measured at a slower cooling rate. Rate dependent behavior arises from finite relaxation times for molecules.

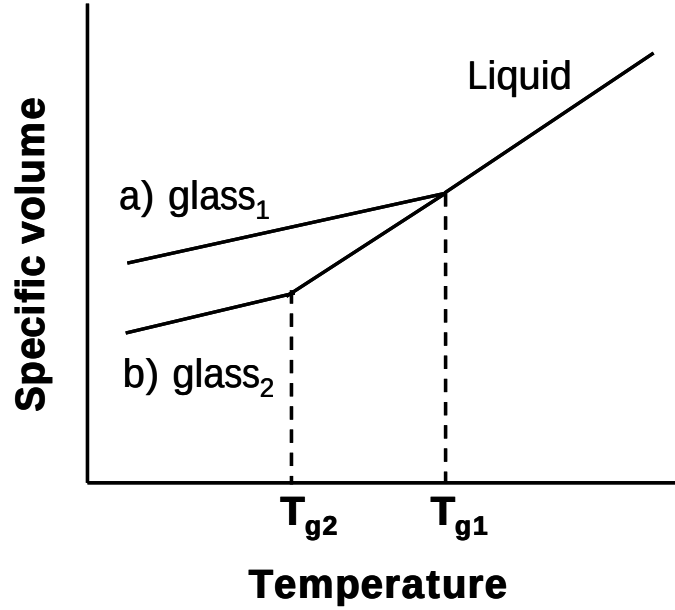


Figure 2.11. Schematic representation of different glass transition temperatures observed for different cooling rates, (a) fast cooling rate (T_{g1}) and (b) a slower cooling rate (T_{g2}).

2.3.4 Factors Affecting the Glass Transition Temperature

2.3.4.1 Effect of Molecular Weight on T_g

Studies showing an increase in T_g with increasing molar mass were first reported by Ueberreiter *et al.*¹²⁵ The theoretical analyses of Fox and Flory suggested that the relationship between T_g and the number average molar mass M_n , could be written as¹⁰²

$$T_g = T_{g\infty} - \frac{K}{(\alpha_R - \alpha_G)M} \quad (2.36)$$

where K is a material dependent constant and $T_{g\infty}$ corresponds to the T_g as $M \rightarrow \infty$. Increasing the number of connected monomers in the system will decrease the free volume since the fraction of end groups decreases. At very high molar masses the glass transition temperature is essentially independent of molar mass. In contrast, T_g is strongly dependent upon molar mass when M_n is small.

2.3.4.2 Effect of Plasticizers

Free volume theory finds a suitable application in predicting the effects of diluents on T_g . As one might expect the presence of plasticizers decreases the glass transition temperature. Equation 2.37 describes the total fractional free volume as a function of temperature.

$$f_T = 0.025 + \alpha_f (T - T_g) \quad (2.37)$$

Equation 2.37 is valid for both the polymer and the diluent. When diluent is added to polymer the fractional free volume can be written as

$$f_T = 0.025 + \alpha_{fp} (T - T_{gp}) V_p + \alpha_{fd} (T - T_{gd}) V_d \quad (2.38)$$

The subscripts p and d in Equation 2.38 represent the polymer and diluent, respectively, and V_p and V_d are the volume fraction, and T_{gp} and T_{gd} are glass transition temperatures for the polymer and diluent, respectively. At T_g for polymer-diluent system $T = T_g$ and $f_T = 0.025$. Rearranging, Equation 2.38 yields Equation 2.39 that describes the behavior of T_g as a function of plasticizer content.¹²⁶

$$T_g = \frac{\alpha_{fp} T_{gp} V_p + \alpha_{fd} (1 - V_p) T_{gd}}{\alpha_{fp} V_p + \alpha_{fd} (1 - V_p)} \quad (2.39)$$

2.3.4.3 Effects of Chain Stiffness, Chemical Structure, and Cross-linking

The characteristic ratio, C_∞ , is an intrinsic measure of polymer chain flexibility, where higher values of C_∞ indicate higher degree of stiffness. T_g of flexible chains will be lower since the activation energy for conformational changes is smaller and these conformational changes can occur at lower temperatures. T_g values for a polymer can be increased by incorporating monomers (as copolymers) that stiffen the polymer chain. A phenyl ring inserted in a polymer backbone is particularly effective in restraining rotation around the polymer backbone thereby increasing T_g .

Another important factor that influences T_g is steric effects. When a macromolecule is symmetrical (i.e. $(CH_2-CH_2)_n$) rotation around the backbone is less hindered than for asymmetrical polymer chains (i.e. $(CH_2-CHX)_n$). Consequently, symmetrical repeating units generally give polymers with lower T_g whereas, polymers possessing bulky pendant groups have hindered rotation around the backbone leading to higher T_g . This effect can be enhanced by increasing the size of the pendant group or introducing polar groups into the polymer structure. On the other hand, *cis*- and *trans*- isomerization and tacticity variations alter chain flexibility and also affect T_g . For example syndiotactic poly(methyl methacrylate) has a $T_g = 115\text{ }^\circ\text{C}$, whereas the isotactic material has $T_g = 45\text{ }^\circ\text{C}$. The energy difference between the two predominant rotational isomers is greater for the syndiotactic configuration than for isotactic configuration. Tacticity effects are quite general for asymmetrical polymer chains and has been discussed by MacKnight *et al.* in detail.¹²⁷

The glass transition temperatures of polymeric materials are highly dependent on the level of crosslinking. In crosslinked systems the free volume is lower, also crosslinking

decreases the conformational entropy of the system. Therefore, qualitatively it can be concluded that crosslinking increases T_g . The cross-linking effects can be taken into account by the following relation,¹²⁸

$$T_g = T_{g\infty} - K / M + K_x p \quad (2.40)$$

where $T_{g\infty}$ is the T_g at infinite molar mass, M is the number average molar mass of the polymer and K_x is a constant and p is the number of cross-links per gram.

2.3.4.4 T_g of Multicomponent Systems

Since the glass transition temperature is an important characteristic for a polymer system, it is useful to predict the T_g of compatible multicomponent systems. It is known that the composition dependence of glass the transition temperature of miscible binary polymer blends can be described by the Gordon-Taylor expression:¹²⁹

$$T_g = \frac{W_1 T_{g,1} + K W_2 T_{g,2}}{W_1 + K W_2} \quad (2.41)$$

In Equation 2.41, T_g is the glass transition temperature of the blend, W_1 and W_2 are the weight fractions of the binary polymer components, and $T_{g,1}$ and $T_{g,2}$ are glass transition temperatures of the two polymers, K is a material specific parameter:

$$K = \frac{\rho_1}{\rho_2} \frac{\Delta\alpha_2}{\Delta\alpha_1} \quad (2.42)$$

where ρ_1 and ρ_2 are the densities of the components 1 and 2, respectively, and $\Delta\alpha_1 = \Delta\alpha_{R,1} - \Delta\alpha_{G,1}$ and $\Delta\alpha_2 = \Delta\alpha_{R,2} - \Delta\alpha_{G,2}$ are the changes in thermal expansion coefficients between the rubbery and glassy states of the components 1 and 2, respectively.

DiMarzio approaches the estimation of T_g for binary polymer blends utilizing the flexible bond fraction, B .¹³⁰⁻¹³² The description has the form of

$$T_g = B_1 T_{g,1} + B_2 T_{g,2} \quad (2.43)$$

where B_1 and B_2 are the fraction of the flexible bonds for the two components. For binary polymer blends, B_i is given by the following expression

$$B_i = \frac{x_i n_i \gamma_i}{\sum_1^2 x_i n_i \gamma_i} \quad (2.44)$$

where γ_i is the number of flexible bonds per monomer unit, x_i is the number of monomer units per molecule, and n_i is the number of molecules of the two components. The weight fraction of the binary polymer system is defined as:

$$W_i = \frac{w_i x_i n_i}{\sum_1^2 w_i x_i n_i} \quad (2.45)$$

Combining the weight fraction yields

$$W_1 = \frac{w_1 B_1 \gamma_2}{w_1 B_1 \gamma_2 + w_2 B_2 \gamma_1} \text{ and } W_2 = \frac{w_2 B_2 \gamma_1}{w_1 B_1 \gamma_2 + w_2 B_2 \gamma_1} \quad (2.46)$$

where w_i is the weight of the monomer unit. Finally Equation 2.43 can be expressed as

$$T_g = B_1 \frac{(w_1 / \gamma_1) W_1 T_{g,1} + (w_2 / \gamma_2) W_2 T_{g,2}}{(w_1 / \gamma_1) W_1 + (w_2 / \gamma_2) W_2} \quad (2.47)$$

Equation 2.47 has the form of the Gordon-Taylor expression:

$$T_g = \frac{W_1 T_{g,1} + K W_2 T_{g,2}}{W_1 + K W_2} \quad (2.48)$$

However, here the K parameter is given by the ratio $\gamma_2 w_1 / \gamma_1 w_2$ rather than by $\alpha_1 \Delta \rho_2 / \alpha_2 \Delta \rho_1$.

Considering the case of similar densities $1 \approx \rho_1 / \rho_2$ and remembering that $(\alpha_R - \alpha_G) \cdot T_g = 0.113$ a constant from Simha-Boyer¹⁰³ rule results in $K \approx T_{g1} / T_{g2}$. Introducing K into Equation 2.41 results the well known Fox equation¹³³

$$1/T_g = W_1/T_{g1} + W_2/T_{g2} \quad (2.49)$$

Hence, T_g of a blend can be easily estimated according to the Fox equation. It should be noted that depending on the nature of the thermodynamic interactions between the components, the glass transition for a blend system could exhibit positive or negative deviation from the Fox equation.

2.3.5 The Glass Transition in Thin Films

The glass transition temperature of thin films is affected by entropic factors such as confinement and interfacial interactions. In many materials atoms or molecules on the surface can be more mobile than those particles buried below the surface. Likewise, the chain segments of a polymer near a free surface, or in the vicinity of air/polymer interface are more mobile due to the greater fractional free volume at the air/polymer interface, hence T_g at the air surface is smaller than its bulk value.¹³⁴⁻¹⁵⁶ In a very recent article, Fakhraai and Forest quantitatively reported that a polymer glass surface can be more mobile than the interior.¹⁵⁰ They found that a several nanometer thick liquid-like layer exists at the surface of polystyrene.¹⁵⁰ They measured the surface mobility by locating nanosize gold spheres (~20 nm diameter) on well defined flat polystyrene (PS) surfaces well below the glass transition temperature. Annealing the samples at 378 K (slightly above the bulk T_g for 641 kg·mol⁻¹ PS) allows the gold nanoparticles to sink a few nanometers into the surface. Removing the gold particles leaves nanosized hemispherical

holes. Upon annealing the surfaces below T_g the filling of the holes were monitored via AFM. The process of recovery of holes back to a flat surface below T_g is much faster than comparable relaxation processes in bulk polystyrene suggesting that the surface of the polymer is indeed in rubbery state at 20 K below the bulk T_g . Previous studies have shown similar deviations from bulk T_g for films less than ~ 40 nm thickness.^{146,157,158} The work of Fakhraai and Forest also indicates that polymer segments in long chains can extend 20 nm or more into the polymer. The range of enhanced surface mobility is at least several nanometers, a value greater than the characteristic length scale of a repeating unit (~ 1 nm). Therefore, the molecular motion is highly cooperative. Since the packing in a glass is tight, a large number of neighbors must collectively adjust their positions in order for a polymer segment to move.

Most studies of surface T_g and cooperative segmental dynamics were conducted on polystyrene samples on silicon substrates^{144-146,154,155} or freely standing films.¹⁵⁹⁻¹⁶⁴ Since macromolecular dynamics are cooperative T_g depression at the surface can extend below the surface. However, in the vicinity of a rigid, impenetrable substrate, polymer chain/substrate interactions are stronger and can lead to restricted chain mobility.^{136,137,159} In this respect the relaxation times associated with chains in the vicinity of the surface, τ_s , in the interior film, τ_f , and in the vicinity of substrate, τ_{sub} , will generally have the relationship $\tau_s > \tau_b > \tau_{sub}$. This suggests that the glass transition is lower at a free surface (air) than at the interface between a polymer and a strongly interacting substrate. Therefore, it can be argued that the depression of T_g observed for polystyrene films on solid substrates could actually be an average of both the surface depression near the air/polymer interface and the slightly higher T_g near the polymer/substrate interface.

However, it is clear that the surface depression must be more dominant than polymer/substrate interactions because the observed surface T_g values are much smaller than the bulk T_g values. Experiments conducted on freely standing polystyrene films are consistent with the effect of two high mobility regions resulting a more significant decrease in T_g compared to the polystyrene samples supported on solid substrates.¹⁵⁹⁻¹⁶¹

Keddie *et al.* quantified the thickness dependence of T_g for polystyrene films supported on solid substrates via an empirical equation:^{145,146}

$$T_g(h) = T_g(\text{bulk}) \left[1 - \left(\frac{A}{h} \right)^\delta \right] \quad (2.50)$$

where $T_g(h)$ is the glass transition temperature of a film with thickness, h for $h < 40$ nm. In this equation, there are two parameters. A , has a unit of length and δ is an empirical indication of the degree of T_g depression with decreasing film thickness. It is clear that larger values of δ reflect a weaker thickness dependence for surface T_g . For the case of polystyrene samples on silicon substrates with $A = 3.2$ nm and $\delta = 1.8$. Studies for PS films on silicon by Torkelson *et al.*, over a broader molar mass range, 5 to 3 000 kg·mol⁻¹, confirmed Equation 2.50 and found no significant molar mass dependence on the film thickness dependence of the surface T_g depression.¹⁵⁸ Conversely, detailed studies of Dutcher *et al.* and Forrest *et al.* on freely standing polystyrene films revealed molar mass does affect surface T_g in some molar mass ranges.¹⁵⁹⁻¹⁶⁴ For low molar mass samples ($M_n < 370$ kg·mol⁻¹), the $T_g(h)$ data were well described by Equation 2.50 with no measurable molar mass dependence. For high molar mass samples ($M_n > 370$ kg·mol⁻¹) T_g values decreased linearly with decreasing film thickness below a threshold film thickness, h_0 :

$$T_g = \begin{cases} T_g^{\text{bulk}} + \alpha(h - h_0), & h < h_0 \\ T_g^{\text{bulk}}, & h > h_0 \end{cases} \quad (2.51)$$

where α characterizes the linear decrease in T_g with decreasing film thickness. The surface T_g behavior was found to depend on the molar mass where α increased with decreasing film thickness. In a recent study, Dutcher *et al.* reported the molar mass dependence of T_g for freely standing poly(methyl methacrylate) PMMA films.¹⁵⁶ For PMMA films T_g decreases linearly with decreasing h , qualitatively agreeing with the results for freely standing high molar mass PS films. However, the degree of T_g depression is much smaller (i.e. by a factor of three) for the high molar mass freely standing PMMA film than for freely standing PS films of comparable thickness and molar mass. These observed differences between freely standing PS and PMMA films suggest that chemical structure also contributes to the magnitude of the surface T_g reduction. This is consistent with two recent studies by Torkelson's group on supported thin films. First, they showed the strength of the thickness dependence of T_g is strongly influenced by the repeating unit structure with side groups having particularly large effects on the overall T_g reduction^{157,158} (i.e. larger reduction of surface T_g were observed for poly(4-tert-butylstyrene (PtBS) compared to a PS samples having comparable thicknesses). Second, the investigation of PS and styrene/methyl methacrylate (S/MMA) random copolymers revealed that as styrene content decreased from 100 mol% to 22 mol%, T_g actually increased as film thickness decreased.¹⁴⁷ In addition, it has been shown that increasing the alkyl chain length of poly(n-alkyl methacrylate) samples increased the surface T_g because of increases the polymer chain stiffness.¹⁵³

Differences in the surface T_g behavior for polymer thin films supported on substrates are typically attributed to the specific interactions between the polymer and the substrate. The presence of attractive substrate interaction reduces the mobility of chain segments and can overwhelm fractional free volume effects at free interfaces. Both poly(methyl methacrylate) PMMA, and poly(vinyl pyridine) (PVP) thin film systems supported on silica substrates exhibit T_g values that are greater than the corresponding bulk values as film thickness decreases.^{146,165} This observation is due to the fact that the polar interactions of the PMMA and PVP chain segments with the oxide layer of the substrate are stronger since PMMA and PVP can hydrogen bond with hydroxyl groups which are present on a silica surface. In contrast, PMMA films supported on gold show T_g decreases with decreasing thickness since there are no hydroxyl groups on the gold surface and no other strongly attractive polymer/substrate interactions.¹⁴⁷ Other studies have also shown that T_g reductions due to the higher fractional free volume at the surfaces can be altered by controlling polymer/substrate interactions.^{147,152,166-168} In addition grafting of chain ends or side groups to the substrate may increase the surface T_g .^{169,170}

As one might expect nanoconfinement also influences the thermal expansion behavior of thin polymer films.^{145,146,171-175} Keddie *et al.* showed an exponential decay of the glassy thermal expansion coefficient, α_g as a function of film thickness for polystyrene films supported on hydrogen terminated silicon substrates.¹⁴⁵ Below a critical thickness ($h < 40$ nm) α_g values increase as the film thickness decreased, whereas, the α values corresponding to the rubbery state, α_R , did not show any thickness dependence having values $\sim 7.2 \times 10^{-4} \text{ K}^{-1}$ which are consistent with the bulk values of $5.5\text{-}6.5 \times 10^{-4} \text{ K}^{-1}$.^{176,177}

The increased α_G values could be explained by the contribution of the mobile liquid-like layer, which will be proportionally greater for thinner films. For thick films, α_G values reach a constant value of $\sim 2.0 \times 10^{-4} \text{ K}^{-1}$ which is similar to reported bulk values of 1.9 to $2.2 \times 10^{-4} \text{ K}^{-1}$.^{176,177} However, as the film gets thinner, the α_G values increase towards the α_R value. Keddie *et al.* also highlighted that the thermal expansion behavior is highly sensitive to thermal history as one might expect for any glassy system. Furthermore, it has been clearly shown that polymer thin film formation can lead to nonequilibrium conformations of polymer chains with residual stresses in confined geometries.¹⁷⁸⁻¹⁸² Therefore, different values for the thermal expansion coefficients for thin films in the glassy state below a critical thickness ($< 40 \text{ nm}$) may be associated with residual stresses from the film preparation where the relaxation of these stresses may influence measured T_g and α values.¹⁸³⁻¹⁸⁵

2.3.6 Methods for Studying the Glass Transition Temperature

The classical method for determining the T_g is dilatometry where specific volume is determined as a function of temperature. The temperature where the slope changes, is taken as T_g (Figure 2.11). The slope is related to the thermal expansion coefficient, α and α shows a discontinuity at T_g . Dilatometry is a quick and inexpensive method for determining T_g values of polymers.¹⁸⁶ The only disadvantage is that it requires moderate amounts of samples. In addition to dilatometry, dynamic thermal analysis (DTA) and a newer method differential scanning calorimetry (DSC) have been extensively employed to determine T_g . Both methods show changes in the heat capacity and yield peaks at temperatures where endothermic and exothermic transitions occur. The DSC method

utilizes a system that provides energy at varying rates to the sample and the reference to maintain a constant temperature for sample and reference. The DSC output plots heat flow [power per unit mass, (W/g) provided to the system] against temperature. By this improved method, the areas under the peaks can be quantitatively related to the enthalpy changes.¹⁸⁷ In addition, mechanical methods such as thermal mechanical analysis (TMA), and dynamic mechanical analysis (DMA) also provide direct determinations of the transition temperature since the glass to rubber transition arise is accompanied by a softening of the material. A TMA instrument measures the deformation of a sample under low static loads as a function of temperature and measures change in modulus of the polymer before and after the glass transition. For DMA, the loss modulus and compliance exhibit maxima in the glass transition region.

Currently, DSC instruments are capable of measuring samples as small as a few milligrams. The methods used to identify surface glass transition temperatures differ from the techniques used for bulk materials because of the small sample sizes (sub microgram). As a consequence, thin films techniques must possess greater sensitivity than bulk systems. Hellman designed the first nanocalorimeter on a chip, for the study of surface T_g .^{188,189} The chip-based calorimeter allows very small mass (i.e. spincoated polymer film) samples to be investigated. However, this technique as applied to polymers still has many experimental challenges, such as control of scanning rate linearity, calibration of baseline heat capacity, accuracy of the temperatures and heat flow. Therefore, surface sensitive techniques such as ellipsometry, fluorescence, brillouin scattering, AFM, and X-ray reflectivity, has been more commonly utilized to measure surface T_g .^{145,146,157,163,190-196} In our experiments we measure surface T_g for thin

polymer films by ellipsometry. The discontinuity in the thermal expansion coefficient before and after T_g is detected as the films are heated at a constant rate. The details of thermal expansion coefficient and surface T_g detection for thin polymer films by ellipsometry measurements can be found in Chapter 3 (Section 3.4.1).

2.4 Experimental Techniques

The important experimental techniques and filler materials that were extensively used for the preparation and characterization of polymer thin films for the projects in this dissertation will be introduced and reviewed in this section.

2.4.1 Langmuir-Blodgett (LB) Technique

The Langmuir-Blodgett (LB) technique was first introduced by Irving Langmuir.¹⁹⁷ Subsequent improvement came from by Katherine Blodgett.^{198,199} The LB-technique is used to deposit a monolayer or multilayer of amphiphilic molecules onto a solid substrate from the surface of a liquid.¹⁹⁷⁻¹⁹⁹ Monolayers of amphiphilic molecules which are transferred onto solid substrates are known as Langmuir-Blodgett (LB) films, on the other hand amphiphilic molecules on liquid surfaces are called Langmuir films. The term subphase is used to refer to a liquid surface on which a Langmuir monolayer is spread. Langmuir films can be formed as monomolecular or multilayer films depending on the surface pressure of the film.

2.4.1.1 Monolayer Systems and Subphase Materials

Typically water is used as a subphase for Langmuir film studies. However, other liquids such as mercury, glycerol, etc. have been utilized for Langmuir film studies.^{200,201} Amphiphilic monolayer forming materials are usually utilized for LB deposition. The

amphiphilic materials have a polar head group and a hydrophobic tail group. In these types of materials the polar head groups are the part of the amphiphiles that attach to the subphase. On the other hand, the hydrophobic tail groups inhibit dissolution of the molecule into the subphase and resulting in a layer at the air/subphase interface.²⁰² The solubility of amphiphilic molecules will decrease as the hydrophobicity of the tails increases. When amphiphilic molecules have sufficiently long enough hydrophobic tails they may form two-dimensional (2D) insoluble films on the subphase. It is known that various classes of small molecules such as long-chain fatty acids, alcohols, esters, and phospholipids can form stable Langmuir films at the air/water interface.²⁰³ All of these molecules possess a polar head group and at least one long hydrocarbon tail. Long-chain carboxylic acids such as stearic acid were widely used in the early studies of Langmuir films.^{197,198,201,202,204} The syntheses of amphiphilics with multiple polar head groups and varying numbers and lengths of hydrophobic tail groups provide a wide variety of chemical species that can form stable Langmuir films at the air/water interface.²⁰⁵ It is also possible to find various classes of amphiphilic polymeric materials that form stable Langmuir films at the air/water interface. Some examples of amphiphilic polymers are: poly(siloxane)s such as poly(dimethylsiloxane)s (PDMS),²⁰⁶⁻²⁰⁹ poly(acrylate)s and poly(methacrylate)s such as poly(tert-butyl acrylate) (PtBA), poly(tert-butyl methacrylate) (PtBMA) and poly(methyl methacrylate) (PMMA),²¹⁰⁻²¹² polyesters such as poly(lactic acid) (PLA)^{213,214} and poly(ϵ -caprolactone) (PCL),^{215,216} and polyethers such as high molar mass poly(ethylene oxide) (PEO).²¹⁷ In addition to these polymeric species fullerene derivatives,²¹⁸ organometallic compounds,²¹⁹ and branched polymers²²⁰ have also been utilized to form stable Langmuir films.

Much of the focus on Langmuir films can be attributed to their "2D" vs. 3D (i.e. area vs. volume) conformations. Langmuir films provide excellent model systems for studying molecules and interactions of molecules in nearly 2D systems. Likewise, the subphase (i.e. water) surface is an ideally smooth surface without defects. Furthermore, thermodynamic variables such as temperature, surface pressure, which is analog to pressure in 3D, and area per molecule, which is analogous to molar volume in 3D, can be easily controlled for Langmuir film studies. Utilizing Langmuir films, intermolecular interactions as well as monolayer/subphase interactions can be studied. These interactions can be varied by altering the properties of polar head groups or hydrophobic tail groups of the amphiphiles or the pH and ionic strength of the subphase. Langmuir films are also used as model systems for biological membranes since phospholipid monolayers can be regarded as one-half of a phospholipid bilayer in a cell. Reports in the literature also show that some amphiphilic molecules form stable bilayers at the air/water interface.¹⁵⁵ Therefore, Langmuir layers are capable of mimicking the biological membrane structure.^{221,222} It should also be also noted that Langmuir films studies are essential for the fabrication of oriented high quality LB-films with controlled thicknesses.

2.4.1.2 Monolayer Phases in a Langmuir Film

In order to prepare a Langmuir film, amphiphilic molecules are dissolved in an appropriate solvent such as chloroform. Next the solution is spread onto the subphase (i.e. water). After allowing sufficient time for the solvent to evaporate, the area available to amphiphilic molecules are reduced to form a film at the air/water interface. The film undergoes different thermodynamic phase transitions as the area available to the amphiphilic molecules on the subphase is reduced (i.e. compression). These phase

changes can be detected by measuring the surface pressure (Π) as a function of molecular area (A) at a constant temperature. Π is the 2D analog to pressure in 3D and is defined as,

$$\Pi = \gamma_0 - \gamma \quad (2.52)$$

where γ_0 is surface tension of pure water and γ is the surface tension of a film covered surface. A Π - A isotherm is obtained by plotting surface pressure as a function of molecular area at a constant temperature. The Π - A isotherm can be regarded as the 2D analog of a P - V isotherm in a 3D system. Agnes Pockles was the first person who used barriers to constrain oil films on a liquid subphase.²²³ In the late 1800s, she performed the first isotherm measurements in her kitchen using oil films on water in a container where she was able to detect the surface pressure. Afterwards, her Π - A isotherm of stearic acid was considered to be the first isotherm study for a Langmuir film.²²³⁻²²⁵ In addition Lord Rayleigh repeated some of Pockles' work and deduced the oil layers on the water surface were monomolecular.²²⁶ Another important discovery was made by William Bate Hardy in 1912. He reported that oils without functional polar groups did not spread on the water subphase and added that the oils with polar functional groups may have an orientation on the water surface.²²⁷ Hardy proposed that these orientations can be induced by long range cohesive forces between the molecules; however, Irving Langmuir later showed that the forces between the molecules were short range and acted only between molecules in contact. Irving Langmuir extended the experimental methods to study insoluble monolayers at the air/water interface. Langmuir is also the first person to provide to an extensive interpretation of monolayer structures at the molecular

level.¹⁹⁷⁻²⁰⁴ Different monolayer phases that can be observed for Π -A isotherms of common amphiphiles will be explained in the following paragraphs of this section.

When the amphiphilic molecules are spread onto the subphase at very low concentrations, the amphiphiles may exist in a 2D gaseous (G) phase. In the gaseous phase there are no or very weak interactions between the amphiphilic molecules. For gaseous monolayers, the surface pressure asymptotically approaches zero as the surface area available to the amphiphiles is increased. In the gaseous phase, area, A , is very large compared to the molecular dimensions of the amphiphiles. At this point, it should be noted that the long hydrocarbon tails of the amphiphiles may actually contact the subphase. Technically all monolayer forming amphiphiles can exhibit a gaseous phase. The molecules in this phase have a surface vapor pressure when the molecules are sufficiently separated from each other. However, the surface vapor pressures for most materials are extremely small at typical experimental conditions. This feature makes the experimental investigation of gaseous monolayer phases extremely difficult.^{201,228} It is possible to model the Π -A characteristics for gaseous monolayers via a 2D analog to the 3D ideal gas law. Based on the kinetic theory of gases, the molecules in the monolayer are assumed to move with an average kinetic energy of $kT/2$ per degree of translational freedom where k is the Boltzmann constant and T is the temperature. It should be noted that the translational degrees of freedom for molecules on the surface are two for a total kinetic energy of kT . The kinetic energy and the surface pressure (Π) are then related by the 2D ideal gas law:^{201,202}

$$\Pi A = kT \quad (2.53)$$

where A is the area per molecule.

As a monolayer in the gas phase is compressed, a phase where interactions between neighboring molecules become important can form. One type of monolayer phase is called a liquid-expanded (LE) phase. In the LE phase, the hydrophobic tails of the molecules are randomly oriented but the head groups are forced to contact with the subphase. As shown in Figure 2.12 the formation of a LE phase is usually preceded by a constant pressure region in the Π -A isotherm. This plateau represents the coexistence of the G and LE phases in the monolayer that precedes a pure LE phase [Figure 2.12 (a)]. The Π -A isotherm of a monolayer in the LE phase exhibits greater curvature than a gaseous monolayer, therefore its angle relative to the x-axis as surface pressure approaches zero is sharper than the curve observed for the gaseous monolayers. The existence of a LE phase in simple long-chain compounds is dependent on the length of hydrophobic tails and the temperature. An increase in hydrophobic chain length increases the van der Waals forces between the molecules resulting in enhanced cohesive interaction. Similarly, a decrease in the temperature decreases thermal motion which helps the film to condense. Under conditions where lateral interactions between the molecules are very strong a direct transition from a gaseous phase to a condensed (LC) monolayer phase could occur as shown in Figure 2.12 (b). Alternatively, as the LE monolayer phase is compressed further, the molecules may pack closely enough to form a condensed (LC) phase.

In the condensed monolayer phases, the headgroups are constrained on the subphase and the hydrophobic tails are closely packed. Hydrophobic tails might have either a tilted or untilted arrangement as shown in Figure 2.12 (c).^{201,202} In 1922, Adam first observed a kink in the isotherm of a condensed monolayer upon further compression and the

compressibility of the monolayer further decreased beyond this kink.²²⁹ Initially, the kink was considered to be a phase transition between the LC and solid (S) phases of the monolayer. However, it is now understood that the hydrophobic tails are aligned parallel to each other in both LC and solid phases and the only difference between the two phases is the orientation of the tails relative to the subphase. The tails are either aligned tilted at an angle or perpendicular with respect to the subphase for LC and S phases, respectively.²⁰² Therefore, both LC and solid phases can be named as condensed phases. The condensed phases may be observed with a plateau that shows the coexistence of the LE and condensed monolayer phases in the Π -A isotherm. This is followed by a transition to the purely condensed phases. The Π -A plot for the condensed monolayer will have a sharper slope compared to the LE monolayer due to the low compressibility of strongly interacting hydrophobic tails. A typical molecular area for a condensed monolayer is close to the cross-sectional area of the head groups.²⁰²

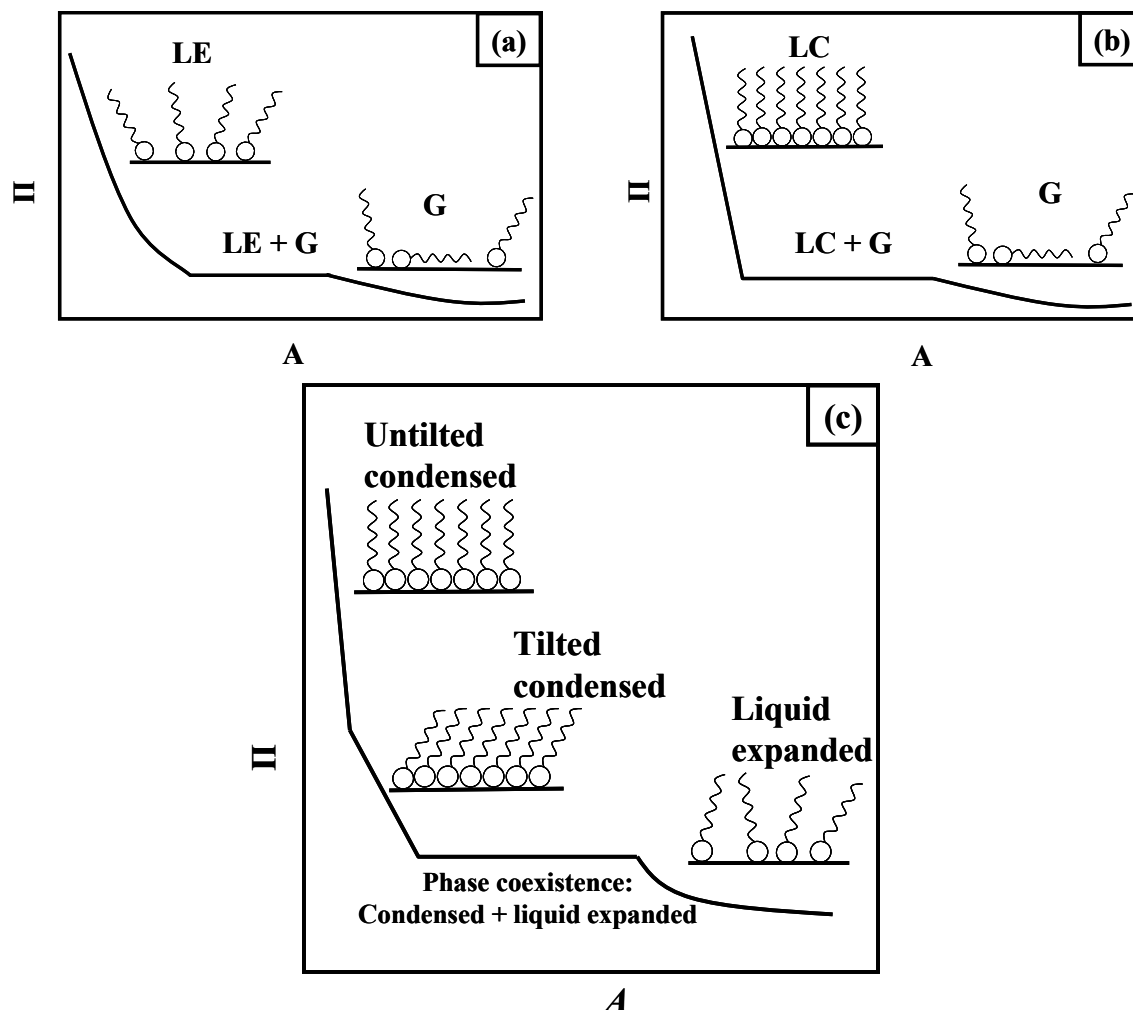


Figure 2.12. Schematic representation of a generalized Π -A isotherms of Langmuir monolayers showing (a) G to LE, (b) G to LC, and (c) LE to LC phase transitions.²⁰²

Further compression beyond the condensed phases results in a state where decreasing the surface area can not increase the surface pressure any further. At this point the area of the monolayer decreases if the pressure is kept constant or the surface pressure decreases if the monolayer is held at constant area. This state is termed as the collapsed state and the surface pressure corresponding to the onset of the collapsed state is known as collapse pressure. The molecules are in a high energy state and the monolayer structure is

distorted whereby molecules are forced out of the interphase to form multilayers to minimize the energy resulting from close packing of molecules. Likewise, LE monolayers that do not form condensed phases can also undergo collapse. Most LE phases also collapse by multilayer formation, however, poly(ethylene oxide) collapses by looping into the subphase and dissolution.

Amphiphilic polymers at the air/water interface show simpler Π -A isotherms compared to those of small molecules such as lipids.²³⁰ In general, Π -A isotherms of polymers show a simple gas phase, a liquid-like phase, or a solid-like phase due to the fact that most polymers do not have the long hydrophobic tails. Therefore complicated untilted and tilted phases in Π -A isotherms are not observed for polymer systems. Polymeric Langmuir monolayers are classified as condensed and expanded.²³⁰ However, these terms for polymers have different meanings than the same terms for small molecules. An expanded polymer monolayer shows a slow rise in surface pressure, whereas a condensed polymer monolayer is characterized by a sharper slope on a Π -A isotherm.

2.4.1.3 Langmuir and Langmuir-Blodgett (LB) Film Preparation

Langmuir films and LB-films are prepared on a Langmuir-Blodgett (LB) trough. The trough is filled with the subphase. The trough that is in contact with the subphase is hydrophobic and inert to the organic solvents that are used for dissolving the amphiphiles. The most common material utilized for the trough is poly(tetrafluoroethylene) (PTFE) (i.e. Teflon). Two movable barriers are attached to the troughs to control the surface area occupied by the amphiphilic molecules after spreading. The barriers are made of either hydrophilic Delrin™ or hydrophobic PTFE.

The barrier could be rigidly affixed to the system or could be independent and easily removable for cleaning purposes. Also a pressure sensor that monitors the surface pressure is attached to the LB-trough. Two common ways to measure surface pressure during monolayer compression are the Langmuir balance and the Wilhelmy plate techniques. The measurement techniques are quite different, however, the sensitivities for both techniques are similar ($\sim 10^{-3}$ mN/m).^{201,202}

For the Langmuir balance technique the water surface is separated from the monolayer covered water surface by a divider. Then the force acting on the divider is measured by a float connected to a balance.²³¹ The Wilhelmy plate technique is more commonly used (Figure 2.13) since it provides an absolute measurement of surface tension. The measurement is based on a partial immersion into the subphase of a very thin plate attached to an electrobalance. Then the forces acting on the plate are measured.²³¹ The plate could be made of platinum or filter paper. There are three main forces acting on the plate; downward forces such as gravity and surface tension and upward forces such as buoyancy. The net downward force (F) acting on a rectangular plate of dimensions l , w , t , with a density of ρ_P , immersed to a depth of h in a liquid of density ρ_L , is given by,^{201,202}

$$F = \rho_P g l w t + 2\gamma(t + w) \cos \theta - \rho_L g t w h \quad (2.54)$$

where γ is the surface tension of the liquid, θ is the contact angle and g is acceleration due to gravity. When the plate is completely wetted by water ($\theta = 0^\circ$, $\cos \theta = 1$) and the difference of the net downward force is measured on the Wilhelmy plate for a pure subphase versus a monolayer covered surface. The change in the net downward force is related to surface pressure (Π) by the following expression,^{201,202}

$$\Pi = \gamma_0 - \gamma = \frac{F_0 - F}{2(t + w)} = \frac{\Delta F}{2(t + w)} \quad (2.55)$$

where γ_0 and γ are the surface tensions of the pure water and film covered surfaces, respectively, and F_0 and F are the net downward forces experienced by the plate for the pure water and film covered surfaces, respectively. For a very thin plate, $t \ll w$, Equation 2.55 can be reduced to,

$$\Delta\gamma \cong \frac{\Delta F}{2w} \quad (2.56)$$

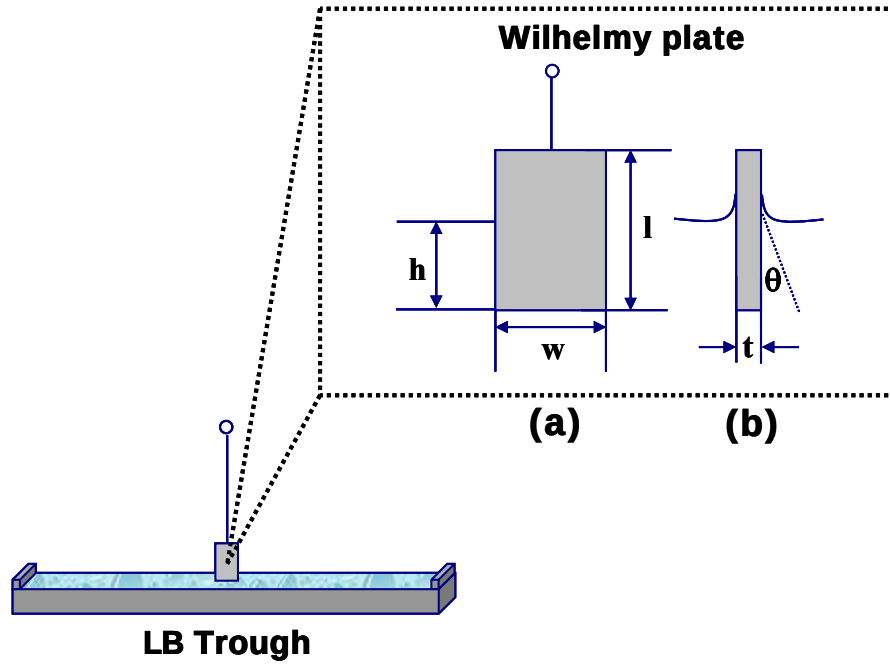


Figure 2.13. A schematic representation of a Wilhelmy plate (a) front view and (b) side view attached to the LB Trough.

2.4.1.4 Langmuir-Blodgett (LB) Film Transfer

Langmuir monolayers can be deposited onto hydrophilic or hydrophobic solid substrates to form multilayer LB-films. The monolayers are transferred from the air/water interface onto solid substrates when the molecules are at their closest packing. (i.e. right before the collapse pressure).²³¹ Generally, the transfer of monolayers by the LB-technique are carried out from the condensed phases. Therefore, the molecular organization in the LB-films depends on the initial orientation of molecules in the condensed monolayers phases.^{201,202} Transfer from condensed phases can provide a high quality film without voids and defects since the molecules are closely packed in the condensed phase.²³¹

The substrate is vertically dipped through the subphase containing the condensed monolayer. There are several vertical LB-deposition patterns such as X, Y, and Z-type transfers. X, Y, and Z deposition patterns are summarized in Figure 2.14 (a-c). The most common type of transfer using a hydrophobic substrate is known as Y-type deposition. Y-type transfer involves the vertical dipping of a hydrophobic substrate through the subphase containing a monolayer. Then the substrate picks up a layer that is one molecule thick. The hydrophobic nature of the substrate and tails of the amphiphilic molecules will allow the idealized transfer depicted in Figure 2.14 (a). On the upstroke, another monolayer is transferred since the polar head groups of the already transferred monolayer will be attracted to the polar head groups of the amphiphiles on the subphase. This process could be repeated until the desired number of monolayers are deposited. A head to head and tail to tail structure is produced for LB-films deposited by Y-type transfer as shown in Figure 2.14 (a). On the other hand, in X-type [Figure 2.14 (b)] and

Z-type [Figure 2.14 (c)] deposition, the amphiphiles are deposited only on the downstroke or upstroke, respectively. Therefore LB-films resulting from X-type and Z-type transfer can have the same orientation in all layers, unlike the alternating head to head and tail to tail attachment for films resulting from Y-type transfer.

The hydrophobicity of air can lead to structural rearrangements in LB-films. During or after the deposition more energetically favored conformations can exist. LB-film studies of octadecyldimethylamine oxide and dioctadecyldimethylammonium chloride via X-ray diffraction and IR have shown that molecules rearranged during LB-transfer.²³² X-type and Y-type films of barium stearate have shown the same intermolecular structure after reorientation.²³³ It has also been reported that the head to head and tail to tail arrangement of docosanoic acid LB-films deposited by Y-type transfer is damaged during deposition at slow dipping rates.²³⁴ It has also been found that the final layer of LB-films tend to have their hydrophobic portions oriented away from the substrate (into the air) independent of the type of deposition.²³⁵

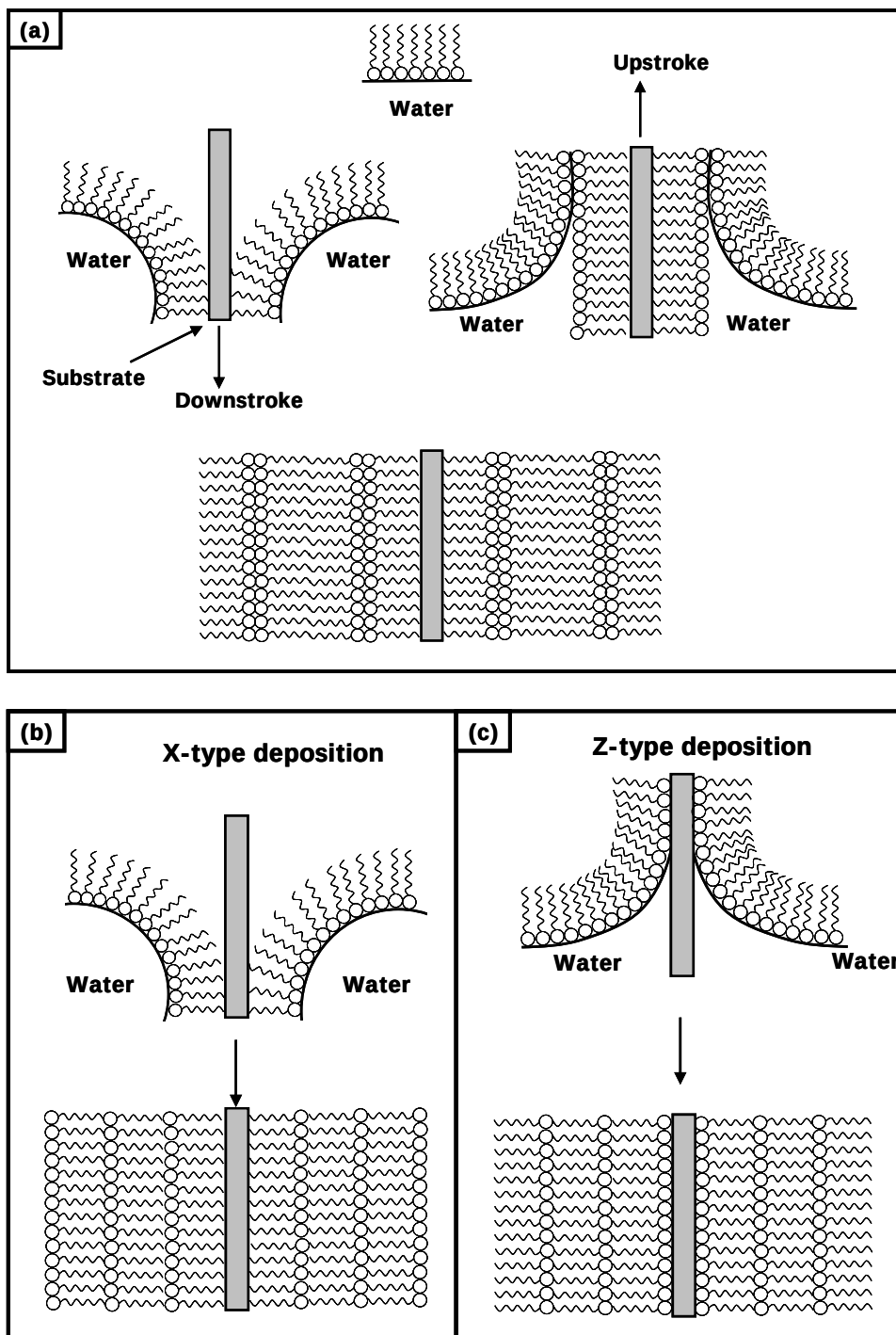


Figure 2.14. Schematic representations of three different LB-deposition methods (a) Y-type, (b) X-type, and (c) Z-type.¹⁵⁶

There are certain points that should be kept in mind in order to increase the quality of Langmuir monolayers and LB-films. These are using pure materials (i.e. amphiphiles, solvent, subphase), rigorous of the cleaning of the trough and barriers, and controlling the temperature of the subphase. One measure of the quality of the LB-films is the transfer ratio (T_R). T_R is the ratio of the decrease in the area occupied by a monolayer on the water surface (A_L) to the area of the substrate passed through the subphase (A_S).²³⁶

$$T_R = \frac{A_L}{A_S} \quad (2.57)$$

The transfer ratio for a perfect transfer equals 1. If molecular rearrangements are present T_R may deviate from 1. Another parameter (ϕ) has been introduced as a metric for the quality of LB-films and the quantity ϕ is defined as,²³⁶

$$\phi = \frac{T_{R,u}}{T_{R,d}} \quad (2.58)$$

where $T_{R,u}$ and $T_{R,d}$ are the transfer ratios for the upstroke and downstroke, respectively. As one may expect perfect Y-, X-, and Z- type deposition will yield $\phi = 1$, 0, and ∞ , respectively.

2.4.2 X-Ray Reflectivity

X-ray reflectivity (XR) has become an important tool for studying the structure and the organization of materials in thin films at the submicron and atomic scales.²³⁷⁻²³⁹ The principle objective of an XR experiment is to determine the one dimensional scattering profile perpendicular to the surface of the material. The information obtained can be related to the chemical and atomic structure. Typically, thickness, electron density and interfacial roughness of the materials can be obtained. The main difference between a

reflectivity and diffraction experiment is that the momentum transfer for the reflectivity experiment is smaller than for diffraction experiments which means the incident angle θ ranges from 0.0° to 3.0° , whereas this angle is between 5° and 70° for a common diffraction experiment. This is why XR (and neutron reflectivity (NR)) is referred to as grazing incidence reflectivity. Both diffraction and reflectivity are elastic scattering techniques where the incident and the reflected wave have the same energy. Both techniques will have constructive or deconstructive interference phenomena, however, the physical reason behind the sources of interference are different. In diffraction, the long range periodical order causes the interference. Conversely, in XR changes in the electron density primarily arise from the sample and substrate. As such, XR can be applied to liquids or amorphous polymers. It is a powerful technique for investigating the structures of organic thin films. XR is highly sensitive to electron density gradients of thin films and is one of the few techniques that can be utilized for determining mass density, thickness, and roughness of thin films along the direction normal to the surface.²⁴⁰⁻²⁴²

2.4.2.1 Basic Principles

The basic idea behind XR is the comparison of measured reflectivity profiles with theoretical Fresnel reflectivity profiles.^{243,244} At an interface of materials having different electron densities x-rays are going to be refracted and reflected. Since the refractive indices of the media at the interface are different for each side, the incoming x-ray undergoes refraction and reflection. For a condensed material irradiated by x-rays the refractive index, n , that depends on the electron density of the volume that is subject to the radiation, is slightly less than one and is given as,

$$n = 1 - \delta + i\beta \quad (2.59)$$

where the dispersion term δ can be written as,

$$\delta = \left(\frac{\lambda_2}{2\pi} \right) r_e N_a \rho \left(\frac{Z + f'}{A} \right) = \left(\frac{\lambda^2}{2\pi} \right) r_e \rho_e \quad (2.60)$$

and the absorption term is,

$$\beta = \left(\frac{\lambda_2}{2\pi} \right) r_e N_a \rho \left(\frac{f''}{A} \right) = \left(\frac{f''}{Z + f'} \right) \delta = \frac{\lambda \mu}{4\pi} \quad (2.61)$$

where λ is the wavelength for x-ray radiation (1.5418 Å), r_e is the classical electron radius (i.e. 2.818×10^{-15}), N_a is the Avogadro's number, ρ is the mass density, Z is the atomic number, A is the atomic mass, ρ_e is the electron density, μ is the linear absorption coefficient, and f' and f'' are real (dispersion) and imaginary (absorption) parts of the dispersion correction, respectively.

On the basis of Equations 2.59 through 2.61 the magnitudes of the δ and β correspond to the electron density of each material. The values for δ and β are in the range around 10^{-5} to 10^{-7} . The magnitude of the β term is a hundred to a thousand times smaller than that of the δ term. The real part of the refractive index, δ in Equation 2.59, is related to the phase-lag of the propagating wave, whereas the imaginary part β is related to the decrease in the propagating wave amplitude. Since the β term is related to the absorption of X-rays and materials absorb x-ray beams at low energies, the importance of the β term is more significant at higher wavelengths.

For two different media having different refractive indices, n_1 and n_2 the refracted angle, θ_2 , for the impinging x-ray beam having an incident angle of θ_1 can be determined by the ratio of the refractive indices of the two media. X-rays also follow Snell's law

previously discussed in Section 2.2.4. For XR, angles are defined relative to the surface rather than relative to the surface normal. However it should be noted that the angles for XR are defined in a different way relative to the surface normal than for visible wavelengths of light described in Section 2.2.4. As a consequence, Snell's law is described in terms of cosines rather than sines:

$$n_1 \cos \theta_1 = n_2 \cos \theta_2 \quad (2.62)$$

If one of the media is air or vacuum, $n_1=1$ and Equation 2.62 reduces to

$$\cos \theta_2 = \frac{1}{n_2} \cos \theta_1 \quad (2.63)$$

As depicted in Figure 2.15, $n_2 < 1$ and $\theta_2 < \theta_1$. There is an angle of refraction for all angles of incidences $\theta_1 > \theta_c$ (the critical angle). At the critical angle θ_2 is zero and Equation 2.63 reduces to,

$$n_2 = \cos \theta_1 = \cos \theta_c \quad (2.64)$$

From Equations 2.62 through 2.64 it follows that total external reflection of the x-rays occurs for incident angles $\theta_{inc} \leq \theta_c$. If the absorption term in Equation 2.59 is neglected the critical angle θ_c can be expressed as,

$$\theta_c = \sqrt{2\delta} \quad (2.65)$$

and for the case of Cu- K_α radiation ($\lambda \sim 1.5418 \text{ \AA}$), typical values of θ_c are on the order of 0.2° and 0.6° for organic to metallic systems.

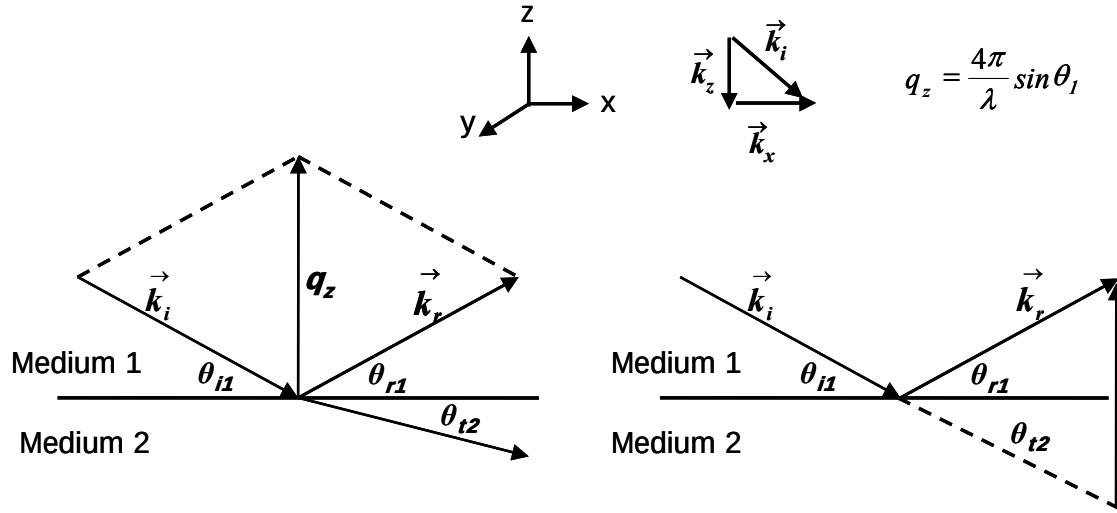


Figure 2.15. Schematic representations of reflection and refraction at an interface with medium₁ and medium₂. θ_{i1} is the angle between the incident ray and the surface, θ_{r1} is the angle between the reflected ray and the surface, and θ_{t2} is the angle between the refracted ray and the surface. The refracted beam reflects the assumption that $n_2 < n_1$.

Data can be acquired in two ways via XR experiments. These are specular and off-specular XR methods. Specular reflection corresponds to the case where the angle of incidence is equal to the angle of reflection. In contrast, the refracted angle differs from the incident angle for off-specular reflection. Here only the principles of specular reflectivity experiments utilized to characterize the films in this thesis will be discussed.

2.4.2.2 Specular XR Experiments

Reflection properties of the x-rays mainly depend on the differences in the wave refractive indices of the media. These differences manifest themselves indirectly in the wave vectors for light propagating in the two media. In vacuum, the magnitude of the wave vector is represented as follows:

$$\left| \vec{k}_i \right| = \left| \vec{k}_r \right| = \frac{2\pi}{\lambda} \quad (2.66)$$

Here both the incident and the reflected angles ($\theta_i = \theta_{il} = \theta_{r1}$ in Figure 2.15) are the same for specular XR experiments and, only the z component of the wave vector, k_z is of interest:

$$k_z = \frac{2\pi}{\lambda} \sin \theta_1 \quad (2.67)$$

For a simple two media (medium 1 and medium 2) experiment, the scattering wave vector, q_z (also shown in Figure 2.15) can be defined as

$$q_z = \frac{4\pi}{\lambda} \sin \theta_1 \quad (2.68)$$

When the interface can be considered as ideal and infinitely sharp, the reflection coefficient is

$$r_{12} = \frac{\sin \theta_1 - n_2 \sin \theta_2}{\sin \theta_1 + n_2 \sin \theta_2} = \frac{k_{z1} - k_{z2}}{k_{z1} + k_{z2}} \quad (2.69)$$

where k_{z1} and k_{z2} are z component of the wave vector for medium 1 and 2, respectively.

On the basis of these reflection coefficients, the Fresnel reflectivity at an interface, R_F , can be written as

$$R_F = r_{12} r_{12}^* = \left| \frac{k_{z1} - k_{z2}}{k_{z1} + k_{z2}} \right|^2 \quad (2.70)$$

In Equation 2.70 r_{12}^* represents the complex conjugate value. k_{z2} can be described as a function of k_{z1} through the electron density difference:

$$k_{z2} = \left(k_{z1}^2 - 4\pi\rho_e \right)^{1/2} = \left(k_{z1}^2 - k_{c1}^2 \right)^{1/2} \quad (2.71)$$

where k_c is the critical value of the k_{z2} . Hence, Equation 2.70 can be expressed as

$$R_F = \frac{\left| 1 - \sqrt{1 - \left(\frac{k_{c2}}{k_{z1}} \right)^2} \right|^2}{\left| 1 + \sqrt{1 - \left(\frac{k_{c2}}{k_{z1}} \right)^2} \right|^2} \quad (2.72)$$

Total external reflection occurs when $k_{z2} < k_{c2}$. Equation 2.72 shows that R_F can be considered as a function of θ_1 or q_z . Furthermore, Equation 2.72 becomes more complicated as additional layers with different refractive indices are added to the system. The situation with two interfaces having three media 1, 2, and 3 is schematically drawn in Figure 2.16. This situation can be perceived as a thin film supported on a solid substrate. Additional terms for the new interfaces, r_{23} and r_{12} are the reflection coefficient for substrate/film and air/film interface, respectively. The reflection coefficient (r) which has contributions from these interfaces can be described as a function of θ and thickness, d :

$$r = \frac{r_{12} + r_{23} \exp(2ik_{z2}d)}{1 + r_{12}r_{23} \exp(2ik_{z2}d)} \quad (2.73)$$

Finally the reflectivity R can be expressed as

$$R = rr^* = \frac{r_{12}^2 + r_{23}^2 + 2r_{12}r_{23} \cos(2ik_{z2}d)}{1 + r_{12}^2 r_{23}^2 + 2r_{12}r_{23} \cos(2ik_{z2}d)} \quad (2.74)$$

Equation 2.74 describes the theoretical reflectivity curves for films having thickness $> \sim 1$ nm. Equation 2.74 shows that the reflectivity profiles will produce a series of maxima

and minima as a function of θ or q_z known as Kiessig fringes.^{245,246} Utilizing the maxima and minima observed for Kiessig fringes, the thickness of the film can be calculated.

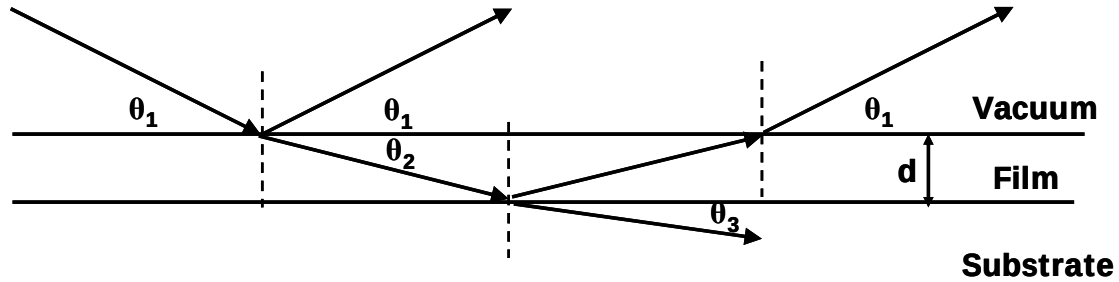


Figure 2.16. Schematic diagram of the x-ray beam path in a thin film with a thickness of d on a supported solid substrate.

2.4.2.2 XR Profile Analyses

The reflectivity, $R(q)$, is the ratio of reflected x-ray intensity to the intensity of the incident x-ray beam coming directly from the source. Figure 2.17 shows a reflectivity vs. scattering wave vector, q , profile for an LB-film on a silicon substrate. Periodic oscillations in $R(q)$, Kiessig fringes, can be observed for $\theta > \theta_c$. Combining the z component of the wave vector q_z and Bragg's law one can deduce the film thickness (d) from the position of the Kiessig fringes:

$$d = \frac{\lambda}{2\Delta k_{z2}} = \frac{2\pi}{\Delta q} \quad (2.75)$$

For the example provided in Figure 2.17, a distinct peak at high angles is noted. This peak, a Bragg peak, indicates the presence of a double layer structure that arises from Y-type deposition of the LB-film.

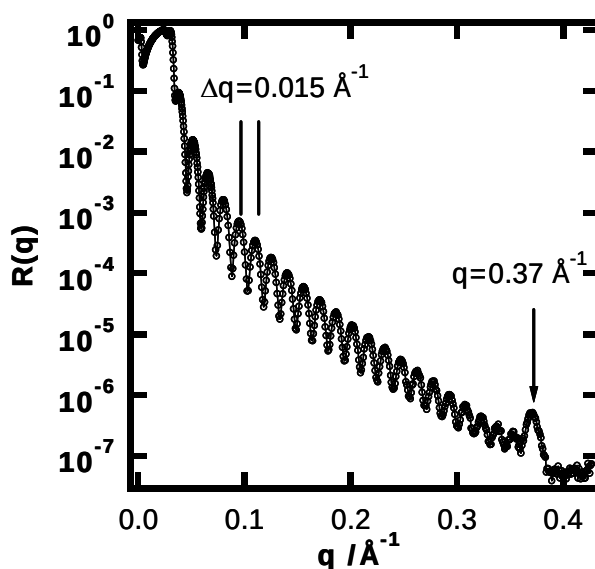


Figure 2.17. An x-ray reflectivity profile for a multilayer LB-film deposited on a H terminated silicon substrate. The oscillations (Kiessig fringes) occur because of the total thickness of the sample. Δq can be used to determine the film thickness from Equation 2.75. The Bragg peak at $q = 0.37 \text{ \AA}^{-1}$ provides the double layer spacing through Bragg's Law.

Recently, data analysis programs for XR experiments have been improved. Full mathematical models combined with regression analyses introduced by Parrat are commonly used.²⁴⁷ Another method to evaluate the film thickness via XR was introduced by Thompson, *et al.*²⁴⁸

Specular reflectivity of X-rays has been used to investigate a wide variety of polymeric systems. XR is a very unique and sensitive technique to study surface structure and surface modification. By simply reducing the angle of incidence the penetration depth can be rapidly changed and in principle allows one to study extremely thin surfaces such as atomic monolayers. For instance, XR have been utilized to

investigate the monolayer structures, phase transitions, and ordering in LB-film systems.²⁴⁹⁻²⁵¹ Extensive applications of XR to LB-films have been reported for evaluating film thickness, surface density, surface roughness, and surface structures.²⁵²⁻²⁵⁵ The first quantitative treatments of reflectivity from LB-films were performed by Pomerantz and Segmuller.^{256,257} Finally it is worth noting that the subsequent experiments revealed the fact that the roughness of the substrate for silicon and silica is reported as ~ 5 Å whereas the roughness for the surface of the polymer film is noted as ~ 6 Å. These results mean that polymer thin films can be prepared on silicon substrates with total roughnesses on the order of ~ 1 nm.²⁵⁸

2.4.3 Ellipsometry

The theoretical framework for ellipsometry was first developed by Drude in 1887 and is still used today.^{259,260} Ellipsometry is an optical technique that characterizes light reflected from interfaces²⁶¹⁻²⁶³ The key feature for ellipsometry is the measurement of the change in the polarization state of the polarized light upon light reflection on a sample. The name ellipsometry refers to the fact that polarized light often becomes elliptically polarized after reflecting from a surface. Elliptically polarized light can be decomposed into two characteristic components, s and p polarized light. The reflectivity of s and p polarized light can be expressed in terms of two ellipsometric angles, Ψ and Δ . For these two angles Ψ is related to the amplitude ratio, and Δ is related to the phase difference, between the s and p polarized light waves. Measurements could be done using spectroscopic sources or can be conducted with a single wavelength laser light source (i.e. typically He:Ne laser, $\lambda = 632.8$ nm). In spectroscopic measurements Ψ and Δ are measured as a function of wavelength. In general, spectroscopic ellipsometry

measurements are carried out in the ultraviolet/visible region, however, measurements in the infrared region have also been performed. Conversely, in single wavelength measurements Ψ and Δ data are usually acquired as a function of incident angle.

The application domain of ellipsometry instruments is quite wide. Since it is a non-destructive rapid measurement technique real time analyses of chemical and physical changes are possible such as *in situ* characterization of thin film growth, etching, or thermal oxidation of surfaces.²⁶⁴⁻²⁶⁷ It should be noted that optical properties and thicknesses of thin films have been widely investigated utilizing ellipsometry measurements.²⁶⁸⁻²⁷² One of the remarkable properties of an ellipsometry measurement is the high precision of the thickness measurements. However, ellipsometry data analyses require an optical model in order to estimate the thickness because the refractive index and thickness are coupled parameter.²⁷³⁻²⁷⁸

2.4.3.1 Basic Principles of Ellipsometry

Maxwell hypothesized that light waves are electromagnetic waves and formulated electromagnetic theory. For electromagnetic waves, the electric field vector, E , and the magnetic field vector, B , are perpendicular to each other. However, these properties do not control the reflection and the transmission properties of the light propagating in different media. In fact it is the complex refractive index, n^* , of the media that controls reflection. Combining the Maxwell boundary conditions and the reflection rule for p-polarized light, the amplitude reflection coefficient for p-polarized is²⁷⁹⁻²⁸⁰

$$r_p \equiv \frac{E_{rp}}{E_{ip}} = \frac{n_t \cos \theta_i - n_i \cos \theta_t}{n_t \cos \theta_i + n_i \cos \theta_t} \quad (2.76)$$

where the subscript p stands for the p-polarized light, and the subscripts i, r and t represent the incident, reflected, and transmitted p-polarized light, respectively. Similarly, the amplitude transmission coefficient for p-polarized light can be written as

$$t_p \equiv \frac{E_{tp}}{E_{ip}} = \frac{2n_i \cos \theta_i}{n_t \cos \theta_i + n_i \cos \theta_t} \quad (2.77)$$

On the other hand, the amplitude reflection and transmission coefficients for s-polarized light can be expressed as,

$$r_s \equiv \frac{E_{rs}}{E_{is}} = \frac{n_i \cos \theta_i - n_t \cos \theta_t}{n_i \cos \theta_i + n_t \cos \theta_t} \quad (2.78)$$

$$t_s \equiv \frac{E_{ts}}{E_{is}} = \frac{2n_i \cos \theta_i}{n_i \cos \theta_i + n_t \cos \theta_t} \quad (2.79)$$

where the subscript s stands for s-polarized light and the subscripts i, r and t represent the incident, reflected, and transmitted s-polarized light, respectively. The above equations for r_p , r_s , t_p , and t_s are known as the Fresnel equations. The Fresnel equations are still valid for the case of a complex refractive index, n^* . Using Snell's Law and a simple trigonometric property (i.e. $\sin^2 \theta + \cos^2 \theta = 1$) the Fresnel equations can be rewritten for the complex refractive index as

$$r_p = \frac{\left(n_t^*/n_i^*\right)^2 \cos \theta_i - \left(\left(n_t^*/n_i^*\right)^2 - \sin^2 \theta_i\right)^{1/2}}{\left(n_t^*/n_i^*\right)^2 \cos \theta_i + \left(\left(n_t^*/n_i^*\right)^2 - \sin^2 \theta_i\right)^{1/2}} \quad (2.80)$$

$$r_s = \frac{\cos \theta_i - \left(\left(n_t^*/n_i^*\right)^2 - \sin^2 \theta_i\right)^{1/2}}{\cos \theta_i + \left(\left(n_t^*/n_i^*\right)^2 - \sin^2 \theta_i\right)^{1/2}} \quad (2.81)$$

Finally Equations 2.78 through 2.81 can be expressed in a polar coordinate system:

$$r_p = |r_p| \exp(i\delta_{rp}) \quad (2.82)$$

$$r_s = |r_s| \exp(i\delta_{rs}) \quad (2.83)$$

$$t_p = |t_p| \exp(i\delta_{tp}) \quad (2.84)$$

$$t_s = |t_s| \exp(i\delta_{ts}) \quad (2.85)$$

It is clear from Equations 2.82 through 2.85, that the reflective and transmissive properties of propagating light can be expressed in term of the amplitude, $|r|$ or $|t|$, and phase, δ .

Up to this stage, the Fresnel equations are considered for a simple ambient surface (i.e air/substrate). Now optical interference effects for a thin film formed on a substrate (ambient/thin-film/substrate) will be discussed. For the analysis of ellipsometry data and the determination of thicknesses for thin films, interference effects are important. Figure 2.18 shows an optical model representation for a thin film supported on a solid substrate. As shown in Figure 2.18 n_0 , n_1 , and n_2 are the refractive index values for air, the film, and the substrate, respectively.

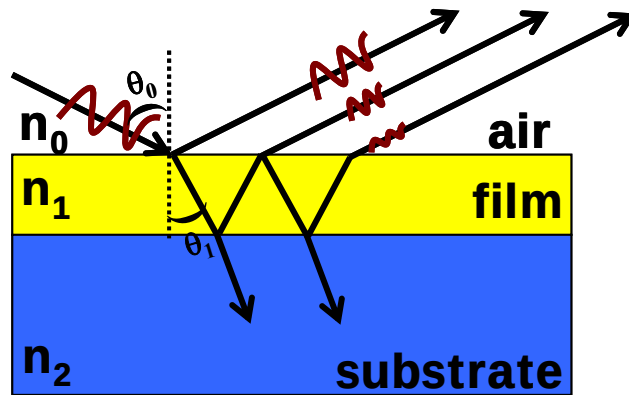


Figure 2.18. Optical interference of light reflected from a thin film on solid substrate.

When the light absorption in a thin film is weak, the incident wave is reflected from two surfaces, the incident medium/film and film/substrate interfaces. The light wave reflected directly from the film surface will interfere with light reflected from the film/substrate interface. In Figure 2.19, the wave amplitude will become larger if the primary (incident medium/film) and secondary (film/substrate) reflected beams are in phase. Conversely, the amplitude of reflected light becomes smaller when the two waves are out of phase.²⁷⁹⁻²⁸⁰ Figure 2.19 explains optical interference in a three medium environment (i.e ambient/thin film/substrate). In Figure 2.19 r_{jk} and t_{jk} shows the amplitude reflection coefficient at each interface. Additionally, the term β is the optical thickness:

$$\beta = \frac{2\pi d}{\lambda} n_1 \cos \theta_1 \quad (2.86)$$

where d denotes the thickness of the thin film, n_1 is the refractive index of the film, λ is the wavelength of the propagating light, and θ_1 is the incident angle.

The general form for the amplitude reflection could be obtained from the Fresnel equations as follows.

$$r_{jk,p} = \frac{n_k^* \cos \theta_j - n_j^* \cos \theta_k}{n_k^* \cos \theta_j + n_j^* \cos \theta_k} \quad (2.87)$$

$$r_{jk,s} = \frac{n_j^* \cos \theta_j - n_k^* \cos \theta_k}{n_j^* \cos \theta_j + n_k^* \cos \theta_k} \quad (2.88)$$

$$t_{jk,p} = \frac{2n_j^* \cos \theta_j}{n_k^* \cos \theta_j + n_j^* \cos \theta_k} \quad (2.89)$$

$$t_{jk,s} = \frac{2n_j^* \cos \theta_j}{n_j^* \cos \theta_j + n_k^* \cos \theta_k} \quad (2.90)$$

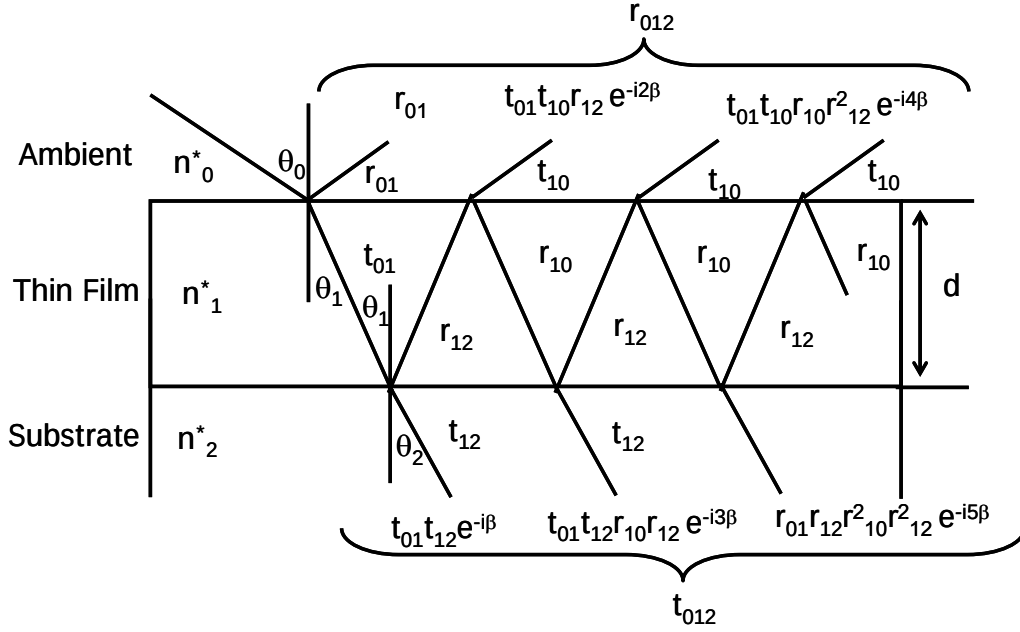


Figure 2.19. Optical interference of light in a thin film on a solid substrate. Optical model for an ambient/thin film/substrate structure is drawn. In this figure, r_{jk} and t_{jk} represents the amplitude coefficients for reflection and transmission from different interfaces.

As shown in Figure 2.19 the amplitude reflection coefficient for the first beam that is directly reflected from the surface is r_{01} . In Figure 2.19 the phase variation arising from the optical path length differences of the beams is proportional to a complex exponential function (i.e. $e^{-i2\beta}$). The second ray is first refracted through the thin film, and then reflected from the substrate, and finally refracted back into the ambient medium as shown in Figure 2.19. By multiplying the phase variation and the individual amplitude coefficients for different rays it is possible to obtain the corresponding amplitude reflection coefficient for each ray shown in Figure 2.19. The summation of the amplitude

reflection coefficients for all rays in the system shown in Figure 2.19 (an infinite number of rays may be present) is:

$$r_{012} = r_{01} + t_{01}t_{10}r_{12}e^{-i2\beta} + t_{01}t_{10}r_{10}r_{12}e^{-i4\beta} + t_{01}t_{10}r_{10}^2r_{12}^3e^{-i6\beta} + \dots \quad (2.91)$$

The infinite series in Equation 2.91 corresponds to via $y = a+ax+ax^2+ax^3+\dots = a/[(1-r)r]$ whereby

$$r_{012} = r_{01} + \frac{t_{01}t_{10}r_{12} \exp(-i2\beta)}{1 - r_{10}r_{12} \exp(-i2\beta)} \quad (2.92)$$

The relationships $r_{10} = -r_{01}$ and $t_{01}t_{10} = 1-r_{01}^2$ yields

$$r_{012} = \frac{r_{01} + r_{12} \exp(-i2\beta)}{1 + r_{01}r_{12} \exp(-i2\beta)} \quad (2.93)$$

Similarly the amplitude transmission coefficient for the ambient medium/thin film/substrate system is

$$t_{012} = \frac{t_{01} + t_{12} \exp(-i2\beta)}{1 + r_{01}r_{12} \exp(-i2\beta)} \quad (2.94)$$

By simply applying Equation 2.92 the amplitude reflection coefficient for s and p polarized light could be obtained. The measured values of Ψ and Δ from ellipsometry are related to the ellipticity (ρ):

$$\rho = \tan \Psi \exp(i\Delta) = \frac{r_p}{r_s} \quad (2.95)$$

The ratio of the amplitude reflection coefficients for s and p polarized light, Equation 2.95, serves as the fundamental equation for ellipsometry where Ψ is related to the attenuation of the amplitude and Δ is related to the phase difference of the p and s polarized light. Another common representation of the ellipticity is

$$\rho = \frac{r_p}{r_s} = \text{Re}(r) + i \text{Im}(r) \quad (2.96)$$

where $\text{Re}(r)$ and $\text{Im}(r)$ are the real and imaginary parts of complex ratio of ellipticity, ρ . The real and imaginary parts of ρ can be easily converted back to the traditional parameters via the following relationships:²⁶¹

$$\tan \Psi = \sqrt{\text{Re}(r)^2 + \text{Im}(r)^2} \quad (2.97)$$

$$\tan \Delta = \frac{\text{Re}(r)}{\text{Im}(r)} \quad (2.98)$$

2.4.3.2 Interpretation of Ellipsometry Data

Polymeric systems such as polymer thin films,²⁸¹⁻²⁸⁴ self assembled layers,^{285,286} Langmuir-Blodgett (LB) films,²⁸⁷ and liquid crystals²⁸⁸⁻²⁹³ have been widely investigated via ellipsometry to obtain optical constants, layer thicknesses, and material compositions. However these parameters are not measured directly rather they are obtained by comparing the ellipsometry data to a model that can be constructed on the basis of the optical dispersion functions discussed in Section 2.2.1. Therefore, the result of the ellipsometry measurements depends on the model. Figure 2.20 shows a flow chart explaining the data analysis procedure for an ellipsometry measurement. The model is used to predict the thickness or the optical constants from the Fresnel equations. Then the calculated values are compared to the experimental data. The unknown material properties are changed until the experimental data matches the theoretical model. The entire model or selected parameters could be changed in order to obtain a better description for the material properties.

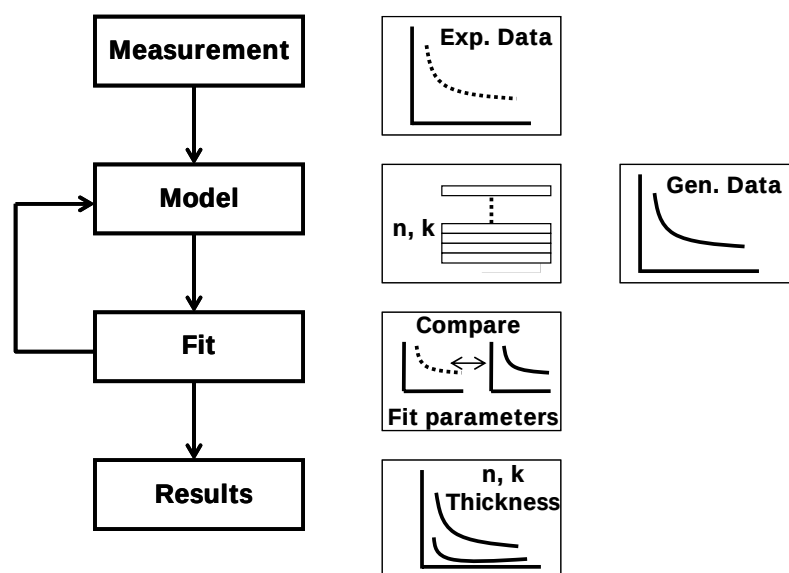


Figure 2.20. A representative data analysis flow chart for ellipsometry measurements.

As one might expect, the quality of the data, which is related to the instrument, angle of incidence, wavelength, and more importantly the quality of the sample is crucial for obtaining reasonable parameters from ellipsometry. Analytical expressions exist for calculating different sample properties. For simple layer systems it is possible to obtain exact solutions, but not from a single measurement. For more complicated systems, such as multiple layers, numerical fitting methods are applied. As such, there is no single approach that is optimal for every system. In many ways, the technique is dependent upon optical simulation software, such as the TFC Companion software used in this thesis. This program provides an interface, whereby setting up multilayer models and fitting of the experimental data is possible. One important point is that multilayer fitting software usually works better for thicker films and multilayer systems because the contribution of interface roughness is smaller, whereas very thin layers are often characterized via direct analyses methods. The details of both approaches will be discussed in Chapter 3 (Experimental and Materials)

In conclusion the approach to analyzing ellipsometry data depends on the properties of interest. While, ellipsometry is a very strong tool for thin film metrology, interpreting the acquired data normally requires more time than the measurement itself.

2.5 Polyhedral Oligomeric Silsesquioxanes (POSS) Model Nanoparticles

Unique polyhedral oligomeric silsesquioxane (POSS) molecules are utilized as nanoparticles for the polymer/nanoparticle blends studied in the temperature dependent experiments of this dissertation. All chemical structures having the empirical formula of $\text{RSiO}_{1.5}$ are known as silsesquioxanes. The R groups could be hydrogen or any alkyl, aryl, arylene, or derivatives of aryl or arylene groups.²⁹⁴ These materials can have random, ladder-like, and cage structures. The cage structure could either be open or closed. Since, the silsesquioxanes derivative cage has approximately spherical topologies they are sometimes referred to as spherosiloxanes.²⁹⁵ POSS is an organic/inorganic hybrid material composed of a rigid inorganic core (i.e. Si-O cage) and a flexible organic corona. POSS molecules are usually regarded as the smallest particles of silica.^{294,296,297} The organic corona provides processability and makes the POSS compatible with polymers, while the rigid inorganic core provides mechanical strength and oxidative stability. Figure 2.21 shows the chemical structures of a heptasubstituted trisilanol-POSS (open cage) and a octasubstituted-POSS (closed cage). Several condensed (complete Si-O cage) and incompletely condensed (partial Si-O cage with multiple Si atoms capped silanols) POSS compounds of different cage sizes (10, 12, and 14 member cages) have been investigated;²⁹⁸ however, this dissertation only focuses on the open cage structure shown in Figure 2.21 (a).

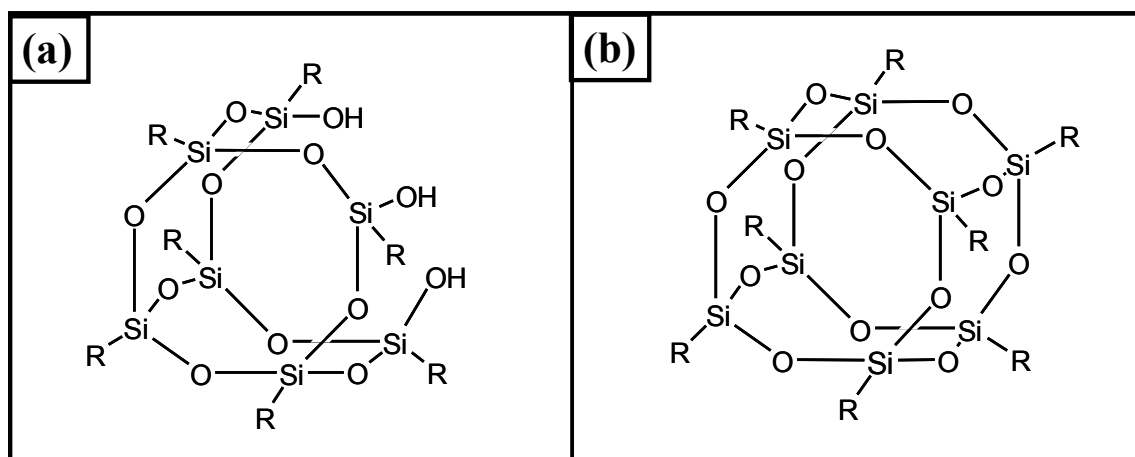
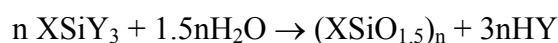


Figure 2.21. Chemical structures for (a) an open cage heptasubstituted trisilanol-POSS, and (b) a closed cage fully functional octasubstituted-POSS. R is most commonly an alkyl, aryl, or arylene substituent.

Different synthetic strategies are available for the synthesis of POSS derivatives.²⁹⁹ The most common process to obtain POSS is via the hydrolytic condensation of trifunctional organosilicon monomers (XSiY_3). In this structure, X is a chemically stable substituent or H, and Y is a highly reactive substituent such as chloride or alkoxy group.³⁰⁰⁻³⁰³ The synthesis of POSS is a difficult process that requires careful control of several factors, such as the concentration of the initial monomer, nature of solvent, type of catalyst, temperature, quantity of water, and the rate of water addition.³⁰⁴ A general chemical equation for the hydrolytic condensation of XSiY_3 monomers to produce polyhedral oligomeric silsesquioxanes is shown in Scheme 2.1. The method usually yields a distribution of products, however, isolation of heptasubstituted trisilanol-POSS in moderate yields has been reported.³⁰⁵ Feher and co-workers have also described a procedure of synthesizing heptasubstituted trisilanol-POSS derivatives via slow hydrolytic condensation of cyclohexyltrichlorosilane in aqueous acetone.³⁰⁶ In addition

synthesis of POSS derivatives by the hydrolytic condensation of modified aminosilanes have been reported.³⁰⁷ Heptasubstituted trisilanol-POSS can be subjected to hydrolytic condensation using a variety of catalysts and heating cycles resulting in the formation of fully functional closed cage POSS derivative with seven ligands of one type and an eight that is chemically different. Frequently, the eight ligand is a polymerizable functional group (acrylate, methacrylate, etc). As a consequence, a variety of copolymers containing POSS have been prepared to create an intriguing class of processible hybrid nanomaterials.³⁰⁸⁻³¹⁴



Scheme 2.1. Hydrolytic condensation of XSiY_3 monomers.²⁵⁶

POSS has received considerable attention because of its rigid framework that resembles silica. It offers a unique opportunity for preparing molecularly dispersed systems. POSS molecules have been incorporated into common polymers via copolymerization, grafting, or blending.^{315,316} POSS has been tested for a variety of applications both as a pure material and in POSS-based polymeric systems. Some potential applications include templates for catalysts,³¹⁷ low-k dielectric materials,³¹⁸ highly porous polymers,³¹⁹ flame retardants,³²⁰ high temperature lubricants,³²¹ dental materials,³²² resist coatings,³²³ and space-survivable coatings.³²⁴⁻³²⁷ Improvements, of thermo-oxidative stability,³²⁸⁻³³⁰ and mechanical properties of polymeric materials as a result of incorporated POSS have also been observed.³³¹⁻³³³ Research has also shown that POSS can increase T_g in composite materials.³³⁴⁻³³⁸ However, the effects of POSS have not been reported on surface glass transition temperatures. Part of this thesis critically

evaluates and brings insight to the surface T_g behavior of POSS containing polymer systems.

2.6 References

- (1) Roberts, G. G. *Adv. Phys.* **1985**, *34*, 475-512.
- (2) Kubono, A.; Okui, N. *Prog. Polym. Sci.* **1994**, *19*, 389-438.
- (3) Konry, T.; Heyman, Y.; Cosnier, S.; Gorgy, K. Marks, R.S. *Electrochimica Acta* **2008**, *53*, 5128-5135
- (4) McCulloch, I.; Man, H. T.; Song, K.; Yoon, H. *J. Appl. Polym. Sci.* **1994**, *53*, 665-676.
- (5) Zhang, J.; Luo, M.; Xiao, H.; Dong, J. *Chem. Mater.* **2006**, *18*, 4-6.
- (6) Subr, V.; Konak, C.; Laga, R.; Ulbrich, K. *Biomacromolecules* **2006**, *7*, 122-130.
- (7) Lynch, I.; de Gregorio, P.; Dawson, K. A. *J. Phys. Chem. B* **2005**, *109*, 6257-6261.
- (8) Park T.; Mirin N.; Lassiter J. B.; Nehl C. L.; Halas N. J.; Nordlander P. *ACS Nano*, **2008**, *2*, 25-32.
- (9) Badr, I. H. A.; Meyerhoff, M. E. *J. Am. Chem. Soc.* **2005**, *127*, 5318-5319.
- (10) Qi, Z.; Honma, I.; Zhou, H. *Anal. Chem.* **2006**, *78*, 1034-1041.
- (11) Lipert, R. J.; Shinar, R.; Vaidya, B.; Pris, A. D.; Porter, M. D.; Liu, G.; Grabau, T. D.; Dilger, J. P. *Anal. Chem.* **2002**, *74*, 6383-6391.
- (12) Thomas, S. W.; ; Amara, J. P.; Bjork, R. E.; Swager, T. M. *Chem. Commun.* **2005**, *36*, 4572-4574.
- (13) Sokuler, M.; Gheber, L. A. *Nano Lett.* **2006**, *6*, 848-853.
- (14) Kim, J. P.; Lee, W. -Y.; Kang, J. -W.; Kwon, S. K.; Kim, J. J.; Lee, J. S. *Macromolecules* **2001**, *34*, 7817-7821.
- (15) Bender, F.; Lange, K.; Barie, N.; Kondoh, J.; Rapp, M. *Langmuir* **2004**, *20*, 2315-2319.
- (16) Matsui, J.; Mitsuishi, M.; Aoki, A.; Miyashita, T. *J. Am. Chem. Soc.* **2004**, *126*, 3708-3709.
- (17) Carotenuto, G.; Her, Y. S.; Matijevic, E. *Ind. Eng. Chem. Res.* **1996**, *35*, 2929-2932.
- (18) Huang, Y.; Paloczi, G. T.; Yariv, A.; Zhang, C.; Dalton, L. R. *J. Phys. Chem. B.* **2004**, *108*, 8606-8613.
- (19) Hoflund, G. B.; Gonzalez, R. I.; Phillips, S. H. *J. Adhes. Sci. Technol.* **2001**, *15*, 1199-1211.
- (20) Wolfe W. L. *The Handbook of Optics*, McGraw-Hill, New York, 1978.
- (21) Klocek P. *Handbook of Infrared Optical Materials*, Marcel Dekker, New York, 1991.
- (22) Palik E. D., *Handbook of Optical Constants of Solids*, Academic Press, San Diego, 1985.
- (23) Palik E. D., *Handbook of Optical Constants of Solids II*, Academic Press, San Diego, 1991.
- (24) Ward L. *The Optical Constants of Bulk Materials and Films*, Institute of Physics Publishing, Bristol, 1994.
- (25) Efimov A. M. *Optical Constants of Inorganic Glasses*, CRC Press, Boca Raton, 1995.
- (26) Winton, P.; Scheiber, W. J. *J. Am. Chem. Soc.* **1939**, *61*, 3449-3451.
- (27) Zillies, J. C; Zwiorek, K.; Winter, G.; *Analyt. Chem.* **2007**, *79*, 4574-4580.

- (28) LeBel, R. G.; Goring, D. A. *J. Chem. Eng. Data* **1962**, 7, 100-101.
- (29) Simmons J. H.; Potter K.S., *Optical Materials*, Academic Press, San Diego, 2000.
- (30) Kasap S. O. *Principles of Electronic Materials and Devices*, McGrawHill, Boston, 2005.
- (31) Fox, M. *Optical Properties of Solids*, Oxford University Press, Oxford, 2001.
- (32) Toyozawa Y. *Optical Processes in Solids*, Cambridge University Press, Cambridge, 2003.
- (33) Looyenga H., *Mol. Phys.* **1965**, 9, 501-511.
- (34) Kumler, W. D. *J. Am. Chem. Soc.* **1935**, 57, 100-100.
- (35) Van Rysselberghe, P. *J. Phys. Chem.* **1932**, 36, 1152-1155.
- (36) Sankin, A.; Martin, C. C.; Lipkin, M. R. *Anal. Chem.* **1950**, 22, 643-649.
- (37) Foss, J. G.; Schellman, J. A. *J. Chem. Eng. Data* **1964**, 9, 551-553.
- (38) Samuni, A.; Czapski, G. *J. Phys. Chem.* **1970**, 74, 4592-4594.
- (39) Kurtz, S. S.; Lipkin, Jr. M. R. *J. Am. Chem. Soc.* **1941**, 63, 2158-2163.
- (40) Sinyukov, A. M.; Hayden, L. M. *J. Phys. Chem. B.* **2004**, 108, 8515-8522.
- (41) Mattoussi, H.; Srinivasarao, M.; Kaatz, P. G.; Berry, G. C. *Macromolecules* **1992**, 25, 2860-2868.
- (42) Baur, M. E.; Knobler, C. M.; Horsma, D. A.; Perez, P. *J. Phys. Chem.* **1970**, 74, 4594-4596.
- (43) Cauchy, A.L. *Bull. Sci. Math.* **1830**, 14, 6-10.
- (44) Cauchy, A.L. *M'emoire sur la Dispersion de la Lumiere*, Calve, Prague, 1836.
- (45) Smith, D.Y.; Inokuti, M.; Karstens, W. *J. Phys.: Cond. Matt.*, **2001**, 13, 3883-3893.
- (46) Ghosh, G.; Endo, M.; Iwasaki, T. *J. Light Wave Technol.* **1994**, 12, 1338-1342.
- (47) Ghosh, G. *Appl. Opt.*, **1997**, 36, 1540-1546.
- (48) Ghosh, G. *Phys. Rev. B*, **1998**, 57, 8178-8180.
- (49) Adachi, S. *Optical properties of crystalline and amorphous semiconductors*, Kluwer Academic Publishers, London, 1999.
- (50) Arwin, H.; Jansson, R. *Electrochimica Acta*, **1994**, 39, 211-215.
- (51) Goldwasser, E. L.; Benjamin, W. A. *Optics, waves, atoms, and nuclei: an introduction*, New York, Amsterdam, 1965.
- (52) Heavens, O. S.; Ditchburn, R. W. *Insights into optics*, John Wiley&Sons, Chichester, New York, 1987.
- (53) Jenkins, F. A.; White, H. E. *Fundamental of optics*, McGraw-Hill Book Company, New York, 1976.
- (54) Sheng, M. Y.; Wu, Y. H.; Feng, S. Z. *Appl. Opt.* **2007**, 46, 7049-7053.
- (55) Mendez, J. A.; Roblin, M. L. *Opt. Commun.* **1975**, 13, 142-147.
- (56) Berreman, D. W. *J. Opt. Soc. Am.* **1972**, 62, 502-510.
- (57) Leroy, J. L. *Polarization of light and astronomical observation*, Gordon and Breach Science Publishers, Amsterdam, Netherlands, 2000.
- (58) Maurer, A. *Lasers: light wave of the future*, New York, Arco Pub., 1982.
- (59) Weber, M. *Handbook of laser wavelengths*, Boca Raton, CRC Press, 1999.
- (60) Hakfoort, C. *Optics in the age of Euler: conceptions of the nature of light*, Cambridge University Press, Cambridge; New York, 1994.

- (61) Bhatia, A. B. *Monographs on the Physics and Chemistry of Materials*, Oxford Pergamon Press, New York 1969.
- (62) Vasicek, A. *Optics of thin films*, North-Holland Publishing Company, Amsterdam, 1960.
- (63) Thomas Preston, *The theory of light* M. A., London, Macmillan and Co., 1901.
- (64) Knittl, Z. *Optics of thin films; an optical multilayer theory*, John Wiley & Sons, London, 1976.
- (65) Fu, Z.; Santore, M. M. *Colloid Surface A*, **1998**, *135*, 63.
- (66) Bradley, T. F. *Ind. Eng. Chem. Analytical edition* **1931**, *3*, 304-309.
- (67) Nam, S. H.; Kang, J. W.; Kim, J. J. *Optics Commun.* **2006**, *266*, 332-335.
- (68) Karimi, M.; Albrecht, A.; Heuchel, M.; Weigel, T.; Lendlein, A.; *Polymer* **2008**, *49*, 2587-2594.
- (69) Zhao, C.; Park, C.; Prasad, P. N.; Zhang, Y.; Ghosal, S.; Burzynski, R. *Chem. Mater.* **1995**, *7*, 1237-1242.
- (70) Davy, K. W. M.; Braden, M. *Biomaterials* **1992**, *13*, 1043-1046.
- (71) Joo, W.; Park, M. S.; Kim, J. K. *Langmuir* **2006**, *22*, 7960-7963.
- (72) Linn, N. C.; Sun C. H.; Jiang, P. *Appl. Phys. Lett.* **2007**, *91*, 101108.
- (73) Zhang, X. -T.; Sato, O.; Taguchi, M.; Einaga, Y.; Murakami, T.; Fujishima, A. *Chem. Mater.* **2005**, *17*, 696-700.
- (74) Takazawa, K.; Kitahama, Y.; Kimura, Y.; Kido, G. *Nano Lett.* **2005**, *5*, 1293-1296.
- (75) Miller, L. W.; Tejedor, M. I.; Nelson, B. P.; Anderson, M. A. *J. Phys. Chem. B.* **1999**, *103*, 8490-8492.
- (76) Lal, S.; Taylor, R. N.; Jackson, J. B.; Westcott, S. L.; Nordlander, P.; Halas, N. J. *J. Phys. Chem. B.* **2002**, *106*, 5609-5612.
- (77) Yoon, J.; Lee, W.; Thomas, E. L. *Nano Lett.* **2006**, *6*, 2211-2214.
- (78) Billmeyer, F. V. *J. Applied Phys.* **1947**, *18*, 431-434.
- (79) Hahn, F. C.; Macht, L.; Fletcher, D. A. *Ind. Eng.* **1940**, 305.
- (80) Penning, J. P.; van Ruiten, J.; Brouwer, R.; Gabriëls W. *Polymer*, **2003**, *44*, 5869-5876.
- (81) Cranston, E. D.; Gray, D. G. *Coll. Surf. A* **2008**, In press, Available online.
- (82) Smith, W. H.; Saylor, C. P.; Wing, H. J. *Rubber Chem. Technol.* **1933**, *6*, 351.
- (83) Hakme, C.; Stevenson, I.; Voice, A.; *J. Polym. Sci. B* **2007**, *45*, 1950-1958.
- (84) Liaw, D. J.; Huang, C. C.; Chen, W. H. *Polymer* **2006**, *47*, 2337-2348.
- (85) Araki, J.; Wada, M.; Kuga, S.; Okano, T. *Langmuir* **2000**, *16*, 2413-2415.
- (86) American Institute of Physics Handbook, 3rd ed.; McGraw-Hill, New York, 1972.
- (87) Van Krevelen, D. W.; Hoftyzer, P. J. *J. Appl. Polym. Sci.* **1969**, *13*, 871-881.
- (88) Van Krevelen, D. W. *Properties of Polymers, estimation and correlation with chemical structure*, Elsevier Scientific Publishing Co., Amsterdam, 1976.
- (89) McGrath, J. E.; Rasmussen, L.; Shultz, A. R. *Polymer* **2006**, *47*, 4042-4057.
- (90) Yamashita, T.; Hayami, T.; Ishikawa, T.; *J. Photopolym. Sci. Technol.* **2007**, *20*, 353-358.
- (91) Groh, W. *Makromol. Chem.* **1988**, *189*, 2861-2874.

- (92) Seferis, J. C.; Brandrup, J.; Immergut, E. H.; Grulke, E.S. Refractive indices of polymers, *Polymer Handbook*, John&Wiley, New York, 1999.
- (93) Nielsen L. E.; Landel R. F. Mechanical Properties of Polymers and Composites Dekker, New York, 1994.
- (94) Tobolsky, A. V.; McLoughnlin, J. R. *J. Polym. Sci.* **1952**, 8, 543.
- (95) Aknolis, J. J. *J. Chem. Ed.* **1981**, 58, 892.
- (96) Boyer R. F. Encyclopedia of Polymer Science and Technology, Interscience, New York, 1977.
- (97) Shimanouchi, T. J.; Asahina, M.; Enomoto, S. *J. Polym. Sci.* **1962** 59, 93.
- (98) Katz, D.; Zervi, I. G. *J. Polym. Sci.* **1974**, 46, 139.
- (99) Katz, D.; Salee, G. *J. Polym. Sci. A* **1968**, 6, 801.
- (100) Ueberreiter, K.; Kanig, G. *J. Chem. Phys.* **1950**, 18, 399.
- (101) Eyring, H. *J. Chem. Phys.*, **1936**, 4, 283.
- (102) Fox, T. G.; Flory, P. J. *J. Appl. Phys.* **1950**, 21, 581-591.
- (103) Simha, R.; Boyer, R.F. *J. Chem. Phys.* **1962**, 37, 1003-1007.
- (104) Doolittle, A. K. *J. Appl. Phys.* **1951**, 22, 1471.
- (105) Williams, M. L.; Landel, R. F.; Ferry, J. D. *J. Am. Chem. Soc.* **1955**, 77, 3701.
- (106) Atkins, P. W. *Physical Chemistry*, Oxford University Press, New York, 1994.
- (107) Ehrenfest, P. *Leiden Comm. Rev.* **1933**, 43, 219
- (108) Kauzmann, W. *Chemical Reviews* **1948**, 43, 219-256.
- (109) Gibbs, J. H.; Di Marzio, E.A. *J. Chem. Physics* **1958**, 28, 373-383.
- (110) Gibbs, J. H.; Di Marzio, E. A. *J. Chem. Physics* **1958**, 28, 807-813.
- (111) Gibbs, J. H.; Di Marzio *J. Polymer Sci.* **1959**, 40, 121-131.
- (112) Adam, G.; Gibbs J. H. *J. Chem. Phys.* **1965**, 43, 139-146.
- (113) Vijayakumar, C. T.; Kothandaraman, H. *Thermochim. Acta* **1987**, 118, 159-161.
- (114) Miaudet, P.; Derré, A.; Maugey, M.; Zakri, C.; Piccione, P. M.; Inoubli, R.; Poulin, P. *Science* **2007**, 318, 1294-1296.
- (115) Wunderlich, B.; Grebowicz, J. *Adv. Polymer Sci.* **1984**, 60, 1-59.
- (116) Moynihan, C.T. Eastal, A. J.; Wilder, J.; Tucker, J. *J. Phys. Chem.* **1974**, 78, 2673-2677.
- (117) Ellison, C. J.; Broadbelt, L. J.; Torkelson, J. M. *Science* **2005**, 309, 456-459.
- (118) Wang, Y.; Chan, C. M.; Jiang, Y.; Li, L.; Ng, K. M. *Macromolecules* **2007**, 40, 4002-4008.
- (119) Schall, P.; Weitz, D. A.; Spaepen, F. *Science* **2007**, 318, 1895-1899.
- (120) Dagdug L.; Garcia-Colin L. S. *Physica A* **1998**, 250, 133-141.
- (121) Gasemjit, P.; Johannsmann, D.; *J. Polym. Sci. B* 44, **2006**, 3031.
- (122) Fakhraai, Z.; Forrest, J. A. *Science* **2008**, 319, 600-604.
- (123) Buchholz, J.; Paul, W.; Varnik, F.; Binder, K. *J. Chem. Phys.* **2002**, 117, 7364-7372.
- (124) Streit-Nierobisch, S.; Gutt, C.; Paulus M.; *Phys. Rev. B* **2008**, 77, 041410/1-4.
- (125) Jenckel, E.; Ueberreiter, Z. *Phys. Chem.* **1938**, 182, 361.
- (126) Kelly, F. N.; Bueche, F. *J. Polym. Sci.* **1961**, 50, 549.
- (127) Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1968**, 1, 537.
- (128) Fox, T. G.; Loshaek, S. *J. Polym. Sci.* **1955**, 15, 371.
- (129) Gordon, M.; Taylor, J. S. *Appl. Chem.* **1952**, 2, 493-500.

- (130) Di Marzio, E. A. *Polymer* **1990**, *31*, 2294-2298.
- (131) Di Marzio, E. A. *Ann. NY Acad. Sci.* **1981**, *371*, 1.
- (132) Di Marzio, E. A. *Polymer* **1990**, *31*, 2294-2298.
- (133) Fox, T. G. *Bull. Am. Phys. Soc.* **1965**, *1*, 123.
- (134) Wallace, W. E.; Fischer, D. A.; Efimenko, K.; Wu, W.-L.; Genzer, J. *Macromolecules* **2001**, *34*, 5081-5082.
- (135) de Gennes, P. G. *Eur. Phys. J. E* **2000**, *12*, 201.
- (136) Lin, E. K.; Wu, W.; Satija, S. *Macromolecules* **1997**, *30*, 7224-7231.
- (137) Lin, E. K.; Kolb, R.; Satija, S.; Wu, W. *Macromolecules* **1999**, *32*, 3753-3757.
- (138) Mansfield, K. F.; Theodorou, D. N. *Macromolecules* **1991**, *24*, 6283-6294.
- (139) Baschnagel, J.; Binder, K. *Macromolecules* **1995**, *28*, 6808-6818.
- (140) Roth, C. B.; McNerny, K. L.; Jager, F. W.; Torkelson, J. M. *Macromolecules*, **2007**, *40*, 2568-2574.
- (141) Haramina, T.; Kirchheim, R.; Tibrewala, A.; Peiner, E. *Polymer*, **2008**, *49*, 2115-2118.
- (142) Wu, W. L.; Sambasivan, S.; Wang, C. Y.; Wallace, W. E.; Genzer, J.; Fisher, D. A. *Eur. Phys. J. E* **2003**, *12*, 127-132.
- (143) Papaleo, R. M.; Leal, R.; Carreira, W. H.; Barbosa, L. G.; Bulla, A.; Bello, I. *Phys. Rev.* **2006**, *74*, 094203.
- (144) Binder, K. *Adv. Polym. Sci.* **1994**, *112*, 181-299.
- (145) Keddie, J. L.; Jones, R. A.; Cory, R. A. *Faraday Discuss.* **1994**, *98*, 219-230.
- (146) Keddie, J. L.; Jones, R. A.; Cory, R. A. *Europhys. Lett.* **1994**, *27*, 59-64.
- (147) Mundra, M. K.; Ellison, J. C.; Behling, R. E.; Torkelson, J. M. *Polymer*, **2006**, *47*, 7747-7759.
- (148) Lee, J. Y.; Su, K. E.; Edwin, P. C.; Zhang, Q.; Emrick, T.; Crosby, A. J. *Macromolecules*, **2007**, *40*, 7755-7757.
- (149) Dutcher, J. R.; Ediger, M. D. *Science*, **2008**, *319*, 577-578.
- (150) Fakhraei, Z.; Forrest, J. A. *Science*, **2008**, *319*, 600-604.
- (151) Nierobish, S. S.; Gutt, C.; Paulus, Tolan, M. *Phys. Rev.* **2008**, *77*, 041410R.
- (152) Park, C. H.; Kim, J. H.; Ree, M.; Sohn, B. H.; Jung, J. C.; Zin, W. C. *Polymer*, **2004**, *45*, 4507-4513.
- (153) Vogt, B. D.; Campbell, C. G. *Polymer*, **2007**, *48*, 7169-7175.
- (154) Faupel, F.; Zaporotjchenko, V.; Shiferaw, T.; Erichsen, J. *Eur. Phys. J. E* **2007**, *24*, 243-246.
- (155) Zaitseva, V. A.; Zaitsev, B. V.; Rudoy, M. V. *Surface Science*, **2004**, *566*, 821-825.
- (156) Roth, C. B.; Pound, A.; Kamp, S. W.; Murray, C. A.; Dutcher, J. R. *Eur. Phys. J. E.* **2006**, *20*, 441-448.
- (157) Ellison, C. J.; Torkelson, J. M. *Nat. Mater.* **2003**, *2*, 695-700.
- (158) Ellison, C. J.; Mundra, M. K.; Torkelson, J. M. *Macromolecules* **2005**, *38*, 1767-1778.
- (159) Forrest, J. A.; Dalnoki-Veress, K.; Stevens, J. R.; Dutcher, J. R. *Phys. Rev. Lett.* **1996**, *77*, 2002-2005.
- (160) Forrest, J. A.; Mattsson, J. *Phys. Rev. E* **2000**, *61*, R53-R56.
- (161) Mattsson, J.; Forrest, J. A.; Borjesson, L. *Phys. Rev. E* **2000**, *62*, 5187-5200.

- (162) Forrest, J. A.; Dalnoki-Veress, K.; Stevens J. R.; Dutcher, J. R. *Phys. Rev. Lett.* **1997**, *56*, 5705.
- (163) Forrest, J. A.; Dalnoki-Veress, K.; Stevens J. R.; Dutcher, J. R. *Phys. Rev. Lett.* **1998**, *58*, 6109-6114.
- (164) Dalnoki-Veress, K.; Forrest, J. A.; Murray, C.; Gigault, C.; Dutcher, J. R. *Phys. Chem. B* **2000**, *104*, 2460.
- (165) Van Zanten, J. H.; Wallace, W. E.; Wu, W. *Phys. Rev. E* **1996**, *53*, 2053-2056.
- (166) Tsui, O. K. C.; Russel, T. P.; Hawker, C. J. *Macromolecules*, **2001**, *34*, 5535-5539.
- (167) Blum, F. D.; Young, E. N.; Smith, G.; Sitton, O. C.; *Langmuir* **2006**, *22*, 4741-4744.
- (168) Priestley, R. D.; Broadbelt, L. J.; Ellison, C. J.; Torkelson J. M.; *Macromolecules*, **2005**, *38*, 654-657.
- (169) Tate, R. S.; Fryer, D. S.; Pasqualini, S.; Montague, M. F.; de Pablo, J. J.; Nealey, P. F.; *J. Chem. Phys.* **2001**, *115*, 9982-9990.
- (170) Keddie, J. L.; Jones, R. A. L. *Isr. J. Chem.* **1995**, *35*, 21-26.
- (171) Orts, W. J.; Zanten, J. H., Wu, W. L. Satija, S. K. *Phys. Rev. Lett.* **1993**, *71*, 867-870.
- (172) Kanaya, T.; Miyazaki, T.; Watanabe, H.; Nishida, K. Yamana, H.; Tasaki, S. *Polymer* **2003**, *44*, 3769-3773.
- (173) Soles, C. L.; Douglas, J. F.; Jones, R. L.; Wu, W. L. *Macromolecules*, **2004**, *37*, 2901-2908.
- (174) Beaucage, G.; Composto, R.; Stein, R. S. *J. Polym. Sci. B* **1993**, *31*, 319-326.
- (175) Ellison, C. J.; Kim, S. D., Hall, D. B.; Torkelson, J. M. *Eur. Phys. J. E.* **2002**, *8*, 155-166.
- (176) Aharoni, S.M. *J. Appl. Polym. Sci.* **1973**, *42*, 795-803.
- (177) Kovacs, A. J. *J. Appl. Polym. Sci.* **1958**, *30*, 131
- (178) Cohen, Y.; Reich, S. *J. Polym Sci Part B* **1981**, *19*, 599-608.
- (179) Ree, M.; Park, Y. H.; Kim, K.; Kim, S. I.; Cho, C. K.; Park, C. E. *Polymer*, **1997**, *38*, 6333-6345.
- (180) Litteken, C. S.; Strohhband, S.; Dauskardt, R. H. *Acta Mater.* **2005**, *53*, 1955 - 1961.
- (181) Jalali-Jafari, B.; Savaloni, H.; Gholipour-Shahraki, M. *J. Appl. Polym. Sci.* **2007**, *244*, 3620-3638.
- (182) Chung, H.; Joe, Y.; Han, H. *J. Appl. Polym. Sci.* **1999**, *74*, 3287-3298.
- (183) Mukherjee, M.; Bhattacharya, M.; Sanyal, M. K.; Geue, T.; Grenzer, J.; Pietsch, U. *Phys. Rev. E.* **2002**, *66*, 061801.
- (184) Kawana, S.; Jones, R. A. L.; *Eur. Phys. J. E.* **2003**, *10*, 223-230.
- (185) Qasmi, M.; Delobelle, P.; Richard, F. *Surf. Coat. Technol.* **2006**, *200*, 4185-4194.
- (186) Phillip, S.; Wilson, R. S. *Macromolecules* **1973**, *6*, 902-908.
- (187) Victor, J. A.; Kim, S. D.; Klein, A.; Sperling, L. H. *J. Appl. Polym. Sci.* **1999**, *73*, 1763.
- (188) Denglinger, D; Abarra, E.; Allen, K.; Rooney, P.; Messer, M. Watson, S.; Hellman, F. *Rev. Sci. Inst.* **1994**, *65*, 946.
- (189) Zink, B.; Rexaz, B.; Sappey, R.; Hellman, F *Rev. Sci. Inst.* **2002**, *73*, 1841.

- (190) See, Y. K.; Cha, J.; Chang, T.; Ree, M. *Langmuir* **2000**, *16*, 2351-2355.
- (191) Wallace, W. E.; van Zanten, J. H.; Wu, W. L. *Phys. Rev. E* **1995**, *52*, 3329-3332.
- (192) Buddy, D. R.; Tsukruk, Vladimir, V. V. *Scanning probe microscopy of polymers*, American Chemical Society, Washington, DC, 1996.
- (193) Overney, M. R.; Buenviaje, C.; Luginbuhl, R.; Dinelli F. *J. Therm. Analys. Cal.* **2000**, *59*, 205-225.
- (194) Vourdas, N.; Karadimos, G.; Goustouridis, D. *J. Appl. Polym. Sci.* **2006**, *102*, 4764-4774.
- (195) Cappella, B.; Kaliappan, S. K.; Sturm, H. *Macromolecules* **2005**, *38*, 1874-1881.
- (196) Miyazaki, T.; Inoue, R.; Nishida, K. *Eur. Phys. J.* **2007**, *141*, 203-206.
- (197) Langmuir, I. *Trans. Faraday Soc.* **1920**, *15*, 62-74.
- (198) Blodgett, K. B. *J. Am. Chem. Soc.* **1935**, *57*, 1007-1022.
- (199) Blodgett, K. B.; Langmuir, I. *Phys. Rev.* **1937**, *51*, 964-982.
- (200) Barraud, A.; Leloup, J.; Lesieur, P. *Thin Solid Films* **1985**, *133*, 113-116.
- (201) Gaines, G. L. *Insoluble monolayers at liquid-gas interface*, Interscience, New York, 1966.
- (202) Petty, M. C. *Langmuir-Blodgett films: an introduction*, Cambridge University Press, Cambridge, 1996.
- (203) Kaganer, V. M.; Mohwald, H.; Dutta, P. *Rev. Mod. Phys.* **1999**, *71*, 779-819.
- (204) Langmuir, I. *J. Am. Chem. Soc.* **1917**, *39*, 1848-1906.
- (205) Williams, A. A.; Day, B. S.; Kite, B. L.; McPherson, M. K.; Slebodnick, C.; Morris, J. R.; Gandour, R. D. *Chem. Commun.* **2005**, *40*, 5053-5055.
- (206) Buzin, A. I.; Godovsky, Y. K.; Makarova, N. N.; Fang, J.; Wang, X.; Knobler, C. M. *J. Phys. Chem. B* **1999**, *103*, 11372-11381.
- (207) Fox, H. W.; Taylor, P. W.; Zisman, W. A. *J. Ind. Eng. Chem.* **1947**, *39*, 1401-1409.
- (208) Granick, S.; Clarson, S. J.; Formoy, T. R.; Semlyen, J. A. *Polymer* **1985**, *26*, 925- 929.
- (209) Hottle, J. R.; Deng, J. J.; Kim, H. J.; Esker, A. R. *Langmuir* **2005**, *21*, 2250-2259.
- (210) Sutherland, J. E.; Miller, M. L. *J. Polym. Sci., Polym. Lett. Ed.* **1969**, *7*, 871-876.
- (211) Gabrielli, G. ; Guarini, G. G. T. *J. Colloid Interface Sci.* **1978**, *64*, 185-187.
- (212) Kawaguchi, M.; Sauer, B. B.; Yu, H. *Macromolecules* **1989**, *22*, 1735-1743.
- (213) Ni, S.; Lee, W.; Li, B.; Esker, A. R. *Langmuir* **2006**, *22*, 3672-3677.
- (214) Pelletier, I.; Pezolet, M. *Macromolecules* **2004**, *37*, 4967-4973.
- (215) Li, B.; Wu, Y.; Liu, M.-H.; Esker, A. R. *Langmuir* **2006**, *22*, 4902-4905.
- (216) Lee, W. K.; Gardella, J. A. *Langmuir* **2000**, *16*, 3401-3406.
- (217) Cheyne, R. B.; Moffitt, M. G. *Langmuir*, **2006**, *22*, 8387-8396.
- (218) Felder, D; Nava, M. G.; Carreon, M. D. *Chem. Act.* **2002**, *85*, 288-319.
- (219) Nalwa, H. S.; Kakuta, A. *Appl. Organomet. Chem.* **1992**, *6*, 645-678.
- (220) Peleshanko, S.; Gunawidjaja, R.; Petrash S. *Macromolecules*, **2006**, *39*, 4756-4766.

- (221) Kmetko, J.; Kewalramani, S.; Evmenenko, G.; Yu, C.; Dutta, P. *Int. J. NanoSci.* **2005**, *4*, 849-854.
- (222) Rybak, B. M. Ornatska, M.; Bergman, Kathryn N.; Genson, Kirsten L.; Tsukruk, Vladimir V. *Langmuir* **2006**, *22*, 1027-1037.
- (223) Pockles, A. *Nature* **1891**, *43*, 437-439.
- (224) Pockles, A. *Nature* **1893**, *48*, 152-154.
- (225) Pockles, A. *Nature* **1894**, *50*, 223-224.
- (226) Rayleigh, L. *Philos. Mag.* **1899**, *48*, 321-337.
- (227) Hardy, W. B. *Proc. Roy. Soc. London* **1912**, *86*, 610-635.
- (228) Hann, R. A. *Langmuir-Blodgett Films*, Roberts, G. G., Ed.; Plenum Press, New York, 1990.
- (229) Adam, N. K. *Proc. Roy. Soc.* **1922**, *101A*, 516-531.
- (230) Crisp, D. J. *J. Colloid Sci.* **1946**, *1*, 49-70.
- (231) Dynarowicz-Latka, P.; Dhanabalan, A.; Oliveira, O. N., Jr. *Adv. Colloid Interface Sci.* **2001**, *91*, 221-293.
- (232) Myrzakozha, D. A.; Hasegawa, T.; Nishijo, J.; Imae, T.; Ozaki, Y. *Langmuir* **1999**, *15*, 3595-3600.
- (233) Ehlert, R. C. *J. Colloid Sci.* **1965**, *20*, 387-390.
- (234) Grundy, M. J.; Musgrove, R. J.; Richardson, R. M.; Roser, S. J.; Penfold, J. *Langmuir* **1990**, *6*, 519-521.
- (235) Schwartz, D. K. *Surf. Sci. Rep.* **1997**, *27*, 241-334.
- (236) Honig, E. P.; Hengst, J. H.; den Engelsen, D. J. *J. Colloid Interface Sci.* **1973**, *45*, 92-102.
- (237) Lutt, M.; Fitzsimmons, M. R.; Li, D. *J. Phys. Chem. B.* **1998**, *102*, 400-405.
- (238) Evmenenko, G.; Yu, C.-J.; Kewalramani, S.; Dutta, P. *Langmuir* **2004**, *20*, 1698-1703.
- (239) Wu, J. C. Lin, T. L.; Yang, C. P. *Colloid Surface Sci. A* **2006**, *284*, 103-108.
- (240) Lin, T. L.; Wu, J. C.; Jeng, U. S. *J. Appl. Cryst.* **2007**, *40*, 680-683.
- (241) Tiilikainen, J.; Bosund, V.; Tilli, J. M. *J. Phys. D* **2007**, *40*, 6000-6004.
- (242) Koo, J.; Park, S.; Satija, S.; Tikhonov, A.; Sokolov, J. C.; Rafailovich, M. H. Koga, T. *J. Colloid Interface Sci.* **2008**, *318*, 103-109.
- (243) Gibson, P. N. In *Surface and thin film analysis*, Wiley-VCH, Weinheim, 2002.
- (244) Daillant, J.; Gibaud, A. *X-ray and Neutron Reflectivity: Principles and Applications*, Springer, New York, 1999.
- (245) Kiessig, H. *Ann. Physik* **1931**, *10*, 715-768.
- (246) Kiessig, H. *Ann. Physik* **1931**, *10*, 769-788.
- (247) Parratt, L. G. *Phys. Rev.* **1954**, *95*, 359-369.
- (248) Thompson, C.; Saraf, R. F.; Jordan-Sweet, J. L. *Langmuir* **1997**, *13*, 7135-7140.
- (249) Arias-Marin, E.; Arnault, J. C.; Guillon, D.; Maillou, T.; Le Moigne, J.; Geffroy, B.; Nunzi, J. M. *Langmuir* **2000**, *16*, 4309-4318.
- (250) Youm, S. G.; Paeng, K.; Choi, Y. W.; Park, S.; Sohn, D.; Seo, Y. S.; Satija, S. K.; Kim, B. G.; Kim, S.; Park, S. Y. *Langmuir* **2005**, *21*, 5647-5650.
- (251) Karabiyik, U.; Mao, M.; Satija, S. K.; Esker, A. R. *Polym. Prep.* **2007**, *48*, 974-975.

- (252) Matsuda, A.; Sugi, M.; Fukui, T.; Lizima, S.; Miyahara, M.; Otsubo, Y. *J. Appl. Phys.* **1977**, *48*, 771-774.
- (253) Panambur, G.; Robert, C.; Zhang, Y. B.; Bazuin, C. G.; Ritcey, A. M. *Langmuir* **2003**, *19*, 8859-8866.
- (254) Schalchli, A.; Benattar, J. J.; Tchoreloff, P.; Zhang, P.; Coleman, A. W. *Langmuir* **1993**, *9*, 1968-1970.
- (255) Kang, Y. J.; Kim, H.; Kim, E.; Kim, I.; Ha, C. S. *Coll. Surf., A* **2008**, *313*, 585-589.
- (256) Pomerantz, M.; Segmuller, A. *Thin Solid Films* **1980**, *68*, 33-45.
- (257) Pomerantz, M.; Segmuller, A.; Netzer, L.; Sagiv, J. *Thin Solid Films* **1985**, *132*, 153-162.
- (258) Stamm, M.; Majkrzak, C. F. *Polym. Prepr.* **1987**, *28*, 18.
- (259) Drude, P. *Ann. Phys.* **1887**, *32*, 584-625.
- (260) Drude P. *Ann. Phys.* **1888**, *34*, 489.
- (261) Azzam, A.; and Bashara, N. M. *Ellipsometry and polarized light*, North Holland, Amsterdam, 1977.
- (262) Tompkins, H. G.; McGahan, W. A. *Spectroscopic ellipsometry and reflectometry: A user's guide*, John Wiley & Sons, Inc., New York, 1999.
- (263) Tompkins, H. G.; Irene, E. A. Eds, *Handbook of ellipsometry*, William Andrew, New York, 2005.
- (264) Schubert, M. *Infrared ellipsometry on semiconductor layer structures: Phonons, plasmons, and polaritons*, Springer, Heidelberg. 2004.
- (265) An, I.; Li, Y. M.; Nguyen, H. V.; and Collins, R. W. *Rev. Sci. Instrum.* **1992**, *63*, 3842-3848.
- (266) Lyapin, A.; Jeurgens, L. P. H.; Graat, P. C. J.; Mittemeijer, E. J. *J. Appl. Phys.* **2004**, *96*, 7126-7135.
- (267) Platzman, I.; Brener, R.; Haick, H.; Tannenbaum, R. *J. Phys. Chem. C* **2008**, *112*, 1101-1108.
- (268) Tsankov, D.; Hinrichs, K.; Korte, E. H.; Dietel, R.; Roseler, A. *Langmuir* **2002**, *18*, 6559-6564.
- (269) Cresswell J. P. *Langmuir* **1994**, *10*, 3727-3729.
- (270) Nagy, N.; Deak, A.; Horvolgyi, Z.; Fried, M.; Agod, A.; Barsony, I. *Langmuir* **2006**, *22*, 8416-8423.
- (271) Paudler, M.; Ruths, J.; Riegler, H. *Langmuir* **1992**, *8*, 184-189.
- (272) Kohoutek, T.; Orava, J.; Hrdlicka, M.; Wagner, T.; Vlcek, Mil.; Frumar, M. J. *Phys. Chem. Solids* **2007**, *68*, 2376-2380.
- (273) Vedam, K. *Thin Solid Films*, **1998**, *9*, 313-3141.
- (274) Rothen, A. *Rev. Sci. Instrum.* **1945**, *16*, 26-30.
- (275) Paik, W.; Bockris, J. O'M. *Surf. Sci.* **1971**, *28*, 61-68.
- (276) Moule, A. J.; Meerholz, K. *Appl. Phys. Lett.* **2007**, *91*, 061901.
- (277) Merkulov, V. S. *Opt. Spect.* **2007**, *103*, 629-631.
- (278) Aspnes, D. E. *Thin Solid Films* **2004**, *455*, 3-13.
- (279) Hecht, E. *Optics*, Addison Wesley, San Francisco, 2002.
- (280) Born, M.; Wolf, E. *Principles of optics*, Cambridge University Press, Cambridge, 1999.

- (281) Kim, Y.-T.; Allara, D. L.; Collins, R. W.; Vedam, K. *Thin Solid Films* **1990**, *193*, 350-360.
- (282) Postava, K.; Yamaguchi, T; Horie, M. *Appl. Phys. Lett.* **2001**, *79*, 2231-2233.
- (283) Sturm, J.; Tasch, S.; Niko, A.; Leising, G.; Toussaere, E.; Zyss, J.; Kowalczyk, T. C.; Singer, K. D.; Scherf, U.; Huber, J. *Thin Solid Films* **1997**, *298*, 138-142.
- (284) Efremov, M.Y.; Soofi, S. S.; Kiyanova, A. V.; Munoz, C. J.; Burgardt, P.; Cerrina, F.; Nealey, P. F. *Rev. Sci. Instr.* **2008**, *79*, 043903.
- (285) Folkers, J. P.; Laibinis, P. E.; Whitesides, G. M. *Langmuir* **1992**, *8*, 1330-1341.
- (286) Wang, C.; Pan, X.; Sun, C.; Urisu, T. *Appl. Phys. Lett.* **2006**, *89*, 233105.
- (287) Lecourt, B.; Blaudez, D.; Turlet, J. -M. *J. Opt. Soc. Am. A*, **1998**, *15*, 2769-2782.
- (288) Tsankov, D.; Hinrichs, K.; Röseler, A.; Korte, E. H. *Phys. Stat. Sol. A* **2001**, *188*, 1319-1329.
- (289) Govindaraju T.; Bertics P. J.; Raines R. T.; Abbott N. L. *J. Am. Chem.* **2007**, *129*, 11223-11231.
- (290) Schubert, M.; Rheinländer, B.; Cramer, C.; Schmiedel, H.; Woollam, J. A.; Herzinger, C. M.; Johs, B. *J. Opt. Soc. Am. A* **1996**, *13*, 1930-1940.
- (291) Johnson, P. M.; Olson, D. A.; Pankratz, S.; Bahr, C.; Goodby, J. W.; Huang, C. C. *Phys. Rev. E* **2000**, *62*, 8106-8113.
- (292) Abbate, G.; Tkachenko, V.; Marino, A.; Vita, F.; Giocondo, M.; Mazzulla, A.; De Stefano, L. *J. Appl. Phys.* **2007**, *101*, 073105.
- (293) Hilfiker, J. N.; Johs, B.; Herzinger, C. M.; Elman, J. F.; Montbach, E.; Bryant, D. Bos, P. J. *Thin Solid Films* **2004**, *455*, 596-600.
- (294) Pittman, C. U.; Jr.; Li, G. Z.; Ni, H. *Macromol. Symp.* **2003**, *196*, 301-325.
- (295) Bornhauser, P.; Calzaferri, G. *J. Phys. Chem.* **1996**, *100*, 2035-2044.
- (296) Baney, R. H.; Itoh, M.; Sakakibara, A.; Suzuki, T. *Chem. Rev.* **1995**, *95*, 1409-1430.
- (297) Haddad, T. S.; Viers, B. D.; Phillips, S. H. *J. Inorg. Organomet. Polym.* **2001**, *11*, 155-164.
- (298) Gidden J.; Kemper P. R.; Shammel E.; Fee D. P.; Anderson S.; Bowers, M. T. *Int. J. Mass Spectrom.* **2003**, *222*, 63-73.
- (299) Provatas, A.; Matisons, J. G. *Trends Polym. Sci.* **1997**, *5*, 327-332.
- (300) Brown, J. F. Jr. *J. Am. Chem. Soc.* **1965**, *87*, 4317-4324.
- (301) Scott, D. W. *J. Am. Chem. Soc.* **1946**, *68*, 356-358.
- (302) Feher, F. J.; Newman, D. A.; Walzer, J. F. *J. Am. Chem. Soc.* **1989**, *111*, 1741-1748.
- (303) Xu, H.; Yang, B.; Gao, X.; Li, C.; Guang, S. *J. Appl. Polym. Sci.* **2006**, *101*, 3730-3735.
- (304) Harrison, P.G. *J. Organomet. Chem.* **1997**, *542*, 141-183
- (305) Laine, R. M.; Zhang, C.; Sellinger, A.; Viculis, L. *Appl. Organomet. Chem.* **1998**, *12*, 715-723.
- (306) Feher, F. J.; Budzichowski, T. A.; Blanski, R. L.; Weller, K. J.; Ziller, J. W. *Organometallics* **1991**, *10*, 2526-2528.

- (307) Fasce, D. P.; Williams, R. J. J.; Mechin, F.; Pascault, J. P.; Llauro, M. F.; Petiaud, R. *Macromolecules* **1999**, *32*, 4757-4763.
- (308) Haddad, T. S.; Lichtenhan, J. D. *Macromolecules* **1996**, *29*, 7302-7304.
- (309) Tsuchida, A.; Bolln, C.; Sernetz, F. G.; Frey, H.; Muelhaupt, R. *Macromolecules* **1997**, *30*, 2818-2824.
- (310) Lichtenhan, J. D.; Otonari, Y. A.; Carr, M. J. *Macromolecules* **1995**, *28*, 8435-8437.
- (311) Lichtenhan, J. D.; Vu, N. Q.; Carter, J. A.; Gilman, J. W.; Feher, F. J. *Macromolecules* **1993**, *26*, 2141-2142.
- (312) Sellinger, A.; Laine, R. M. *Macromolecules* **1996**, *29*, 2327-2330.
- (313) Bliznyuk, V. N.; Tereshchenko, T. A.; Gumenna, M. A.; Gomza, Yu P.; Shevchuk, A. V.; Klimenko, N. S.; Shevchenko, V. V. *Polymer* **2008**, *49*, 2298-2305.
- (314) Iacono, S. T.; Budy, Stephen M.; Mabry, Joseph M.; Smith, Dennis W. *Polymer* **2007**, *48*, 4637-4645.
- (315) Haddad, T. S.; Stapleton, R.; Jeon, H. G.; Mather, P. T.; Lichtenhan, J. D.; Phillips, S. *Polym. Prepr.* **1999**, *217*, 608-608.
- (316) Paul, R.; Karabiyik, U.; Swift, M. C.; Esker, A. R. *Langmuir*, **2008**, *24*, 5079-5090.
- (317) Feher, F. J.; Budzichowski, T. A. *Polyhedron* **1995**, *14*, 3239-3253.
- (318) Hao, N.; Boehning, M.; Schoenhals, A. *Macromolecules*, **2007**, *40*, 9672-9679.
- (319) Zhang, C.; Babonneau, F.; Bonhomme, C.; Laine, R. M.; Soles, C. L.; Hristov, H. A.; Yee, A. F. *J. Am. Chem. Soc.* **1998**, *120*, 8380-8391.
- (320) Pielichowski, K.; Njuguna, J.; Janowski, B.; Pielichowski, J. *Adv. Polym. Sci.* **2006**, *201*, 225-296.
- (321) Blanski, R.; Leland, J.; Viers, B.; Phillips, S. H. *Proc. Int. Sampe Symp. Exhib.* **2002**, *47*, 1503-1507.
- (322) Dodiuk-Kenig, H.; Maoz, Y.; Lizenboim, K.; Eppelbaum, I.; Zalsman, B.; Kenig, S. *J. Adhes. Sci. and Technol.* **2006**, *20*, 1401-1412.
- (323) Bellas, V.; Tegou, E.; Raptis, I.; Gogolides, E.; Argitis, P.; Iatrou, H.; Hadjichristidis, N.; Sarantopoulou, E.; Cefalas, A. C. *J. Vac. Sci. Technol., B* **2002**, *20*, 2902-2908.
- (324) Gilman, J. W.; Schlitzer, D. S.; Lichtenhan, J. D. *J. Appl. Polym. Sci.* **1996**, *60*, 591-596.
- (325) Gonzalez, R. I.; Phillips, S. H.; Hoflund, G. B. *J. Spacecraft Rockets* **2000**, *37*, 463-467.
- (326) Phillips, S. H.; Gonzalez, R. I.; Blanski, R. L.; Viers, B. D.; Hoflund, G. B. *Proc. Int. SAMPE Symp. Exhibition* **2002**, *47*, 1488-1496.
- (327) Tomczak, S. J.; Marchant, D.; Svejda, S.; Minton, T. K.; Brunsvold, A. L.; Gouzman, I.; Grossman, E.; Schatz, G. C.; Troya, D.; Sun, L.; Gonzalez, R. I. *Mater. Res. Soc. Symp. Proc.* **2005**, *851*, 395-406.
- (328) Huang, J.-C.; He, C.-B.; Xiao, Y.; Mya, K. Y.; Dai, J.; Siow, Y. P. *Polymer* **2003**, *44*, 4491-4499.
- (329) Markovic, E; Clarke, S.; Matisons, J.; Simon, G. P. *Macromolecules* **2008**, *41*, 1685-1692.

- (330) Smentkowski, V. S.; Duong, H. M.; Tamaki, R.; Keenan, M. R.; Ohlhausen, J. A. Tony; Kotula, P. G. *Appl. Surface Sci.* **2006**, 253, 1015-1022.
- (331) Pellice, S. A.; Fasce, D. P.; Williams, R. J. J. *J. Polym. Sci., Part B: Polym. Phys.* **2003**, 41, 1451-1461.
- (332) Fu, B. X.; Gelfer, M. Y.; Hsiao, B. S.; Phillips, S.; Viers, B.; Blanski, R.; Ruth, P. *Polymer* **2003**, 44, 1499-1506.
- (333) Bharadwaj, R. K.; Berry, R. J.; Farmer, B. L. *Polymer* **2000**, 41, 7209-7221.
- (334) Karabiyik, U.; Paul, R.; Swift, M. C.; Esker, A. R. *PMSE Prep.* **2008**, 98, 863-864.
- (335) Xu, H.; Kuo, S. -W.; Lee, J.-S.; Chang, F. C. *Macromolecules* **2002**, 35, 8788-8793.
- (336) Lee, A.; Litchenhan, J. D. *Macromolecules* **1998**, 31, 4970-4974.
- (337) Huang, J. -C.; He, C. -B.; Xiao, Y.; Mya, K. Y.; Dai, J.; Siow, Y. P. *Polymer* **2003**, 44, 4491-4499.
- (338) Song, X. Y.; Geng, H. P.; Li, Q. F. *Polymer* **2006**, 47, 3049-3056.

CHAPTER 3

Materials and Experimental Methods

3.1 Materials

The following compounds were used without further purification: poly(*tert*-butyl acrylate) (PtBA) (number average molar mass, $M_n = 5$ and $23 \text{ kg}\cdot\text{mol}^{-1}$; polydispersity index, $M_w/M_n = 1.12$ and 1.08), and polystyrene (PS) ($M_n = 604$, 76 , and $23 \text{ kg}\cdot\text{mol}^{-1}$; $M_w/M_n = 1.05$, 1.04 , and 1.05 , respectively) samples were obtained from Polymer Source, Inc., and poly(methyl methacrylate) (PMMA) ($M_n = 107 \text{ kg}\cdot\text{mol}^{-1}$, $M_w/M_n = 1.1$) was obtained from Polymer Laboratories, Ltd. A polyhedral oligomeric silsesquioxane (POSS), trisilanolphenyl-POSS (TPP), was obtained from Hybrid Plastics, Inc. Size-exclusion chromatography (SEC) was conducted on a Waters system that was equipped with three in-line PLgel 5mm Mixed-C columns, an autosampler, a 410 RI detector, a Viscotek 270 dual detector, and an in-line Wyatt Technologies miniDawn multiple angle laser light scattering (MALLS) detector at 40°C in tetrahydrofuran (THF) at $1 \text{ mL}\cdot\text{min}^{-1}$ using polystyrene standards. The synthesis and the preparation of trimethylsilylcellulose (TMSC) (degree of substitution, $DS = 2.01$; $M_n = 44 \text{ kg}\cdot\text{mol}^{-1}$) and cellulose nanocrystals are provided elsewhere.^{1,2} Chemical structures for the main compounds in this thesis are provided in Figure 3.1. Chloroform (HPLC grade, EMD Chemicals) was used to prepare $\sim 0.5 \text{ mg}\cdot\text{g}^{-1}$ PtBA and TMSC solutions for Langmuir-Blodgett (LB) film deposition. Spincoated films were prepared from polymer solutions of different weight percent concentrations (wt%) in toluene (HPLC grade, EMD Chemicals). Spincoated films of TMSC and cellulose nanocrystals were prepared from solutions of different weight

percent concentrations (wt%) in toluene (HPLC grade, EMD Chemicals) and water, respectively. The water used in all steps of the experiments was ultrapure water (18.2 MΩ, Millipore, MilliQ Gradient A-10, <10 ppb organic impurities). Ethylene glycol (EG), triethylene glycol (TEG), (reagent plus, >99%, Sigma-Aldrich), and glycerol (ultrapure, HPLC Grade, Alfa-Aesar) were used as different ambient media for polymer systems. In addition, hexane (HPLC grade, EMD Chemicals) was used as the second ambient medium for regenerated cellulose and cellulose nanocrystal films. All other reagents, H₂O₂ (30% by volume), H₂SO₄ (conc.), and NH₄OH (28% by volume) were purchased from EM Science, VWR International, and Fisher Scientific, respectively. Silicon wafers (100) were purchased from Waferworld, Inc.

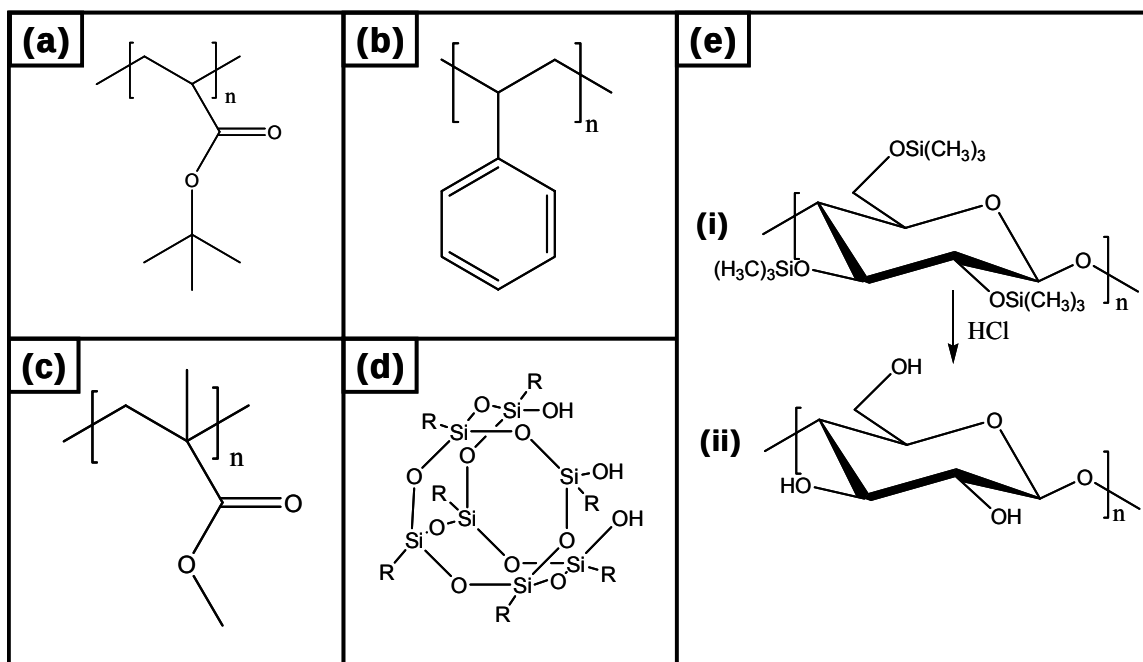


Figure 3.1. Chemical structures of (a) PtBA, (b) PS, (c) PMMA, (d) TPP, and (e) TMSC and regenerated cellulose.

3.2 Cleaning Procedure of Silicon Wafers

The silicon wafers were cleaned in a 5:1:1 (by volume) boiling mixture of $\text{H}_2\text{O}:\text{H}_2\text{O}_2:\text{NH}_4\text{OH}$ for 1 h. After the substrates were rinsed with Millipore water and dried with nitrogen, the substrates were placed in a 7:3 (by volume) mixture of $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$ for 3 h. The substrates were then rinsed with copious amounts of water and dried with nitrogen. At this point, the surface is a hydrophilic silica surface. The hydrophilic silica surface was used to create spincoated films of cellulose nanocrystals. In order to obtain a hydrophobic silicon surface, substrates were dipped into buffered HF solutions (J. T. Baker) for 5 min followed by a short dip into a buffered NH_4F (J. T. Baker) solution to obtain hydrophobic silicon substrates. LB and spincoated films of all systems except for the cellulose nanocrystals were prepared on hydrophobic silicon surfaces.

3.3 Thin Film Preparation

Silicon wafers were used for both LB and spincoated films. Substrates for spincoating were cut into roughly $15 \times 15 \text{ mm}^2$ pieces. LB-films were prepared on $40 \times 40 \text{ mm}^2$ substrates. Following X-ray reflectivity (XR) experiments, LB-films were cut into $15 \times 15 \text{ mm}^2$ pieces for ellipsometry measurements. LB-films were prepared on a standard LB-trough (KSV 2000, KSV Instruments, Inc.) resting on a floating table inside a Plexiglas box. The temperature of the subphase (Millipore water) was maintained at 22.5°C by a water circulation bath. Surface pressure, Π , was monitored via the Wilhelmy plate technique. The trough was filled with Millipore water and the spreading solutions of PtBA, TPP, PtBA/TPP blends, and TMSC were spread to $\Pi = \sim 5 \text{ mN}\cdot\text{m}^{-1}$; i.e. below the transfer pressure to avoid multilayer formation. After allowing ~ 20 min for

the spreading solvent to evaporate the monolayers were compressed to a constant transfer Π below the collapse Π . Transfer Π of 18.5 mN·m⁻¹, 10.5 mN·m⁻¹, 25 mN·m⁻¹ were chosen for PtBA, TPP, and TMSC, respectively. The transfer Π was varied from ~10.5 - 18.5 mN·m⁻¹ for the PtBA/TPP blends depending on the collapse pressure of each blend composition. The compression rate of 10 mm·min⁻¹ and the maximum forward and reverse barrier speeds of 10 mm·min⁻¹ were used during LB-transfers. The dipping rates of the substrate for both up- and downstrokes were set to 10 mm·min⁻¹. Transfer proceeded by Y-type deposition to prepare multilayer LB-films. The LB layers were quantitatively transferred onto hydrophobic silicon substrates with nominal transfer ratios of ~1.0. All spincoated films were prepared from solutions of varying wt% polymer and TMSC in toluene and were spun onto hydrophobic silicon wafers at 2000 rpm for 60 s. In contrast, spincoated films of cellulose nanocrystals were prepared from dispersions of varying wt% cellulose nanocrystals in water and were spun onto hydrophilic silicon wafers at 2000 rpm for 60 s.

3.4 Experimental Techniques

3.4.1 Ellipsometry

3.4.1.1 Multiple Incidence Media (MIM) Ellipsometry

MIM ellipsometry measurements were carried out with a phase modulated ellipsometer (Beaglehole Instruments, Wellington, New Zealand) at a wavelength of 632.8 nm (He:Ne laser) at Brewster's angle. The sample cell is depicted in Figure 3.2. Measurements in air were performed at several different positions in order to confirm the uniformity and the quality of the films through the quartz cell. Measurements with

different ambient media were performed in the same quartz cell. The design of the quartz cell allows us to fill the sample cell with liquid after completing the air measurements without removing the substrate, thereby allowing measurements on the same position of the wafer.

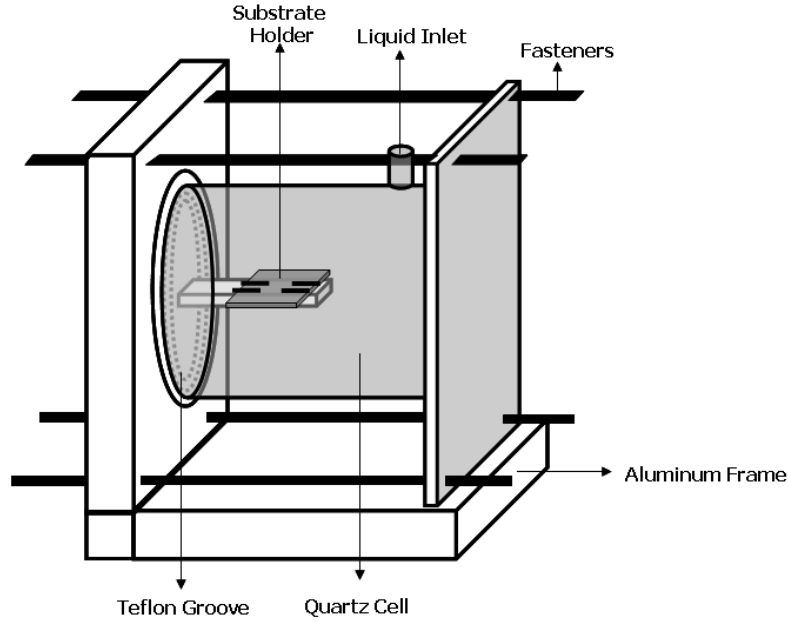


Figure 3.2. Schematic depiction of the multiple incident media (MIM) ellipsometry sample cell.

The fundamental equation for the reflection coefficient in ellipsometry is³

$$r = \frac{r_p}{r_s} = \text{Re}(r) + i \text{Im}(r) = \tan \Psi \exp(i\Delta) \quad (3.1)$$

where r_p and r_s are the reflection coefficients for p and s polarized light, respectively, and Ψ and Δ are the ellipsometric angles. At Brewster's angle, $\text{Re}(r) = 0$, which is equivalent to $\Delta = 90^\circ$. Under these conditions, Equation 3.1 simplifies to:⁴

$$\rho = r = \frac{r_p}{r_s} = i \text{Im}(r) = \tan \Psi \quad (3.2)$$

where ρ is the ellipticity. For the case where the film thickness, D , is much smaller than the wavelength of light, λ , the ellipticity may be expressed as power series in terms of (D/λ) . The first term of this power series provides Drude's Equation:^{5,6}

$$\rho = \frac{\pi}{\lambda} \frac{(\epsilon_1 + \epsilon_2)^{1/2}}{(\epsilon_1 - \epsilon_2)} \int_0^D \frac{(\epsilon - \epsilon_1)(\epsilon - \epsilon_2)}{\epsilon} dz \quad (3.3)$$

where ϵ is the dielectric constant at position z in the film, ϵ_1 is the dielectric constant of the ambient medium, and ϵ_2 is the dielectric constant of the substrate. For the case of homogenous ultrathin films with negligible surface roughnesses, ϵ is a constant (independent of z) and Equation 3.3 becomes

$$\rho = \frac{\pi}{\lambda} \frac{(\epsilon_1 + \epsilon_2)^{1/2}}{(\epsilon_1 - \epsilon_2)} \frac{(\epsilon - \epsilon_1)(\epsilon - \epsilon_2)}{\epsilon} D \quad (3.4)$$

As Mao *et al.*⁷ noted, measurements with two different ambient media, A and B, allows one to eliminate D by taking the ratio

$$\frac{\rho^A}{\rho^B} = \frac{(\epsilon_1^A + \epsilon_2)^{1/2} (\epsilon_1^B - \epsilon_2) (\epsilon - \epsilon_1^A)}{(\epsilon_1^B - \epsilon_2)^{1/2} (\epsilon_1^A - \epsilon_2) (\epsilon - \epsilon_1^B)} \quad (3.5)$$

which leads to an analytical expression for ϵ :

$$\epsilon = \frac{\rho^A \sqrt{\epsilon_1^B + \epsilon_2} (\epsilon_1^A - \epsilon_2) \epsilon_1^B - \rho^B \sqrt{\epsilon_1^A + \epsilon_2} (\epsilon_1^B - \epsilon_2) \epsilon_1^A}{\rho^A \sqrt{\epsilon_1^B + \epsilon_2} (\epsilon_1^A - \epsilon_2) - \rho^B \sqrt{\epsilon_1^A + \epsilon_2} (\epsilon_1^B - \epsilon_2)} \quad (3.6)$$

Once ϵ is known, D can be obtained from Equation 3.4 for either ambient medium. The error analysis for refractive index and thickness obtained through Equations 3.4 and 3.6, are provided with the necessary derivatives in Appendix A1.

3.4.1.2 Multiple Angle of Incidence (MAOI) Measurements

MAOI measurements were carried out with a phase modulated ellipsometer (Beaglehole Instruments, Wellington, New Zealand) at a wavelength of 632.8 nm (Halogen Lamp). Angles were varied between 45° and 80°.

3.4.1.3 Spectroscopic Ellipsometry (SE) Measurements

SE measurements were carried out with a phase modulated ellipsometer (Beaglehole Instruments, Wellington, New Zealand) at an incident angle of 60° over a wavelength range of 230 to 800 nm (halogen and deuterium lamp). X and Y data measured with the phase modulated system can be converted to the traditional parameters Ψ and Δ using the Equations 3.7 through 3.10:

$$\text{Re}(r) = \frac{1 \pm \sqrt{1 - X^2 - Y^2}}{X^2 + Y^2} X \quad (3.7)$$

$$\text{Im}(r) = \frac{1 \pm \sqrt{1 - X^2 - Y^2}}{X^2 + Y^2} Y \quad (3.8)$$

$$\tan \Psi = \sqrt{\text{Re}(r)^2 + \text{Im}(r)^2} \quad (3.9)$$

$$\tan \Delta = \text{Im}(r) / \text{Re}(r) \quad (3.10)$$

In most practical cases the values of $\text{Re}(r)$ and $\text{Im}(r)$ are small enough to use the negative root in the conversion equations (Equations. 3.7 and 3.8). Nonetheless, TFCompanionTM software enables us to directly analyze X and Y data without conversion to obtain thickness and refractive index values. The critical point exciton (CPE) material

approximation was utilized to model the wavelength dependence of the refractive indices for the materials used in this study.

3.4.1.4 Anisotropy Measurements

Anisotropy measurements were carried out with an M2000[®] spectroscopic ellipsometer over the wavelength range from 195 to 1700 nm at J. A. Wollaham Co., Inc. 100 layer LB-films of PtBA and TPP were used to test for the presence of anisotropy. The PtBA optical constants were described using a Kramers-Kronig model. In addition mean squared errors (MSE) were calculated in order to test the difference between experimental data and model predictions. Both anisotropic and isotropic models for refractive indices were tested for this film. The anisotropic models did not provide statistically significant improvements in the fits over the isotropic models (fit quality improved by ~2% in contrast to ~30% improvement for systems where anisotropic measurements are justified). This observation indicates that there is no significant anisotropy in the refractive indices of PtBA and TPP LB-films.

3.4.1.5 Temperature Dependent Ellipsometry Scans

The glass transition temperatures (T_g), the loss of double layer transition temperatures (T_d), and thermal expansion coefficients (α) for PtBA, TPP, and PtBA/TPP blend films were determined using a phase modulated ellipsometer (Beaglehole Instruments, $\lambda = 632.8$ nm) with a homebuilt heating stage. All PtBA/TPP blend LB-films in this study were subjected to the following procedure: 1) The films were initially heated from -10 to 60 °C at a heating rate of 1 °C·min⁻¹ under nitrogen; 2) Following the first heating scans, the samples were rapidly cooled to -10 °C using chilled nitrogen gas (N₂ was passed through a copper coil immersed in a dry ice/ethanol mixture, ~-65 °C), for an effective

cooling rate of $\sim 10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$; and 3) A second heating scan was performed up to $60\text{ }^{\circ}\text{C}$ at $1\text{ }^{\circ}\text{C}/\text{min}$. In addition, the following control experiments were performed with single-component systems. Fresh LB- and spincoated films of pure PtBA and fresh LB-films of TPP were subjected to the following procedure: 1) The films were first heated from -10 to $90\text{ }^{\circ}\text{C}$ at a heating rate of $1\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ under nitrogen; 2) Following the first heating scans, the samples were rapidly cooled to $-10\text{ }^{\circ}\text{C}$ using chilled nitrogen gas for an effective cooling rate of $\sim 10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$; 3) A second heating scan was performed up to $90\text{ }^{\circ}\text{C}$ at $1\text{ }^{\circ}\text{C}\cdot\text{min}$; and then 4) Finally, LB- and spincoated PtBA films were annealed overnight at $90\text{ }^{\circ}\text{C}$ under vacuum and a heating scan from -10 to 90°C was used to compare their thermal characteristics before and after the removal of residual stresses (double layer structure).

The thermal expansion coefficients of the aforementioned films supported on hydrophobic silicon substrates were determined during these heating scans. The ellipticity (ρ) signal changes due to thermal expansion. ρ for sufficiently thin, ($D \ll \lambda$) homogeneous films measured at Brewster's angle are described by Drude's equation (Equation 3.4). The thermal expansion coefficient (α) for condensed matter can be expressed in terms of volume (V) and temperature (T):

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \left(\frac{\partial \ln V}{\partial T} \right)_P \quad (3.11)$$

The linear thermal expansion coefficient for thin films (thickness changes perpendicular to the substrate) can be written as,

$$\alpha = \left(\frac{\partial \ln(D)}{\partial T} \right)_P \quad (3.12)$$

where D is the film thickness. It is evident from Equation 3.12 that the slope of a plot of $\ln(D)$ as a function of T yields the linear thermal expansion coefficient of the film. During our measurements, the dielectric constant of the film was assumed to be independent of T over the limited experimental temperature range. Experimental results show α values (the slope on $\ln D$ vs. T plot) are different before and after a transition. The intersection of these lines with different slopes provides an estimate of the transition temperature. The surface T_g of the thin films were determined from changes in ellipticity during the first, as well as the second heating scans at Brewster's angle.(i.e. from the intersection of the lines corresponding to the glassy and rubbery states). The T_d values of the LB-films films were determined from changes in the ellipticity signal during the first heating scans at Brewster's angle.

3.4.2 X-ray Reflectivity (XR)

XR measurements were performed at the NIST Center for Neutron Research using Cu- K_α radiation with a wavelength of 1.5418 Å on a Bruker AXS-D8 Advance Diffractometer. The thickness of the films were obtained by analyzing the Kiessig fringe spacing following the method of Thomson *et al.*⁸ In this approach, the positions of the minima, q_m , in a plot of the reflectivity, $R(q)$, vs. the scattering wave vector, $q = (4\pi/\lambda)\sin\theta$ where θ is the scattering angle, are used to obtain the film thickness, D . According to Thomson *et al.*:⁸

$$\sqrt{q_m^2 - q_c^2} = Q_m(q) = \frac{2\pi}{D}m \quad (3.13)$$

where q_c is the critical wavevector, and q_m is the wavevector corresponding to the minimum index, m , of the refraction corrected minima. Hence, D can be obtained for a

plot of Q_m vs. m . This method was validated by also fitting the reflectivity curves with a single layer model with both a silicon/polymer and polymer/air roughness in Microsoft Excel.^{9,10}

3.4.3 Bulk Characterization via Differential Scanning Calorimetry (DSC)

5 wt% solutions of TPP, PtBA, or TPP/PtBA blends were prepared in chloroform for solution casting. Cast samples were allowed to dry for 3 days followed by overnight annealing under vacuum at 35 °C to remove residual solvent. These samples were analyzed by differential scanning calorimetry (DSC) (TA instrument DSC-Q100) operating under nitrogen. Two heating scans were performed by heating the samples (~8-10 mg) from -10 °C to 60 °C at 10 °C·min⁻¹. Following the first scans, all samples were cooled to -10 °C at 10 °C·min⁻¹. Second heating scans from -10 °C to 60 °C at 10 °C·min⁻¹ were used to determine bulk T_g .

3.5 References

- (1) Beck-Candanedo, S.; Roman, M.; Gray, D. G. *Biomacromolecules* **2005**, *6*, 1048-1054.
- (2) Muller, F.; Beck, U. *Das Papier* **1978**, *32*, 25-31.
- (3) Azzam, R. M. A.; Bashara, N. M. *Ellipsometry and Polarized light*, Elsevier: Amsterdam, 1987.
- (4) Beaglehole, D.; Christenson, H. K. *J. Phys. Chem.* **1992**, *96*, 10933-10937.
- (5) Drude, P. *Ann. Phys.* 1889, *36*, 532-560.
- (6) Lekner, J. *Theory of Reflection*; Nijhoff: Amsterdam, 1988.
- (7) Mao, M.; Zhang, J.; Yoon, R.; Ducker, W. A. *Langmuir* **2004**, *20*, 1843-1849.
- (8) Thomson, C.; Saraf, R. F.; Jordan-Sweet, J. L. *Langmuir* **1997**, *13*, 7135-7140.
- (9) Esker, A. R.; Gröll, H.; Satija, S. K.; Han, C. C. *J. Polym. Sci., Part B* . **2004**, *42*, 3248-3257.
- (10) Welp, K. A.; Co, C.; Wool, R. P. *J. Neutron Res.* **1999**, *8*, 37-46.

CHAPTER 4

Determination of Thicknesses and Refractive Indices of Polymer Thin Films by Multiple Incident Media Ellipsometry

4.1 Abstract

Single wavelength ellipsometry measurements at Brewster's angle provide a powerful technique for characterizing ultrathin polymer films. By conducting the experiments in different ambient media, simultaneous determinations of a film's thickness and refractive index are possible. Poly(tert-butyl acrylate) (PtBA) Langmuir-Blodgett films serve as a model system for the simultaneous determination of thickness and refractive index (1.45 ± 0.01 at 632 nm). Thickness measurements on films of variable thickness agree with X-ray reflectivity results ± 0.8 nm. The method is also applicable to spincoated films where refractive indices of PtBA, polystyrene, and poly(methyl methacrylate) are found to agree with literature values within experimental error.

4.2 Introduction

Precise control of film thickness is often a critical parameter in ultrathin polymer coatings. Several microscopy^{1,2} and reflectivity^{3,4} methods such as profilometry, atomic force microscopy (AFM), and X-ray reflectivity (XR) have been developed for measuring the thicknesses of polymer thin films in the nanometer regime. However, measurements should be rapid and non-destructive for researchers who require routine determinations of film thickness prior to further surface characterization. Ellipsometry is a rapid, non-contact, and non-destructive method for probing thickness and refractive index in

nanoscale polymer coatings through changes in polarization upon the reflection of light from a surface.⁵ The technique is applicable for both *ex-situ* measurements in air and *in-situ* experiments in liquid media. Like other reflectivity techniques, thickness determinations via ellipsometry are complicated by the need to know the film's optical properties. As the refractive index and the thickness are correlated parameters in ellipsometry, it is not possible to uniquely obtain both parameters through a single measurement at a constant wavelength for ultrathin films.⁶ Spectroscopic ellipsometers overcome this problem by making measurements at multiple wavelengths under the assumption that the refractive index of the film can be optically modeled as a function of wavelength over the studied range. Making this assumption often requires some prior knowledge of the refractive index and absorbance properties of the film. This problem is further complicated by the fact that the bulk refractive indices may not be applicable for ultrathin interfaces with thickness < 5 nm.⁷ One way to circumvent this problem for single wavelength instruments is the use of multiple incident media (MIM). This technique has previously been applied to silicon surfaces with an oxide layer,⁸ self-assembled monolayers on silicon substrates,^{9,10,11} and water adsorbed on chromium slides.¹²

The MIM technique requires two ambient media whose refractive indices should be significantly different from each other. The task of choosing the ambient media is complicated by the fact that the medium should be chemically and physically inert (non-swelling). In addition, a liquid cell that is compatible with the variable angle setup must be constructed. The most common cell design described in the literature is trapezoidal in shape to ensure that the incident and reflected light enter and leave the cell at normal

incidence, thereby avoiding changes in the polarization state. Other cell designs having hollow prism shapes have also been reported.¹² In this paper, a quartz cylinder sample cell (described in Chapter 3, Figure 3.2)¹¹ has been used with a phase modulated ellipsometer to conduct the MIM ellipsometry measurements on polymer films. The advantage of the cylindrical cell design is that it does not require a fixed incident angle, whereby Brewster's angle can be easily scanned so long as the cylindrical cell is properly centered with respect to the axis of rotation of the arms of the ellipsometer.

Like ellipsometry, X-ray reflectivity (XR) and neutron reflectivity (NR) can reliably measure a polymer film's thickness with angstrom level resolution. For single component homogenous films with small surface roughnesses, the Kiessig fringe patterns unambiguously yield a film's thickness.^{13,14,15} Comparative XR and spectroscopic ellipsometry studies can be found in the literature.^{16,17,18} As shown in this study, the MIM method enables one to simultaneously determine the refractive index and thickness of a thin film. In this respect, MIM ellipsometry is comparable to the use of multiple ambient media and polarized neutrons to try to solve the phase problem in neutron reflectivity.¹⁹⁻²⁴ The advantage of the MIM ellipsometry technique over XR and NR is the fact that it can be done much more quickly (< 5 min).

In this study the Langmuir-Blodgett (LB) technique²⁵ is used to transfer poly(tert-butyl acrylate) (PtBA) films onto solid substrates from a water subphase. PtBA LB-films are ideal for testing the MIM technique on polymer thin films because quantitative LB-transfer²⁶ by Y-type deposition yields films whose thicknesses linearly correlate with the number of deposited layers and films that do not swell in water.²⁷ Results obtained via MIM ellipsometry are then compared to XR results to validate the method. Finally, the

technique is applied to spincoated systems of PtBA, polystyrene (PS), and poly(methyl methacrylate) (PMMA) to demonstrate general applicability.

4.3 Results and Discussion

Experimental details for this and all subsequent chapters are provided in Chapter 3. All ellipticity data in this data chapter obtained at Brewster's angle represent averages of measurements obtained at six different spots on the films.

4.3.1 XR Characterization of PtBA LB-Films

All LB-films of PtBA were analyzed by XR for comparative purposes. Figure 4.1 shows a representative XR profile for a 10 layer LB-film of PtBA. For $q > q_c$, $R(q)$ exhibits periodic oscillations, Kiessig fringes, which arise from interference between X-rays reflected from the silicon/polymer and polymer/air interfaces. The spacing of the maxima or minima are related to the film thickness through Bragg's Law.¹⁵ Thomson *et al.*²⁸ used this feature to provide a refraction corrected analysis scheme, whereby model independent values of film thickness can be obtained from Equation 3.13 (Chapter 3). This analysis scheme is demonstrated in the inset of Figure 2. In addition, the reflectivity profile in Figure 4.1 was fit using a multilayer algorithm^{29,30} and the film thickness is $D = 10.1 \pm 0.08$ nm with root-mean-square roughnesses at the silicon/polymer and polymer/air interfaces of $\sigma_s \sim 0.6$ nm and $\sigma_p \sim 0.8$ nm, respectively. These parameters are summarized in Table 1 for all PtBA LB-films.

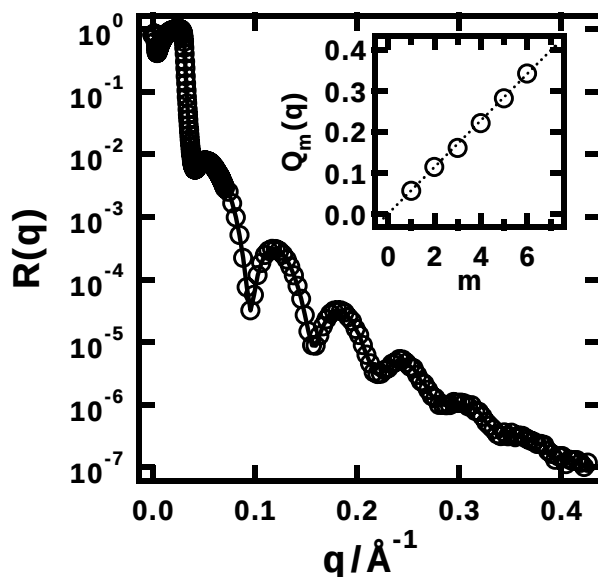


Figure 4.1. A representative XR profile for a 10 layer PtBA LB-film. The open circles are the experimental data and the solid line corresponds to the fit obtained through a multilayer algorithm.^{29,30} The inset shows $Q_m(q)$ vs. m which is used to obtain D according to the method of Thomson *et al.*²⁸

Table 4.1. X-Ray reflectivity data for PtBA LB-films.

#of Layers	X-Ray Reflectivity			
	Thickness		Roughness ^b	
	D /nm ^a	D /nm ^b	σ_p /nm	σ_s /nm
4	4.2	4.3	0.99	0.43
6	6.1	6.2	0.77	0.54
8	8.1	8.0	0.73	0.53
10	10.1	10.1	0.84	0.56
12	12.2	12.2	0.91	0.49
16	15.8	15.9	0.87	0.50
20	19.4	19.6	0.61	0.49

^aUtilizing Equation 3.13 ; ^bFit utilizing a multilayer algorithm²⁹

A plot of D vs. the number of LB-layers (Figure 4.2) shows a linear relationship that is consistent with quantitative LB-transfer via Y-type deposition. The slope of the line for the X-ray data in Figure 3 yields the thickness of a single PtBA layer, d , in a LB-film transferred at $\Pi = 18 \text{ mN.m}^{-1}$. The value obtained from Figure 3, $d = 0.96 \pm 0.01 \text{ nm}$, is in good agreement with previously published values.^{26,27} These films and measurements serve as references for the subsequent analyses of the ellipsometry data.

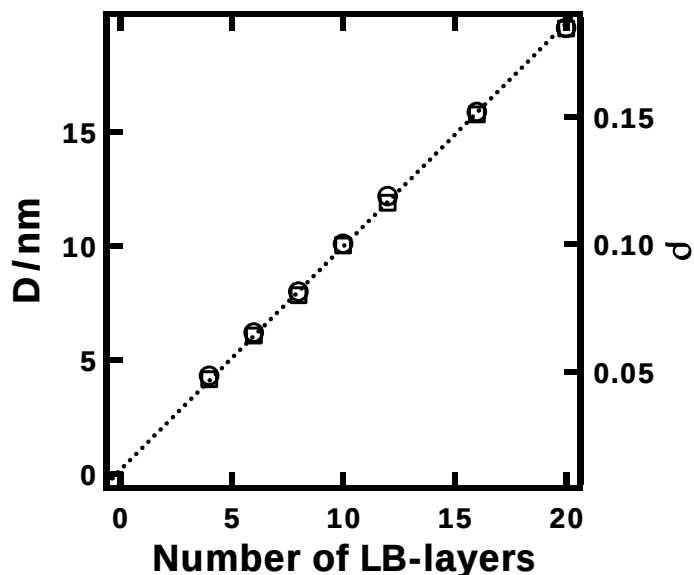


Figure 4.2. D determined by X-ray reflectivity ($\circ$, left-hand axis), and ρ obtained from ellipsometry at Brewster's angle in air ($\square$, right-hand axis) as a function of the number of LB layers. One standard deviation error bars on the XR and ellipsometry data are smaller than the size of the data points.

4.3.2 MIM Ellipsometry for PtBA LB-Films

Figure 4.2 also contains ellipticity, ρ , plotted against the right-hand y-axis as a function of the number of LB-layers for PtBA LB-films measured in air. A linear

relationship between ρ and the number of LB-layers is observed for PtBA LB-films. This result is consistent with quantitative LB-transfer^{26,27} and the applicability of Equation 3.4. Figure 4.3 shows the same ellipticity data measured in air as Figure 4.2, along with ρ data measured in water ($n_2 = 1.333$, $\varepsilon_2 = 1.777$). Figure 4.3 clearly shows that there is also a linear relationship between ρ and the number of layers transferred for films measured in water. At this stage, the analysis of the MIM ellipsometry data can proceed along two paths: Approach 1 - The refractive index and thickness of each film can be determined according to Equations 3.6 and 3.4; and Approach 2 - The slope of each curve in Figure 4.3 can be used to obtain $\rho^{\text{air}}/\text{layer}$ and $\rho^{\text{water}}/\text{layer}$. These values can then be used to determine the refractive index and thickness, d , per layer through Equations 3.6 and 3.4. Approach 2 has the advantage that surface roughnesses neglected in the derivation of Equation 3.4 from Equation 3.3, will only affect the intercepts of the lines in Figure 4.3 and not the slopes as long as the roughness values are more or less constant between different films. As seen in Table 2, this condition is true for the PtBA LB-films. Hence, Approach 2 is expected to provide the most reliable values of n . Nonetheless, Approach 1 will be discussed first.

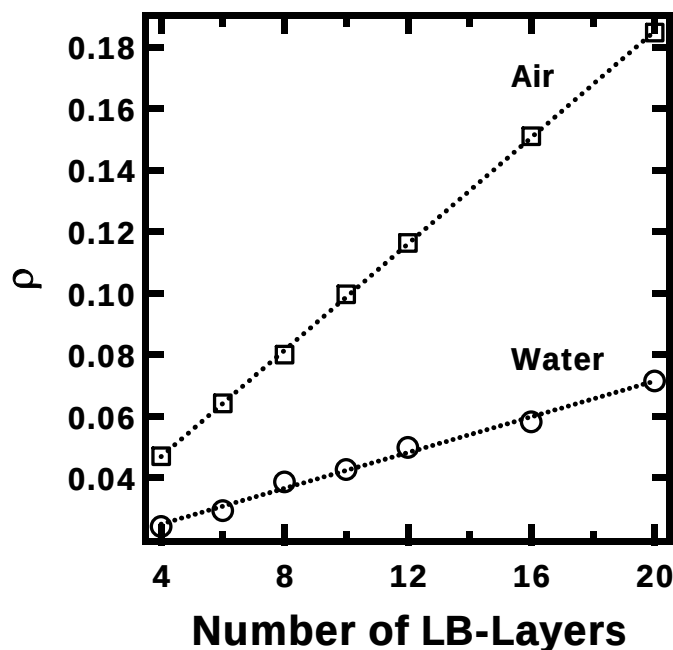


Figure 4.3. MIM ellipsometry data for PtBA LB-films in air (□) and in water (○) at a wavelength of 632 nm. One standard deviation error bars for the ellipsometry data are smaller than the size of the data points.

In addition to data obtained via X-ray reflectivity for PtBA LB-films (Table 1), Table 2 also contains the thickness and refractive index values for each film obtained from measurements in air and in water through Equation 3.6 and 3.4 by Approach 1. As shown in Table 1 and Table 2, the agreement between the XR data and the ellipsometry data is excellent with less than 1 nm deviation, i.e. the deviation is essentially the surface roughness. The error estimates on D and n in Table 1 represents $\pm$ one standard deviation and are obtained from a propagation of error calculation (Appendix A1). Table 1 also shows that n values are largely independent of the number of layers transferred, with an average value of $n = 1.47 \pm 0.01$. Upon closer inspection for differences, it should be noted

that the largest deviations are observed for the thinnest films. Greater deviation for thinner films should not be surprising as the polymer/substrate and polymer/air or polymer/water interfacial roughnesses neglected in the derivation of Equation 3.4 will make the largest contributions to the observed ρ values from ellipsometry on a percentage basis for the thinnest films.

Turning to Approach 2, the slopes of $\rho^{\text{air}}/\text{layer} = (8.64 \pm 0.06) \times 10^{-3}$ and $\rho^{\text{water}}/\text{layer} = (2.9 \pm 0.1) \times 10^{-3}$ in Figure 4.3 yield $d = 0.91 \pm 0.01$ nm/layer and $n = 1.45 \pm 0.01$ from Equations 3.4 and 3.6, respectively. Here, the error estimates are obtained from the same propagation of error calculation used for Approach 1. The value of d is in excellent agreement with the value from XR and published results.^{26,27} Utilizing the n value obtained from Approach 2, it is also possible to calculate D for each film. These values are also summarized in Table 2. As expected, the thickness values deduced in this manner exhibit the greatest deviation for the thinnest films. Nonetheless, the conclusion is clear; so long as Drude's equation is valid, the MIM ellipsometry values provide unambiguous values of refractive index and film thickness. Moreover, D from XR and ellipsometry agree within a nm. At this stage it should be noted that we found no evidence to support the presence of air bubbles at the hydrophobic polymer surface for measurements at polymer/water interfaces.¹¹ This observation is consistent with the fact that film roughnesses for LB and spincoated polymer films tend to be $> \sim 0.5$ nm, i.e. larger than the window necessary to observe nanobubbles.^{31,32}

Table 4.2. Ellipsometry data for PtBA LB-films obtained from MIM ellipsometry experiments.

#of Layers	Ellipsometry		n ^a
	Thickness		
	D /nm ^a	D /nm ^b	
4	4.4±0.1	4.9±0.1	1.46±0.01
6	6.2±0.1	6.7±0.1	1.48±0.01
8	7.6±0.2	8.4±0.1	1.48±0.01
10	9.8±0.8	10.4±0.6	1.46±0.02
12	11.4±0.7	12.2±0.1	1.47±0.01
16	15.1±0.3	15.8±0.2	1.45±0.02
20	18.6±0.9	19.4±0.8	1.45±0.02
		Average ^c	1.47±0.01
		Approach 2 ^c	1.45±0.01

^aUtilizing Approach 1; ^bUtilizing Approach 2;

^cOne standard deviation error bars

4.3.3 MIM Ellipsometry Studies for Spincoated PtBA Films

Having obtained a reasonable value of $n = 1.45 \pm 0.01$ from MIM ellipsometry measurements on LB-films utilizing Approach 2, the data analysis scheme could then be applied to spincoated PtBA films. Figure 4.4 (a) shows ρ plotted as a function of the spincoating solution concentration (wt% PtBA) for measurements in air and in water. As expected for a spincoated film,¹⁷ the plot of ρ vs. the wt% concentration of the PtBA spincoating solution is nearly linear. Next, Approach 1 is used to deduce the thickness and refractive index of each film through Equations 3.4 and 3.6, respectively. The results for D and n are summarized in Table 4.3, and the ellipticity values from Figure 4.4 (a) are now plotted against D in Figure 4.4 (b). Figure 4.4 (b) shows a linear relationship between ρ and D as expected from Equation 3.3. Next the data in Figure 4.4 (b) are fit with a linear relationship to obtain $\rho^{\text{air}}/\text{nm} = (9.52 \pm 0.09) \times 10^{-3} \text{ nm}^{-1}$ and $\rho^{\text{water}}/\text{nm} =$

$(2.8 \pm 0.2) \times 10^{-3} \text{ nm}^{-1}$. From the values of $\rho^{\text{air}}/\text{nm}$ and $\rho^{\text{water}}/\text{nm}$ it is now possible to deduce $n = 1.44 \pm 0.01$ for spincoated PtBA from Equation 3.6 via Approach 2. This value is in excellent agreement with the value of $n = 1.45 \pm 0.01$ obtained from PtBA LB-films by Approach 2. Hence, one can conclude that MIM ellipsometry also can be safely applied to spincoated films, where isotropic refractive indices ($n_{||} = n_{\perp}$) are expected and, films of different thickness provide a self-consistency check and reliable refractive index values. As noted in the Experimental Section (3.4.1.4) PtBA LB-films do not exhibit anisotropic refractive indices.

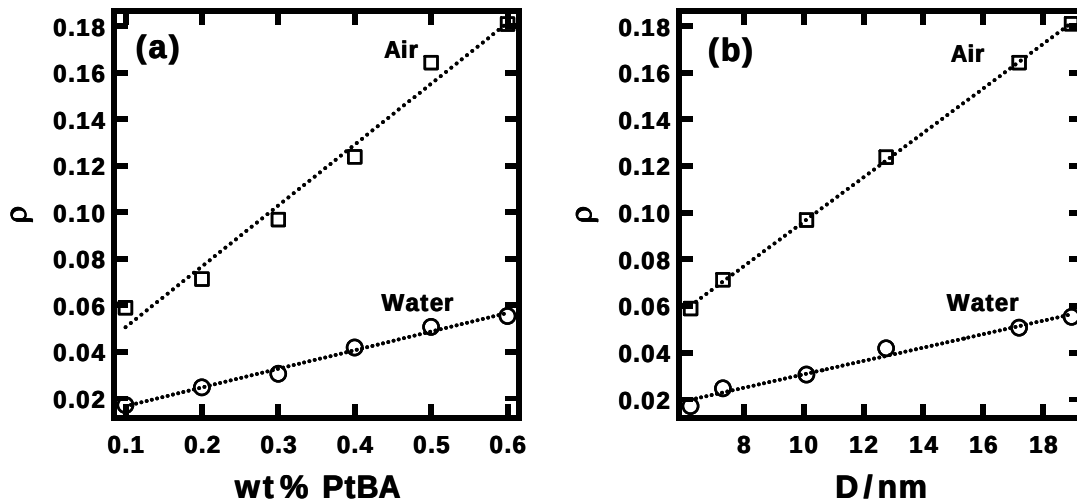


Figure 4.4. (a) ρ vs. the wt% PtBA in the spincoating solution. (b) ρ vs. D deduced from MIM ellipsometry data for spincoated systems of PtBA in air ($\square$) and in water ($\circ$) at a wavelength of 632 nm. One standard deviation error bars on ρ are smaller than the size of the data points. The thickness values in (b) are obtained by analyzing the air and water measurements for a given film from (a) via Approach 1.

Table 4.3. Thickness and refractive index values for spincoated PtBA films deduced from MIM ellipsometry data.

wt %	D /nm ^a	n ^a
0.1	6.2±0.2	1.43±0.01
0.2	7.3±0.2	1.46±0.01
0.3	10.1±0.2	1.45±0.01
0.4	12.8±0.8	1.46±0.01
0.5	17.2±0.7	1.44±0.01
0.6	19.0±0.4	1.44±0.02
	Average ^b	1.45±0.01
	Approach 2 ^b	1.44±0.01

^aUtilizing Approach 1

^bOne-standard deviation error bars

4.3.4 MIM Ellipsometry Studies for PtBA Films in Different Ambient Media

In order to further confirm that MIM ellipsometry is a suitable technique to measure the thickness and refractive index values for polymer thin films in non-solvent systems, three other non-solvent systems, ethylene glycol (EG, $n_2=1.431$, $\varepsilon_2=2.048$), triethylene glycol (TEG, $n_2=1.455$, $\varepsilon_2=2.120$), and glycerol, ($n_2=1.472$, $\varepsilon_2=2.169$), were used for both LB- and spincoated systems of PtBA films. MIM ellipsometry measurements for LB- and spincoated systems of PtBA in different ambient media are provided in Figure 4.5 and 4.6, respectively. The results obtained from different media, Tables 4.3 and 4.4, are in excellent agreement with the previously discussed X-ray and MIM ellipsometry results in Tables 4.2 and 4.3. Tables 4.4 and 4.5 summarize the thickness and refractive index values for LB- and spincoated films, respectively. These results along with XR data confirm that water does not swell PtBA films, a necessary condition for applying MIM ellipsometry to polymer films.

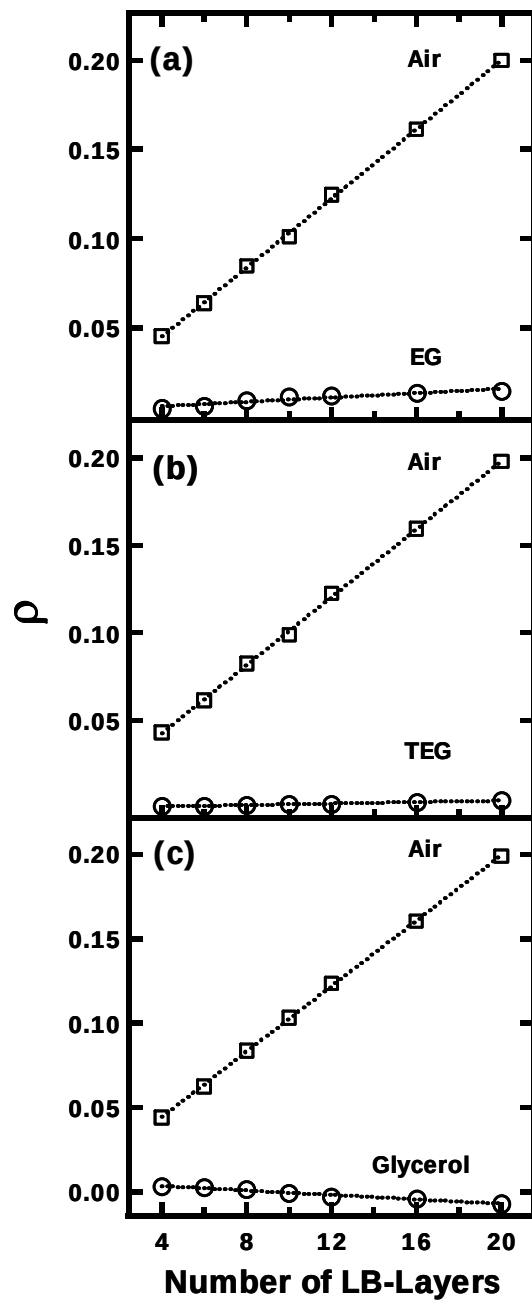


Figure 4.5. MIM ellipsometry data for PtBA LB-films (a) air (□) and ethylene glycol (EG) (○), (b) air (□) and triethylene glycol (TEG) (○), and (c) air (□) and glycerol (○).

One standard deviation error bars on ρ are smaller than the size of the data points.

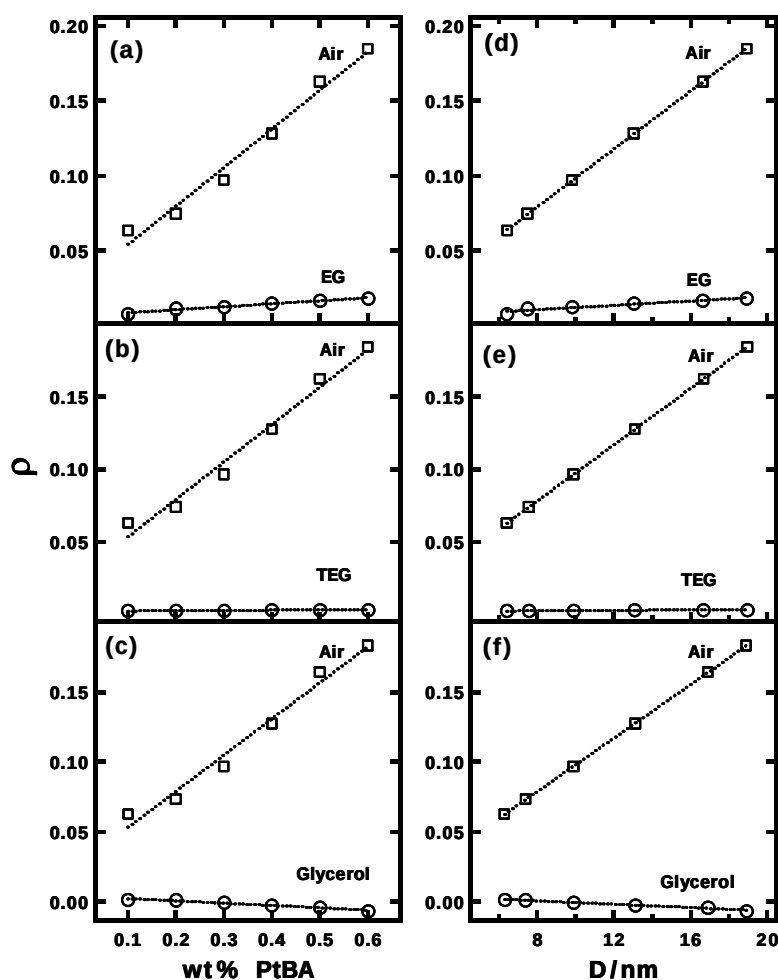


Figure 4.6. MIM ellipsometry data for spincoated PtBA films. ρ obtained for measurements made in (a) air ($\square$) and ethylene glycol (EG) ($\circ$), (b) air ($\square$) and triethylene glycol TEG ($\circ$), and (c) air ($\square$) and glycerol ($\circ$) are plotted vs. wt% PtBA of spincoating solution. d, e, and f contain the same data in a, b, and c, respectively plotted as a function of the thickness obtained via Approach 1 for each film. One standard deviation error bars on ρ are smaller than the size of the symbols for the data points.

Table 4.4. Thickness and refractive index values for PtBA LB-films deduced from MIM ellipsometry experiments in different media.

# of Layers	EG		TEG		Glycerol	
	D /nm ^a	n ^a	D /nm ^a	n ^a	D /nm ^a	n ^a
4	4.6±0.1	1.47±0.01	4.4±0.2	1.47±0.01	4.4±0.1	1.49±0.01
6	6.5±0.1	1.46±0.01	6.3±0.1	1.46±0.01	6.3±0.1	1.49±0.01
8	8.6±0.2	1.47±0.01	8.5±0.2	1.46±0.01	8.5±0.6	1.48±0.01
10	10.3±0.2	1.47±0.01	10.1±0.1	1.46±0.01	10.5±0.1	1.47±0.01
12	12.8±0.1	1.46±0.01	12.6±0.1	1.46±0.01	12.7±0.1	1.46±0.01
16	16.6±0.5	1.46±0.01	16.3±0.1	1.46±0.01	16.4±0.1	1.47±0.01
20	20.7±0.2	1.46±0.01	20.3±0.2	1.46±0.01	20.5±0.2	1.46±0.01
Average ^b		1.46±0.01		1.46±0.01		1.47±0.01
Approach 2 ^b		1.45±0.01		1.45±0.01		1.46±0.01

^aUtilizing Approach 1; ^bOne-standard deviation error bars

Table 4.5. Thickness and refractive index values for spincoated PtBA films deduced from MIM ellipsometry experiments in different media.

wt %	EG		TEG		Glycerol	
	D /nm ^a	n ^a	D /nm ^a	n ^a	D /nm ^a	n ^a
0.1	6.1±0.4	1.48±0.01	6.4±0.1	1.48±0.01	6.3±0.1	1.48±0.01
0.2	7.3±0.6	1.49±0.01	7.6±0.1	1.47±0.01	7.4±0.1	1.48±0.01
0.3	9.7±0.3	1.48±0.01	9.9±0.1	1.47±0.01	9.9±0.2	1.47±0.01
0.4	12.9±0.1	1.47±0.01	13.1±0.1	1.46±0.01	13.1±0.3	1.47±0.01
0.5	16.5±0.1	1.47±0.01	16.7±0.2	1.46±0.01	16.9±0.2	1.46±0.01
0.6	18.7±0.2	1.47±0.01	18.9±0.2	1.46±0.01	18.9±0.2	1.46±0.01
Average ^b		1.48±0.01		1.47±0.01		1.47±0.01
Approach 2 ^b		1.45±0.01		1.46±0.01		1.45±0.01

^aUtilizing Approach 1; ^bOne-standard deviation error bars

4.3.5 Application of MIM Ellipsometry to PS and PMMA in Different Ambient Media

As a final test, three different molar masses of PS and one molar mass of PMMA were examined by MIM ellipsometry in aqueous media, EG, TEG, and glycerol. Both PS and PMMA are known to form films with negligible refractive index anisotropy.^{33,34} MIM ellipsometry measurements of spincoated 23 kg·mol⁻¹, 76 kg·mol⁻¹, 604 kg·mol⁻¹ PS films and, a PMMA film in different ambient media are shown in Figures 4.7 through 4.10. Table 4.6 contains a summary of refractive index values obtained for these polymer films via Approach 2 in different media. The data in Table 4.6 exhibit excellent agreement between the experimental and refractive index values in the literature.³⁵ Thickness and refractive index values obtained by Approach 1 in various media for individual polymer films are summarized in Tables 4.7 through 4.10.

Table 4.6. Refractive index values for PS and PMMA spincoated films calculated from MIM ellipsometry measurements made in different ambient media.

Polymer ^a	$n_{\text{Water}}^{\text{b,c}}$	$n_{\text{EG}}^{\text{b,c}}$	$n_{\text{TEG}}^{\text{b,c}}$	$n_{\text{Glycerol}}^{\text{b,c}}$
604 kg·mol ⁻¹ PS (1.59)	1.60±0.02	1.60±0.01	1.61±0.01	1.60±0.02
76 kg·mol ⁻¹ PS (1.59)	1.61±0.02	1.60±0.02	1.61±0.01	1.60±0.01
23 kg·mol ⁻¹ PS (1.59)	1.60±0.02	1.61±0.01	1.60±0.02	1.59±0.02
PMMA (1.49)	1.48±0.01	1.48±0.01	1.49±0.01	1.49±0.01

^aParenthesis indicate literature values for the refractive index³⁹

^bUtilizing Approach 2

^cOne standard deviation error bars

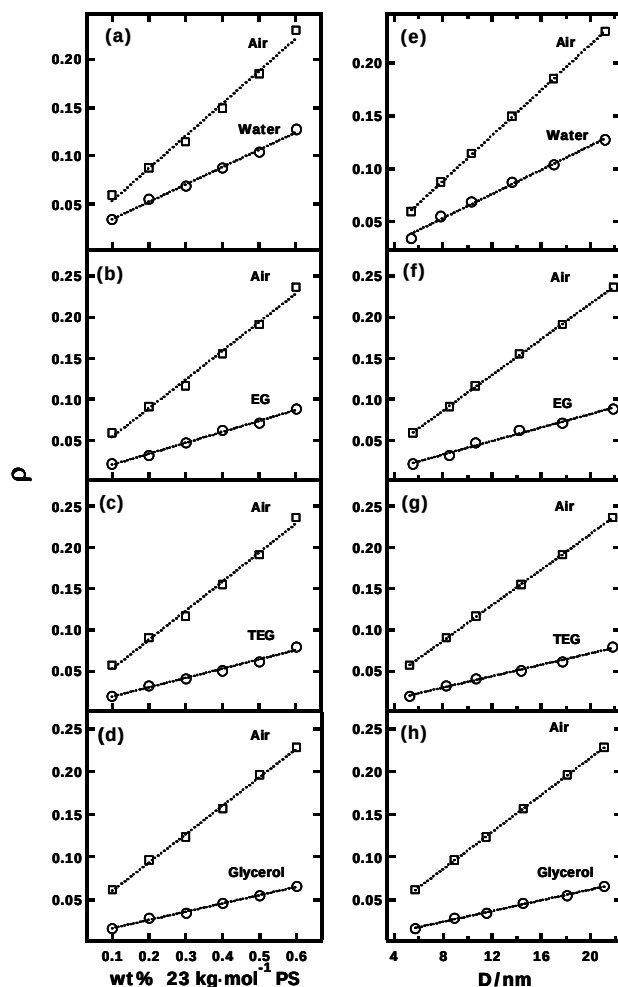


Figure 4.7. MIM ellipsometry data for spincoated $23 \text{ kg}\cdot\text{mol}^{-1}$ PS films. ρ obtained for measurements made in (a) air ($\square$) and water ($\circ$), (b) air ($\square$) and ethylene glycol (EG) ($\circ$), (c) air ($\square$) and triethylene glycol (TEG) ($\circ$), and (d) air ($\square$) and glycerol ($\circ$) are plotted vs. wt% PS of spincoating solution. e, f, g, and h contain the same ρ data as a, b, c, and d, respectively, plotted as a function of the thickness obtained via Approach 1 for each film. One standard deviation error bars on ρ are smaller than the size of the symbols for the data points.

Table 4.7. Thickness and refractive index values for $M_n = 23 \text{ kg}\cdot\text{mol}^{-1}$ PS spincoated films obtained from MIM ellipsometry measurements made in different ambient media.

wt %	Water		EG	
	D /nm ^a	n ^a	D /nm ^a	n ^a
0.1	5.4±0.2	1.62±0.02	5.5±0.1	1.58±0.01
0.2	7.8±0.3	1.68±0.02	8.5±0.1	1.59±0.01
0.3	10.4±0.9	1.65±0.04	11.6±0.1	1.63±0.01
0.4	13.6±0.6	1.64±0.01	14.2±0.2	1.63±0.01
0.5	17.0±0.2	1.62±0.03	17.7±0.1	1.60±0.01
0.6	21.2±0.8	1.61±0.01	21.9±0.2	1.61±0.01
Average ^b		1.64±0.03		1.61±0.02
Approach 2 ^b		1.60±0.02		1.61±0.01
wt %	TEG		Glycerol	
	D /nm ^a	n ^a	D /nm ^a	n ^a
0.1	5.3±0.1	1.62±0.01	5.7±0.1	1.63±0.01
0.2	8.3±0.5	1.63±0.02	8.9±0.9	1.60±0.01
0.3	10.7±0.1	1.63±0.01	11.5±0.2	1.58±0.02
0.4	14.3±0.2	1.61±0.01	14.5±0.8	1.60±0.01
0.5	17.7±0.1	1.60±0.01	18.1±0.1	1.59±0.01
0.6	21.8±0.2	1.63±0.01	21.1±0.2	1.60±0.01
Average ^b		1.62±0.01		1.60±0.01
Approach 2 ^b		1.60±0.02		1.59±0.01

^aUtilizing Approach 1; ^bOne standard deviation error bars

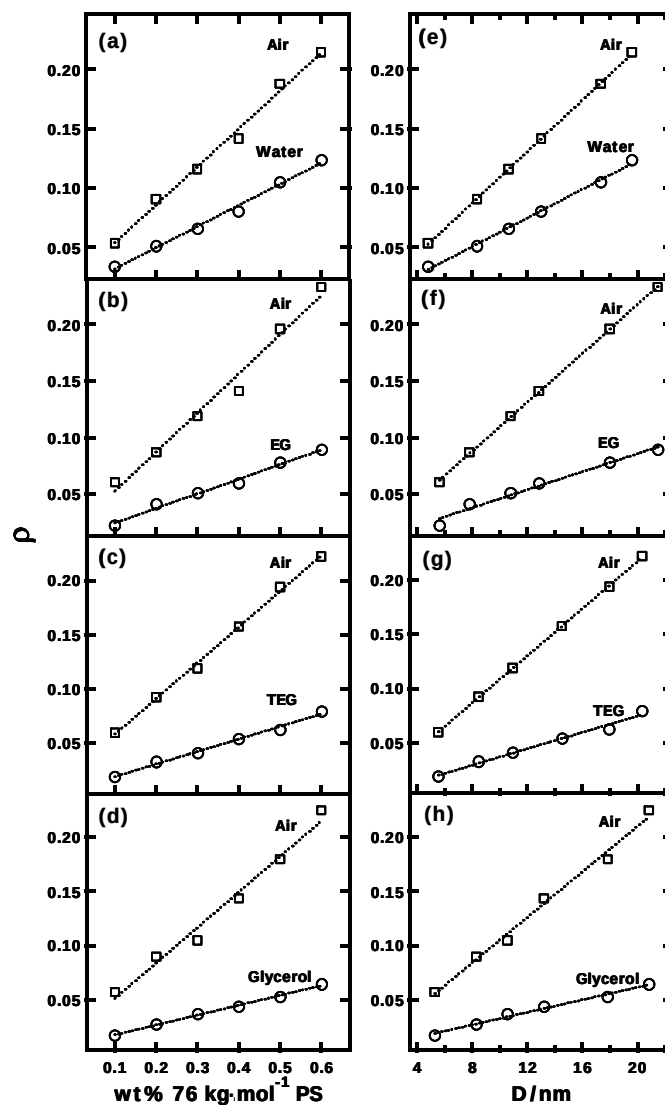


Figure 4.8. MIM ellipsometry data for spincoated $76 \text{ kg}\cdot\text{mol}^{-1}$ PS films. ρ obtained for measurements in (a) air ($\square$) and water ($\circ$), (b) air ($\square$) and ethylene glycol (EG) ($\circ$), (c) air ($\square$) and triethylene glycol TEG ($\circ$), and (d) air ($\square$) and glycerol ($\circ$) are plotted vs. wt% PS of the spincoating solution. e, f, g, and h contain same ρ data as a, b, c, and d, respectively, plotted as a function of the thickness obtained via Approach 1 for each film. One standard deviation error bars on ρ are smaller than the size of the symbols for data points.

Table 4.8. Thickness and refractive index values for $M_n = 76 \text{ kg}\cdot\text{mol}^{-1}$ PS spincoated films obtained from MIM ellipsometry measurements made in different ambient media.

wt %	Water		EG	
	D /nm ^a	n ^a	D /nm ^a	n ^a
0.1	4.8±0.2	1.69±0.04	5.6±0.1	1.60±0.01
0.2	8.3±0.1	1.62±0.02	7.8±0.2	1.68±0.01
0.3	10.6±0.2	1.62±0.02	10.8±0.2	1.65±0.02
0.4	13.0±0.1	1.62±0.01	12.8±0.1	1.64±0.01
0.5	17.3±0.2	1.61±0.01	18.0±0.2	1.62±0.01
0.6	19.6±0.2	1.63±0.01	21.5±0.2	1.61±0.01
Average ^b		1.63±0.03		1.63±0.03
Approach 2 ^b		1.61±0.02		1.60±0.02
wt %	TEG		Glycerol	
	D /nm ^a	n ^a	D /nm ^a	n ^a
0.1	5.5±0.1	1.60±0.01	5.5±0.1	1.60±0.01
0.2	8.5±0.2	1.62±0.01	8.5±0.2	1.62±0.01
0.3	10.9±0.2	1.62±0.01	10.9±0.2	1.62±0.01
0.4	14.5±0.1	1.61±0.01	14.5±0.1	1.61±0.01
0.5	18.0±0.4	1.60±0.02	18.0±0.4	1.60±0.02
0.6	20.3±0.2	1.63±0.01	20.3±0.2	1.63±0.01
Average ^b		1.61±0.01		1.61±0.01
Approach 2 ^b		1.61±0.01		1.61±0.01

^aUtilizing Approach 1; ^bOne standard deviation error bars

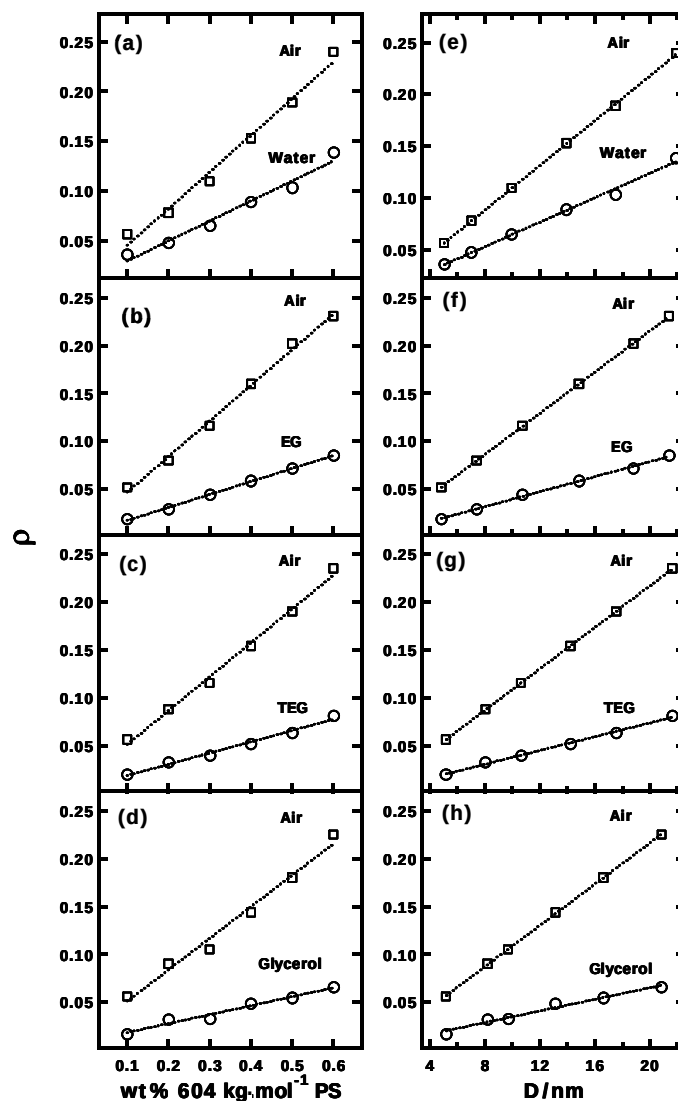


Figure 4.9. MIM ellipsometry data for of spincoated $604 \text{ kg}\cdot\text{mol}^{-1}$ PS films. ρ obtained for measurements in (a) air ($\square$) and water ($\circ$), (b) air ($\square$) and ethylene glycol (EG) ($\circ$), (c) air ($\square$) and triethylene glycol (TEG) ($\circ$), and (d) air ($\square$) and glycerol ($\circ$) are plotted vs. wt% PS of the spincoating solution. e, f, g, and h, contain the same ρ data as a, b, c, and d, respectively plotted as a function of the thickness obtained via Approach 1 for each film. One standard deviation error bars on ρ are smaller than the sizes of the symbols for the data points.

Table 4.9. Thickness and refractive index values for $M_n = 604 \text{ kg}\cdot\text{mol}^{-1}$ PS spincoated films obtained from MIM ellipsometry measurements made in different ambient media.

wt %	Water		EG	
	D /nm ^a	n ^a	D /nm ^a	n ^a
0.1	5.0±0.1	1.69±0.04	4.8±0.2	1.59±0.01
0.2	7.0±0.1	1.67±0.02	7.4±0.1	1.60±0.02
0.3	9.9±0.1	1.65±0.01	10.7±0.1	1.61±0.01
0.4	13.9±0.1	1.64±0.01	14.8±0.1	1.60±0.01
0.5	17.5±0.2	1.60±0.01	18.8±0.1	1.59±0.01
0.6	21.9±0.6	1.63±0.02	21.4±0.2	1.60±0.01
Average ^b		1.65±0.03		1.60±0.01
Approach 2 ^b		1.60±0.02		1.60±0.01
wt %	TEG		Glycerol	
	D /nm ^a	n ^a	D /nm ^a	n ^a
0.1	5.2±0.1	1.62±0.03	5.2±0.1	1.62±0.03
0.2	8.0±0.5	1.63±0.02	8.0±0.5	1.63±0.02
0.3	10.6±0.1	1.62±0.01	10.6±0.1	1.62±0.01
0.4	14.2±0.1	1.61±0.01	14.2±0.1	1.61±0.01
0.5	17.6±0.1	1.61±0.01	17.6±0.1	1.61±0.01
0.6	21.6±0.2	1.62±0.02	21.6±0.2	1.62±0.02
Average ^b		1.62±0.01		1.62±0.01
Approach 2 ^b		1.61±0.01		1.61±0.01

^aUtilizing Approach 1; ^bOne-standard deviation error bars

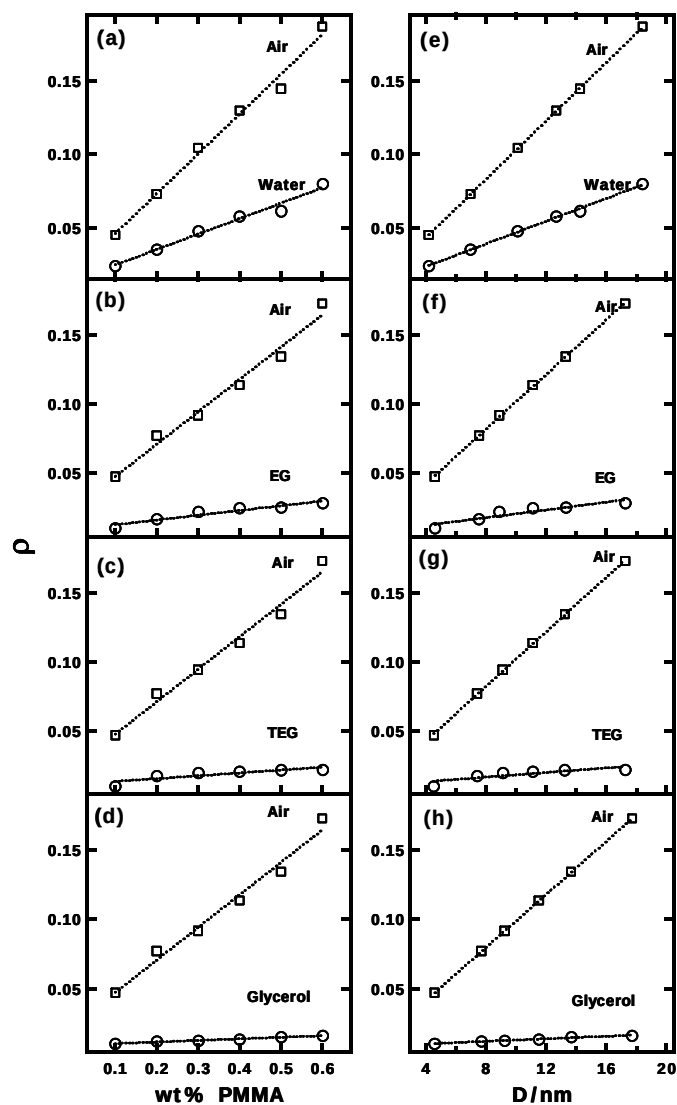


Figure 4.10. MIM ellipsometry data for spincoated PMMA films. ρ obtained for measurements in (a) air ($\square$) and water ($\circ$), (b) air ($\square$) and ethylene glycol (EG) ($\circ$), (c) air ($\square$) and triethylene glycol (TEG) ($\circ$), and (d) air ($\square$) and glycerol ($\circ$) are plotted vs. the wt% of the spincoating solution. e, f, g, and h contain the same data as a, b, c, and d, respectively, as a function of the thickness obtained via Approach 1 for each film. One standard deviation error bars on ρ are smaller than the size of the symbols for the data points.

Table 4.10. Thickness and refractive index values for PMMA spincoated films obtained from MIM ellipsometry measurements made in different ambient media.

wt %	Water		EG	
	D /nm ^a	n ^a	D /nm ^a	n ^a
0.1	4.2±0.1	1.59±0.02	4.6±0.1	1.51±0.01
0.2	7.0±0.1	1.55±0.01	7.6±0.3	1.51±0.01
0.3	10.1±0.1	1.53±0.01	8.9±0.1	1.53±0.01
0.4	12.7±0.1	1.52±0.01	11.1±0.2	1.52±0.02
0.5	14.3±0.1	1.51±0.02	13.3±0.3	1.50±0.02
0.6	18.4±0.6	1.51±0.02	17.3±0.3	1.49±0.01
Average ^b		1.54±0.03		1.51±0.01
Approach 2 ^b		1.49±0.01		1.48±0.01
wt %	TEG		Glycerol	
	D /nm ^a	n ^a	D /nm ^a	n ^a
0.1	4.5±0.1	1.53±0.01	4.5±0.1	1.53±0.01
0.2	7.4±0.3	1.54±0.01	7.4±0.3	1.54±0.01
0.3	9.1±0.1	1.53±0.01	9.1±0.1	1.53±0.01
0.4	11.1±0.2	1.52±0.01	11.1±0.2	1.52±0.01
0.5	13.3±0.3	1.51±0.02	13.3±0.3	1.51±0.02
0.6	17.3±0.2	1.49±0.01	17.3±0.2	1.49±0.01
Average ^b		1.52±0.02		1.52±0.02
Approach 2 ^b		1.47±0.02		1.47±0.02

^aUtilizing Approach 1; ^bOne-standard deviation error bars

4.3.6 Spectroscopic Ellipsometry (SE) and Multiple Angle of Incidence (MAOI) Ellipsometry Measurements

Simultaneous determinations of thickness and refractive index values for the thin films used in this study via SE or MAOI ellipsometry measurements yield estimates with significantly larger errors. Hence, one approach for evaluating SE and MAOI ellipsometry data is to measure thick films and determine n . Once n is known, it serves as a fixed parameter for determining D . Therefore, 100 layer LB-films of PtBA (93.2±1.3 nm) and thicker spincoated films of PtBA, PMMA, and three different molar masses of PS were prepared to determine n for the various materials. The refractive

indices and thicknesses of these films deduced from SE and MAOI ellipsometry measurements are summarized in Table 4.11. The refractive index values as a function of wavelength are provided through Figures 4.11 through 4.16. It is important to note that the n values are not significantly different from the MIM results. Furthermore, D values deduced from SE and MAOI ellipsometry data with fixed n yield D values that agree with MIM ellipsometry within experimental error. Tables 4.12-4.17 summarize the MAOI and SE results relative to the previous MIM results.

Table 4.11. Thickness and refractive index values ($\lambda = 632.8$ nm) for thick spincoated films obtained from SE and MAOI ellipsometry measurements.

	MAOI		SE	
	D /nm	n	D /nm	n
PtBA (100 LB-Layers)	95.2±1.4	1.46±0.01	93.2±1.3	1.44±0.01
PtBA (spincoated)	129.1±4.2	1.45±0.01	128.3±3.5	1.44±0.01
PS(23 kg·mol ⁻¹)	207.6±4.8	1.60±0.01	202.1±4.0	1.60±0.01
PS(76 kg·mol ⁻¹)	197.2±5.3	1.60±0.01	197.2±3.5	1.60±0.01
PS(604 kg·mol ⁻¹)	202.8±3.4	1.60±0.01	195.4±4.3	1.60±0.01
PMMA	147.3±4.7	1.48±0.01	145.5±5.6	1.49±0.01

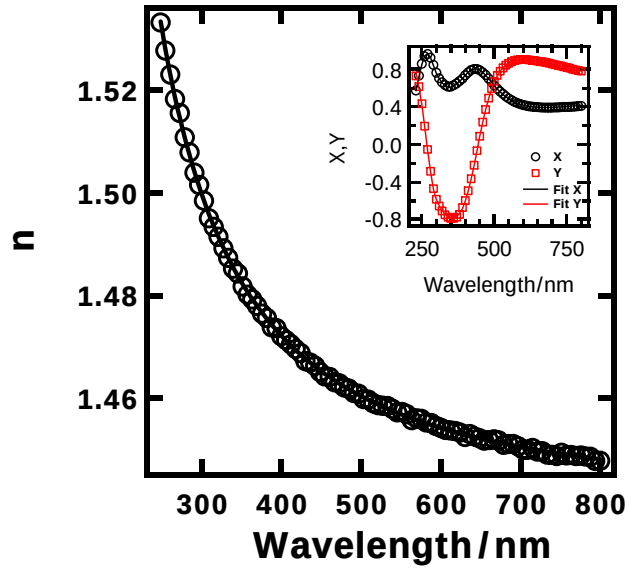


Figure 4.11. Refractive index values for a 100 layer PtBA LB-Film (93.2 ± 1.3 nm) as a function of wavelength. Empirical relationships for n as a function of wavelength via the Cauchy equations (solid lines) are provided for the PtBA LB-film with $n_{\text{PtBA}}(\lambda) = 1.4403 + 4938.9/\lambda^2 + 7.6420 \cdot 10^6/\lambda^4 + 2.5070 \cdot 10^{12}/\lambda^6$. Deviations between the empirical Cauchy equations and the n values obtained from SE ellipsometry are < 0.001 for $230 \text{ nm} < \lambda < 800 \text{ nm}$. The inset shows the experimental data and model fits of the $X(\circ)$ and $Y(\square)$ data over a wavelength range of 250-800 nm.

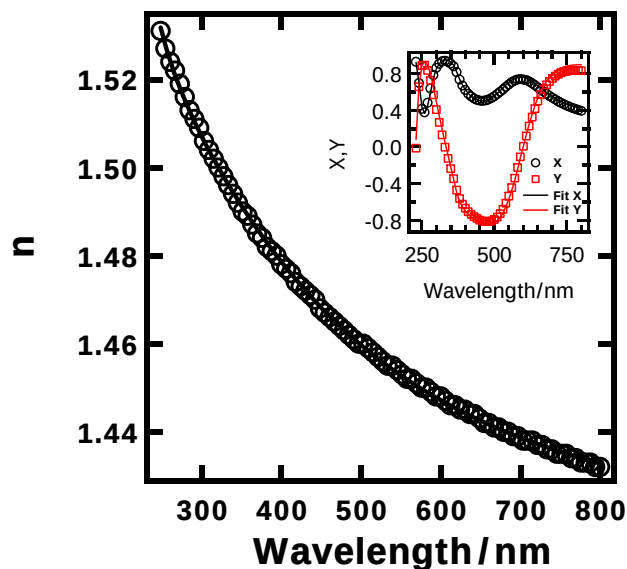


Figure 4.12. Refractive index values of a spincoated PtBA film (128.3 ± 3.5 nm) as a function of wavelength. Empirical relationships for n as a function of wavelength via the Cauchy equations (solid lines) are provided for the PtBA spincoated system with $n_{\text{PtBA}}(\lambda) = 1.4553 + 4635.6/\lambda^2 + 6.8655 \cdot 10^6/\lambda^4 + 2.3816 \cdot 10^{12}/\lambda^6$. Deviations between the empirical Cauchy equations and the n values obtained from SE ellipsometry are <0.001 for $230 \text{ nm} < \lambda < 800 \text{ nm}$. The inset shows the experimental data and model fits of the X($\circ$) and Y($\square$) data over a wavelength range of 250-800 nm.

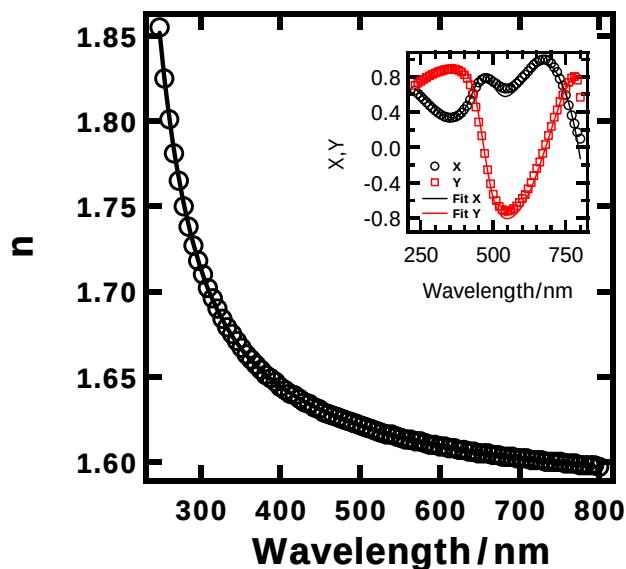


Figure 4.13. Refractive index values of a spincoated $M_n = 23 \text{ kg}\cdot\text{mol}^{-1}$ PS film ($202.1 \pm 4.0 \text{ nm}$) as a function of wavelength. Empirical relationships for n as a function of wavelength via the Cauchy equations (solid lines) are provided for the $23 \text{ kg}\cdot\text{mol}^{-1}$ PS with $n_{\text{PS}}(\lambda) = 1.57908 + 12383.2/\lambda^2 - 6.8002 \cdot 10^8/\lambda^4 + 5.9001 \cdot 10^{13}/\lambda^6$. Deviations between the empirical Cauchy equations and the n values obtained from SE ellipsometry are < 0.001 for $230 \text{ nm} < \lambda < 800 \text{ nm}$. The inset shows the experimental data and model fits of the X($\circ$) and Y($\square$) data over a wavelength range of 250-800 nm.

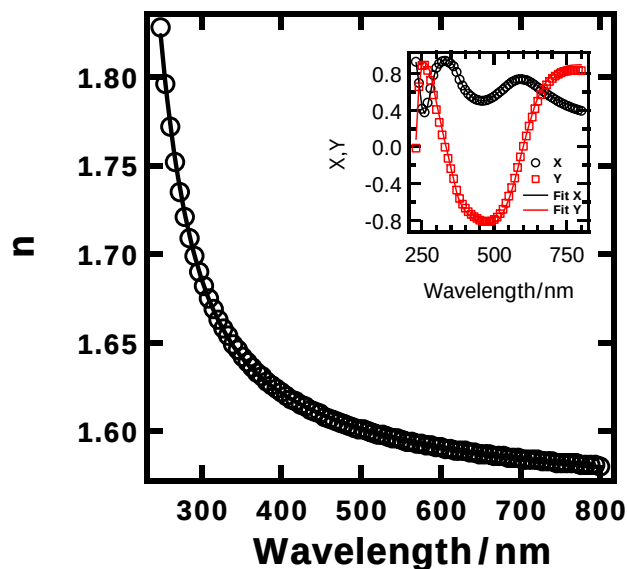


Figure 4.14. Refractive index values of a spincoated $M_n = 76 \text{ kg}\cdot\text{mol}^{-1}$ PS film ($197.2 \pm 3.5 \text{ nm}$) as a function of wavelength. Empirical relationships for n as a function of wavelength via the Cauchy equations (solid lines) are provided for the $76 \text{ kg}\cdot\text{mol}^{-1}$ PS with $n_{\text{PS}}(\lambda) = 1.5633 + 11599/\lambda^2 - 7.6826 \cdot 10^8/\lambda^4 + 6.45056 \cdot 10^{13}/\lambda^6$. Deviations between the empirical Cauchy equations and the n values obtained from SE ellipsometry are < 0.001 for $230 \text{ nm} < \lambda < 800 \text{ nm}$. The inset shows the experimental data and model fits of the X($\circ$) and Y($\square$) data over a wavelength range of 250-800 nm.

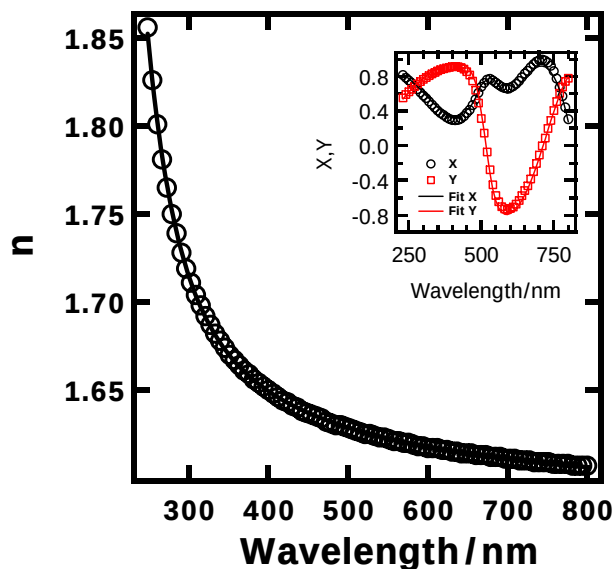


Figure 4.15. Refractive index values of a spincoated $M_n = 604 \text{ kg}\cdot\text{mol}^{-1}$ PS ($195.4 \pm 4.3 \text{ nm}$) as a function of wavelength. Empirical relationships for n as a function of wavelength via the Cauchy equations (solid lines) are provided for the $604 \text{ kg}\cdot\text{mol}^{-1}$ PS with $n_{\text{PS}}(\lambda) = 1.5894 + 11739/\lambda^2 - 7.3434 \cdot 10^8/\lambda^4 + 6.25005 \cdot 10^{13}/\lambda^6$. Deviations between the empirical Cauchy equations and the n values obtained from SE ellipsometry are < 0.001 for $230 \text{ nm} < \lambda < 800 \text{ nm}$. The inset shows the experimental data and model fits of the X($\circ$) and Y($\square$) over a wavelength range of 250-800 nm.

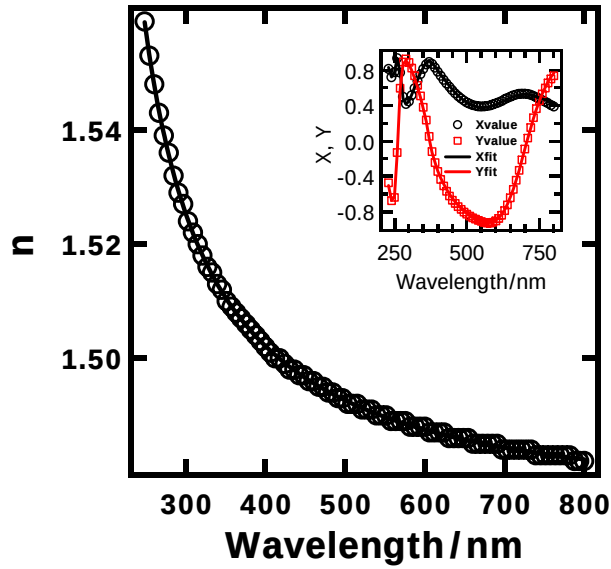


Figure 4.16. Refractive index values of a spincoated PMMA film (145.5 ± 5.6 nm) as a function of wavelength. Empirical relationships for n as a function of wavelength via the Cauchy equations (solid lines) are provided for the PMMA with $n_{\text{PMMA}}(\lambda) = 1.4752 + 4626.4/\lambda^2 - 1.06194 \cdot 10^8/\lambda^4 + 8.6036 \cdot 10^{12}/\lambda^6$. Deviations between the empirical Cauchy equations and the n values obtained from SE ellipsometry are < 0.001 for $230 \text{ nm} < \lambda < 800 \text{ nm}$. The inset shows the experimental data and model fits of the X($\circ$) and Y($\square$) data over a wavelength range of 250-800 nm.

Table 4.12. Thicknesses of PtBA LB-films obtained from XR and MIM ellipsometry, and from SE and MAOI ellipsometry measurements utilizing the optical constants deduced from thick films.

Layer#	D /nm (XR ^a)	D /nm (MIM ^b)	D /nm (MAOI)	D /nm (SE)
4	4.2	4.4±0.1	5.1±1.1	4.2±2.3
6	6.1	6.2±0.1	6.4±0.6	5.7±1.1
8	8.1	7.6±0.2	9.0±0.6	7.4±1.2
10	10.1	9.8±0.8	10.4±0.4	9.5±1.3
12	12.2	11.4±0.7	13.7±0.5	12.9±1.4
16	15.8	15.1±0.3	15.4±0.4	14.7±1.4
20	19.4	18.6±0.9	19.4±0.4	19.5±1.2

^aFit utilizing a multilayer algorithm;²⁹ ^bUtilizing Approach 1

Table 4.13. Thicknesses of spincoated PtBA films obtained from MIM ellipsometry, and SE and MAOI ellipsometry measurements utilizing the optical constants deduced from thick films.

wt%	D /nm (Ellipsometry ^a)	D /nm (MAOI)	D /nm (SE)
1	6.2±0.2	6.8±0.5	6.2±1.5
2	7.3±0.2	7.1±0.4	7.0±1.4
3	10.1±0.2	9.9±0.5	8.8±1.5
4	12.8±0.8	12.6±0.5	12.2±1.6
5	17.2±0.7	17.3±0.5	16.5±1.6
6	19.0±0.4	19.0±0.5	17.7±1.7

^aUtilizing Approach 1

Table 4.14. Thicknesses of spincoated $M_n = 23 \text{ kg}\cdot\text{mol}^{-1}$ PS films obtained from MIM ellipsometry and SE and MAOI ellipsometry measurements utilizing the optical constants deduced from thick films.

wt%	D /nm (Ellipsometry ^a)	D /nm (MAOI)	D /nm (SE)
1	5.4±0.2	5.7±0.9	4.9±1.7
2	7.8±0.3	7.5±0.5	7.4±1.8
3	10.4±0.9	10.2±0.4	10.9±1.7
4	13.6±0.6	13.8±0.4	12.6±1.3
5	17.0±0.2	17.3±0.6	17.4±1.8
6	21.2±0.8	21.1±0.5	20.6±1.5

^aUtilizing Approach 1

Table 4.15. Thicknesses of spincoated $M_n = 76 \text{ kg}\cdot\text{mol}^{-1}$ PS films obtained from MIM ellipsometry and SE and MAOI ellipsometry measurements utilizing the optical constants deduced from thick films.

wt%	D /nm (Ellipsometry ^a)	D /nm (MAOI)	D /nm (SE)
1	4.8±0.2	4.8±0.7	3.9±1.6
2	8.3±0.1	9.3±0.8	8.2±1.7
3	10.6±0.2	10.3±0.4	9.8±1.6
4	13.0±0.1	13.1±0.3	12.8±1.6
5	17.3±0.2	16.4±0.3	16.3±1.5
6	19.6±0.2	20.9±0.4	19.3±1.4

^aUtilizing Approach 1

Table 4.16. Thicknesses of spincoated $M_n = 604 \text{ kg}\cdot\text{mol}^{-1}$ PS films obtained from MIM ellipsometry and SE and MAOI ellipsometry measurements utilizing the optical constants deduced from thick films.

wt%	D /nm (MIM ^a)	D /nm (MAOI)	D /nm (SE)
1	5.0±0.1	5.1±1.2	4.8±1.9
2	7.0±0.1	7.2±0.8	7.1±1.9
3	9.9±0.1	9.6±0.9	10.2±1.4
4	13.9±0.1	14.3±0.6	12.4±1.1
5	17.5±0.2	17.3±0.3	17.1±1.3
6	21.9±0.6	21.7±0.4	22.1±1.2

^aUtilizing Approach 1

Table 4.17. Thicknesses of spincoated PMMA films obtained from MIM ellipsometry and SE and MAOI ellipsometry measurements utilizing the optical constants deduced from thick films.

wt%	D /nm (MIM ^a)	D /nm (MAOI)	D /nm (SE)
1	4.2±0.1	4.1±1.1	5.1±1.4
2	7.0±0.1	7.1±1.0	7.8±1.5
3	10.1±0.1	10.2±0.6	9.5±1.6
4	12.7±0.1	12.6±0.5	12.8±1.2
5	14.3±0.1	14.9±0.2	14.1±1.4
6	18.4±0.6	18.1±0.3	19.1±1.1

^aUtilizing Approach 1

The most commonly used electronic model to analyze ellipsometry data is the Harmonic Oscillator Approximation (HOA).³⁶ Here we report our results utilizing the Critical Point Exciton (CPE) material approximation³⁷ which is an extension to the HAO model used for various polymers. The CPE parameters (Chapter 2, Equation 2.15) are summarized in Table 2.18 for the polymer systems that are used in this study.

Table 4.18. CPE parameters for PtBA, PS, and PMMA.

Parameter	UV_{term}	A_i	E_c	Γ_i	ϕ_i
PtBA(LB-film)	1.90	1.293	7.66	0.620	6.151
PtBA(Spincoated)	2.01	1.213	7.43	0.610	6.201
PS(23 kg·mol ⁻¹)	2.25	1.168	5.94	0.132	6.104
PS(76 kg·mol ⁻¹)	2.20	1.355	6.09	0.194	6.268
PS(604 kg·mol ⁻¹)	2.32	1.187	6.02	0.171	6.138
PMMA	2.03	0.912	7.344	0.025	3.211

4.4 Conclusions

This chapter provides a detailed comparison between thickness measurements obtained by XR and those obtained by various ellipsometry techniques. As shown in this chapter, MIM ellipsometry provides rapid and unambiguous film thickness and refractive index values for ultrathin films that lack anisotropic refractive indices. Deviations between thickness values deduced from XR and ellipsometry agree within ± 1 nm, i.e. $\pm$ the surface roughness. Likewise, the deduced refractive index values are in excellent agreement with the literature. Moreover, the results are in quantitative agreement with more traditional ellipsometric techniques (SE and MAOI ellipsometry) without making any prior assumptions about n . In this study, water insoluble polymers were used. Hence water was a natural choice for the second medium. Measurements with other non-solvents are consistent with water being a non-swelling non-solvent. Moreover, the

different media used in this study demonstrate that it should be possible to find a number of non-swelling non-solvents for any given polymer. As such, MIM ellipsometry is a suitable technique for evaluating most polymer films. The sole requirements are that the second medium does not swell the film and that the film is isotropic (i.e. $n_{||}=n_{\perp}$). As will be shown in the next chapter, MIM ellipsometry can be applied to anisotropic materials, however, some ambiguity exists about the exact meaning of n .

4.5 References

- (1) Fian, A.; Haase, A.; Stadlober, B.; Jakopic, G.; Matsko, N. B.; Grogger, W.; Leising, G. *Analy. Bioanaly. Chem.* **2008**, *390*, 1455-1461.
- (2) Dementeva, O. V.; Zaitseva, A. V.; Kartseva, M. E.; Ogarev, V. A.; Rudoy, V. M. *Colloid Journal* **2007**, *69*, 278-285.
- (3) Shelley, P. H.; Booksh, K. S.; Burgess, L. W.; Kowalski, B. R. *Appl. Spectrosc.* **1996**, *50*, 119-125.
- (4) See, T. J.; Byun, G. S.; Jin, K. S.; Heo, K.; Kim, G.; Kim, S. Y.; Cho, I.; Ree, M. *J. Appl. Cryst.* **2007**, *40*, 620-625.
- (5) Azzam, R. M. A.; Bashara, N. M. *Ellipsometry and Polarized light*, Elsevier: Amsterdam, 1987.
- (6) Arvin, H.; Aspnes, D. E. *Thin Solid Films* **1986**, *138*, 195-207.
- (7) Irene, E. A. *Solid-State Electron.* **2001**, *45*, 1207-1217.
- (8) Landgren, M.; Joensson, B. *J. Phys. Chem.* **1993**, *97*, 1656-1664.
- (9) Kattner, J.; Hoffmann, H. *J. Phys. Chem. B* **2002**, *106*, 9723-9729.
- (10) Ayupov, B. M.; Sysoeva, N. P. *Cryst. Res. Technol.* **1981**, *16*, 503-512.
- (11) Mao, M.; Zhang, J.; Yoon, R.; Ducker, W. A. *Langmuir* **2004**, *20*, 1843-1849.
- (12) McCrackin, F. L.; Passaglia, E.; Stromberg, R. R.; Steinberg, H. L. *J. Res. Natl. Bur. Std.* **1963**, *67*, 363-367.
- (13) Kiessig, H. *Ann. Phys.* **1931**, *10*, 715-768.
- (14) Russell, T. P. *Mater. Sci. Rep.* **1990**, *5*, 171-271.
- (15) Richter, A. G.; Guico, R.; Shull, K.; Wang, J. *Macromolecules* **2006**, *39*, 1545-1553.
- (16) Biswas, A.; Poswal, A. K.; Tokas, R. B.; Bhattacharyya, D. *Appl. Surf. Sci.* **2008**, *254*, 3347-3356.
- (17) Ishizaki, T.; Saito, N.; SunHyung, L.; Ishida, K.; Takai, O. *Langmuir* **2006**, *22*, 9962-9966.
- (18) Kohli, S.; Rithner, C. D.; Dorhout, P. K.; Dummer, A. M.; Menoni, C. S. *Rev. Sci. Instrum.* **2005**, *76*, 1-5.
- (19) Majkrzak, C. F.; Berk, N. F. *Phys. Rev. B* **1998**, *58*, 15416-15418.
- (20) Majkrzak, C. F.; Berk, N. F.; Dura, J. A.; Satija, S. K.; Karim, A.; Pedulla, J.; Deslattes, R. D. *Physica B: Condensed Matter* **1998**, *248*, 338-342.
- (21) Majkrzak, C. F.; Berk, N. F. *Phys. Rev. B* **1995**, *52*, 10827-10830.
- (22) Majkrzak, C. F.; Berk, N. F.; Silin, V.; Meuse, C. W. *Phys. Rev. B* **2000**, *283*, 248-252.
- (23) Schreyer, A.; Majkrzak, C. F.; Berk, N. F.; Grull, H.; Han, C. C. *J. Phys. Chem. Solids* **1999**, *60*, 1045-1051.
- (24) Majkrzak, C. F.; Berk, N. F.; Krueger, S.; Dura, J. A.; Tarek, M.; Tobias, D.; Silin, V.; Meuse, C. W.; Woodward, J.; Plant, A. L. *Biophys. J.* **2000**, *79*, 3330-3340.
- (25) Blodgett, K. B. *J. Am. Chem. Soc.* **1934**, *56*, 495-495.
- (26) Esker, A. R.; Mengel, C.; Wegner, G. *Science* **1998**, *280*, 892-895.
- (27) Mengel, C.; Esker, A. R.; Meyer, W. H.; Wegner, G. *Langmuir* **2002**, *18*, 6365-6372.

- (28) Thomson, C.; Saraf, R. F.; Jordan-Sweet, J. L. *Langmuir* **1997**, *13*, 7135-7140.
- (29) Esker, A. R.; Gröll, H.; Satija, S. K.; Han, C. C. *J. Polym. Sci., Part B* . **2004**, *42*, 3248-3257.
- (30) Welp, K. A.; Co, C.; Wool, R. P. *J. Neutron Res.* **1999**, *8*, 37-46.
- (31) Tyrrell, J. W. G.; Attard, P. *Langmuir* **2002**, *18*, 160-167.
- (32) Poynor, A.; Hong, L.; Robinson, I. K.; Granick, S.; Zhang, Z.; Fenter, P. A. *Phys. Rev. Lett.* **2006**, *97*, 266101-266105.
- (33) Machell, J. S.; Greener, J.; Contestable, B. A. *Macromolecules* **1990**, *23*, 186-194
- (34) Natansohn, A. L.; Hore, D. K. *J. Phys. Chem. B* **2002**, *106*, 9004-9012.
- (35) Brandrup, J.; Immergut, E. H.; Grulke, E. A. *Polymer Handbook*; John-Wiley: New York, 1999.
- (36) Adachi, S. *Optical Properties of Crystalline and Amorphous Semiconductors*, Kluwer Academic Publishers, London, 1999.
- (37) Arwin, H.; Jansson, R. *Electrochimica Acta*, **1994**, *39*, 211-215.

CHAPTER 5

Optical Characterization of Cellulose Derivatives via Multiple Incident Media Ellipsometry

5.1 Abstract

Ellipsometry measures the relative intensity and the phase shift between the parallel and perpendicular components of polarized light reflecting from a surface. Single wavelength ellipsometry measurements at Brewster's angle provide a powerful technique for characterizing ultrathin polymeric films. In this study multiple incident media (MIM) ellipsometry is utilized to simultaneously obtain the refractive indices and thicknesses of thin films of trimethylsilylcellulose (TMSC), regenerated cellulose, and cellulose nanocrystals. Experiments were conducted in air and water for TMSC, and in air and hexane for regenerated cellulose and cellulose nanocrystals. The refractive indices of TMSC, regenerated cellulose, and cellulose nanocrystals are found to be 1.46 ± 0.01 , 1.51 ± 0.01 , and 1.51 ± 0.01 , respectively.

5.2 Introduction

Model cellulose surfaces are important for elucidating how cellulose, hemicellulose, and lignin self-assemble to form the hierarchical structure of the cell wall.¹⁻⁴ Likewise, model surfaces provide model substrates for studying the enzymatic degradation of lignocellulosic materials.^{5,6} On the other hand the swelling behavior of cellulose surfaces in aqueous media attracts great attention from both fundamental and applied sciences in terms of performance and potential applications of cellulose based materials in the paper and textile industries.^{7,8,9} It is clear that, in such applications where the cellulose is in

contact with a liquid medium, techniques that are applicable for in situ characterization are desirable. In addition, prior to further surface treatment and subsequent surface analysis, it is important to characterize and explore initial surface characteristics, eg. film thickness and refractive index. Many techniques have been developed that can be used to measure the thicknesses and refractive indices of thin films such as refractometry,¹⁰ waveguide prism couplers,¹¹ surface plasmon resonance spectroscopy,^{12,13} polarizing interference microscopy,¹⁴ variable-angle single wavelength ellipsometry,^{15,16} and spectroscopic ellipsometry.¹⁷ Of these, ellipsometry as a rapid, non-contact, and non-destructive method is ideal for measuring thickness and refractive index in nanoscale coatings through changes in polarization upon the reflection of light from the surface. In addition, the simultaneous determination of film thickness and refractive index is possible through multiple incident media (MIM) ellipsometry.^{18,19}

Thickness determinations via ellipsometry are complicated by the need to know the film's optical properties. Refractive index and thickness are correlated parameters in ellipsometry, hence, it is not possible to uniquely obtain both parameters through a single measurement at a constant wavelength for thin films.²⁰ Spectroscopic ellipsometers overcome this problem by conducting measurements at multiple wavelengths. However, the refractive index of the film needs to be optically modeled as a function of wavelength. As a consequence some prior knowledge of the refractive index of the film at some point in the sampled wavelength window is usually desired. Another complication is that the bulk refractive indices may not be applicable for thin films with thicknesses < 5 nm.²¹ In order to avoid these problems for single wavelength instruments MIM ellipsometry can be utilized. This technique has previously been applied to silicon surfaces with an oxide

layer,²² self-assembled monolayers on silicon substrates^{19,23,24} and water adsorbed on chromium slides.²⁵ MIM ellipsometry requires two ambient media whose refractive indices are different from each other. Additionally, the ambient media should be chemically and physically inert to the surface. Moreover, the liquid sample cell should be compatible with a variable angle ellipsometry setup. The most common cell design reported in the literature has a trapezoidal shape that allows the incident and reflected light to enter and leave the sample cell at normal incidence, thereby avoiding changes in the polarization state of the light. Another cell design is a hollow prism.²⁵ In our study, a cylindrical quartz sample cell, schematically shown in Figure 3.2, has been used with a phase modulated ellipsometer to conduct MIM ellipsometry measurements on cellulose based films. This cylindrical cell design does not require a fixed incident angle, therefore; Brewster's angle can be easily scanned.

The focus of this chapter is the use of MIM ellipsometry to probe the optical properties of model cellulose surfaces. Cellulose is a naturally abundant polymer in the cell walls of plants and is widely used in the wood, paper, and textile industries. One of the greatest complications associated with obtaining model cellulose surfaces is that cellulose is insoluble in most common organic solvents. Recently, there have been efforts to directly prepare model cellulose surfaces.²⁶⁻²⁹ However, issues with uniformity and surface roughness for these approaches can complicate detailed optical characterization of the resulting films. Therefore, instead of using cellulose directly, more readily soluble cellulose derivatives have been used for the preparation of some model surfaces in this study. Trimethylsilylcellulose (TMSC) has been deposited onto substrates by the Langmuir–Blodgett technique³⁰ and spincoating.³¹ The resulting TMSC films are easily

converted back into cellulose via vapor phase HCl hydrolysis.³¹ As a basis for comparison, model cellulose surfaces are also obtained by spincoating aqueous cellulose nanocrystal suspensions.³² TMSC LB-films are ideal for testing the MIM ellipsometry technique because quantitative LB-transfer by Y-type deposition yields films whose thicknesses linearly increase as a function of the number of layers.^{30,33-38} Hence, results for TMSC LB-films help to validate subsequent MIM ellipsometry studies on spincoated TMSC, regenerated cellulose, and cellulose nanocrystal films.

5.3 Results and Discussion

Experimental details for this and all subsequent chapters are provided in Chapter 3. All ellipticity data in this data chapter obtained at Brewster's angle represent averages of measurements obtained at six different spots on the films.

5.3.1 Multiple Incidence Media (MIM) Ellipsometry for TMSC LB-Films

MIM ellipsometry is utilized to investigate LB-films of TMSC. Figure 5.1 shows ellipticity, ρ , as a function of the number of TMSC LB-layers for data obtained in air ($n_2 = 1$, $\epsilon_2 = n_2^2 = 1$) and water ($n_2 = 1.333$, $\epsilon_2 = n_2^2 = 1.777$). A linear relationship between ρ and the number of TMSC LB-layers is observed for both data sets. Here it should be noted that LB-deposition allows precise control over the film thickness by varying the number of deposited layers. Furthermore, Figure 5.1 indicates that film thicknesses are in a regime where Equation 3.4 should be valid for data analysis. Analysis of the MIM ellipsometry data in Figure 5.1 can proceed in two ways: Approach 1 - The refractive index and thickness of each film can be determined according to Equation 3.6 and 3.4; and Approach 2 - The slope of each curve in Figure 5.1 can be used to obtain $\rho^{\text{air}}/\text{layer}$ and $\rho^{\text{water}}/\text{layer}$, thereby allowing one to deduce the refractive index and thickness per

layer, d , through Eqs. 3.6 and 3.4, respectively. The total thickness of the film, D , is then calculated from Equation 3.4 using n derived from the slopes and ρ data measured in air or water. In this study ρ data measured in air was used to compute D .

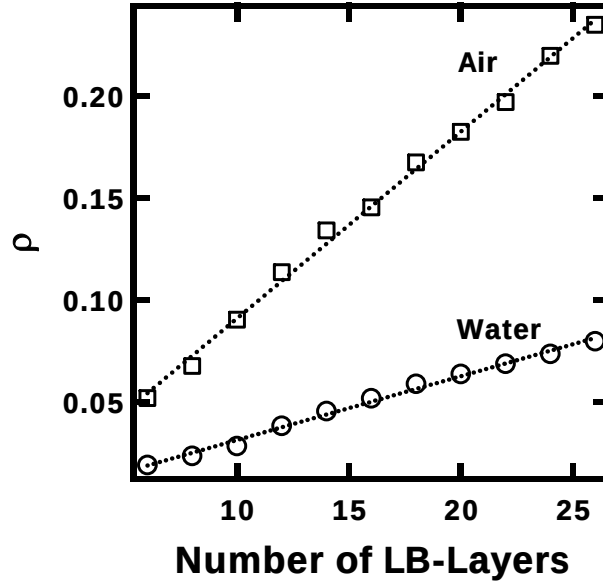


Figure 5.1. ρ vs. the number of layers in TMSC LB-films measured in air ($\square$) and water ($\circ$) at Brewster's angle and a wavelength of 632 nm. One standard deviation error bars for ρ are smaller than the size of the symbols used to represent the data.

Approach 1: Table 5.1 contains thickness and refractive index values for each film obtained from measurements in air and water utilizing Equations 3.4 and 3.6 by Approach 1. Table 5.1 shows that n values are independent of the number of layers transferred, with an average value of $n = 1.46 \pm 0.01$. The refractive index value obtained by Approach 1 is in agreement with a previous study of TMSC ($n = 1.44 \pm 0.01$) by Holmberg *et al.*³³

Approach 2: The slopes of $\rho^{\text{air}}/\text{layer} = (9.20 \pm 0.04) \times 10^{-3}$ and $\rho^{\text{water}}/\text{layer} = (3.1 \pm 0.1) \times 10^{-3}$ in Figure 5.1 yield $d = 0.95 \pm 0.01$ nm and $n = 1.46 \pm 0.01$ utilizing Equations 3.4 and 3.6, respectively. The monolayer thickness obtained via Approach 2 is in agreement with the published values for TMSC LB-films.³⁵ Utilizing the n value obtained from Approach 2 and ρ values obtained from measurements in air, it is possible to calculate D for each film. These values are also summarized in Table 5.1. The conclusion is clear, so long as Drude's equation is valid, the MIM ellipsometry results provide unambiguous values of refractive index and film thickness that agree well with the literature when a non-swelling non-solvent is used.

Table 5.1. MIM ellipsometry results of TMSC LB-films^a

#of Layers	Ellipsometry		
	Thickness		n^b
	D/nm^b	D/nm^c	
4	5.2 ± 0.2	5.3 ± 0.2	1.47 ± 0.01
6	6.9 ± 0.1	6.8 ± 0.2	1.46 ± 0.01
8	9.4 ± 0.3	9.1 ± 0.1	1.45 ± 0.02
10	11.7 ± 0.1	11.2 ± 0.4	1.46 ± 0.01
12	13.8 ± 0.8	13.4 ± 0.3	1.46 ± 0.02
14	14.9 ± 0.3	14.8 ± 0.2	1.47 ± 0.01
16	17.2 ± 0.2	17.4 ± 0.1	1.47 ± 0.01
18	18.7 ± 0.2	19.1 ± 0.1	1.46 ± 0.01
20	20.2 ± 0.3	20.6 ± 0.2	1.46 ± 0.02
22	22.7 ± 0.5	23.0 ± 0.3	1.46 ± 0.01
24	24.2 ± 0.4	24.8 ± 0.3	1.46 ± 0.01
	Average		1.46 ± 0.01
	Approach 2		1.46 ± 0.01

^aOne-standard deviation error bars

^bUtilizing Approach 1

^cUtilizing Approach 2 with ρ data measured in air

5.3.2 MIM Ellipsometry Studies for Spincoated TMSC Films

After obtaining a value of $n = 1.46 \pm 0.01$ from MIM ellipsometry measurements on LB-films of TMSC via the slope-based Approach 2, the data analysis procedure was next applied to spincoated systems of TMSC. Figure 5.2 (a) has ρ plotted as a function of the spincoating solution concentration (wt% TMSC in toluene) for measurements in air and water. As expected for a spincoated film, the plot of ρ vs. the wt% concentration of the TMSC spincoating solution is essentially linear, but more scattered than the analogous plot ρ vs. number of LB-layers for LB-films. This result is not surprising since the preparation of the spincoated films does not allow one to control film thickness as well as the LB-technique. However, Approach 1 can be used to deduce the refractive index and thickness of each film through Equations 3.6 and 3.4, respectively. The results for D and n are summarized in Table 5.2, and the ellipticity values from Figure 5.2 (a) are then plotted against D in Figure 5.2 (b). Figure 5.2 (b) shows a nearly linear relationship between ρ and D as expected from Equation 3.4. Next the data in Figure 5.2 (b) are fit with a linear relationship to obtain $\rho^{\text{air}}/\text{nm} = (9.64 \pm 0.08) \times 10^{-3} \text{ nm}^{-1}$ and $\rho^{\text{water}}/\text{nm} = (3.1 \pm 0.3) \times 10^{-3} \text{ nm}^{-1}$. From the values of $\rho^{\text{air}}/\text{nm}$ and $\rho^{\text{water}}/\text{nm}$ it is now possible to deduce $n = 1.45 \pm 0.01$ from Equation 3.6 for spincoated TMSC via Approach 2. This value is in excellent agreement with the value of $n = 1.46 \pm 0.01$ obtained from TMSC LB-films by Approach 2 and the literature value of $n = 1.44 \pm 0.01$.³³ Therefore, we can conclude that MIM ellipsometry can also be applied to spincoated films.

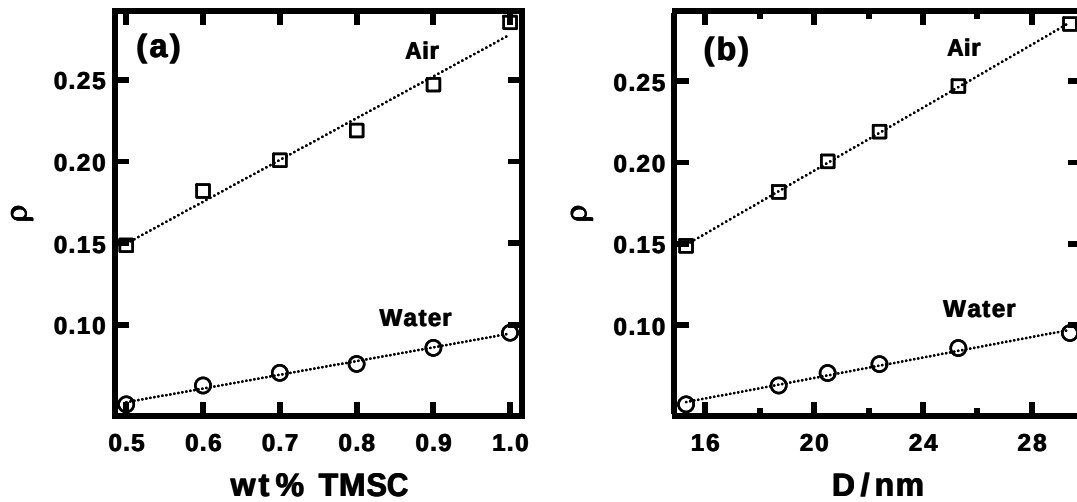


Figure 5.2. (a) ρ vs. the wt% TMSC of the spincoating solution. (b) ρ vs. D obtained from MIM ellipsometry data utilizing Approach 1 for spincoated TMSC films in (a). Symbols correspond to measurements in air ($\square$) and water ($\circ$) at a wavelength of 632 nm. One standard deviation error bars for ρ are smaller than the size of the symbol used to represent the data.

Table 5.2. Thickness and refractive index values for spincoated TMSC films^a deduced from MIM ellipsometry data.

wt %	D / nm^b	n^b
0.5	15.3 ± 0.2	1.46 ± 0.01
0.6	18.7 ± 0.1	1.46 ± 0.01
0.7	20.5 ± 0.3	1.47 ± 0.01
0.8	22.4 ± 0.2	1.46 ± 0.01
0.9	25.3 ± 0.2	1.46 ± 0.01
1.0	29.4 ± 0.2	1.46 ± 0.01
Average		1.46 ± 0.01
Approach 2		1.45 ± 0.01

^aOne-standard deviation error bars

^bUtilizing Approach 1

5.3.3 MIM Ellipsometry Studies of Cellulose Films Regenerated from TMSC Films

Next, the MIM ellipsometry method is suitable for characterizing both "LB" and "spincoated" films of regenerated cellulose derived from the TMSC films of the previous sections. Here, hexane ($n_2 = 1.375$, $\epsilon_2 = n_2^2 = 1.890$) serves as a non-swelling non-solvent. Analogous plots to those in Figure 5.2 in air and hexane are provided in Figure 5.3 for regenerated cellulose films. The refractive index and thickness results are summarized in Tables 5.3 and 5.4 for "LB" and "spincoated" regenerated cellulose films, respectively. Here it should be noted that upon acid catalyzed hydrolysis of TMSC the thickness values decrease by ~56%. The refractive index value for regenerated cellulose is found to be $n = 1.51 \pm 0.01$. In addition, the "monolayer thickness" reduces from 0.95 ± 0.01 nm for TMSC to 0.38 ± 0.01 nm for the regenerated cellulose. These results agree well with previously reported monolayer thickness values for TMSC and regenerated cellulose.³⁵ The refractive index of the thin film changes from 1.46 ± 0.01 for TMSC to 1.51 ± 0.01 for the regenerated cellulose films. The measurements reveal no significant difference between the refractive indices of the LB or spincoated films. The refractive index value reported for cotton cellulose ranges from 1.53-1.58 and is anisotropic (values perpendicular vs. parallel to the cellulose backbone).³⁹ However the lower refractive index value ($n = 1.51 \pm 0.01$) obtained via MIM ellipsometry for regenerated cellulose is consistent with a previously reported value ($n = 1.49 \pm 0.02$) from ellipsometry studies.³³

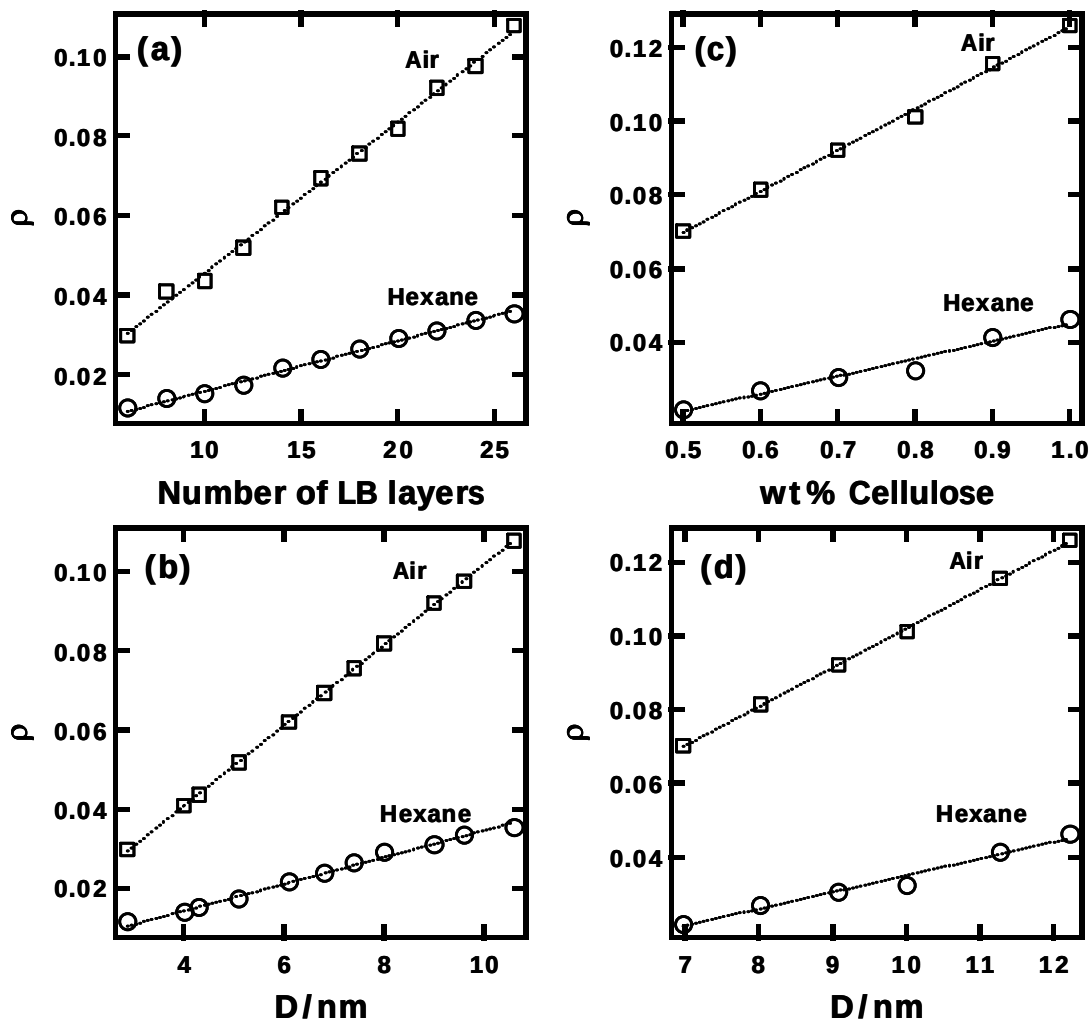


Figure 5.3. (a) ρ vs. the number of LB-layers in the precursor TMSC film and (b) ellipticity vs. film thicknesses obtained from MIM ellipsometry data utilizing Approach 1 for cellulose films regenerated from TMSC LB-films. (c) Ellipticity vs. wt % concentration of TMSC in the spincoating solution and (d) ellipticity vs. film thicknesses obtained from MIM ellipsometry data utilizing Approach 1 for cellulose films regenerated from spincoated TMSC films. Symbols correspond to measurements in air ($\square$) and hexane ($\circ$) at a wavelength of 632 nm. One standard deviation error bars on ρ are smaller than the size of the symbols used to represent the data.

Table 5.3. Thickness and refractive index values obtained by MIM ellipsometry for cellulose films regenerated from TMSC LB-films.^a

#of Layers	Ellipsometry		n ^b
	Thickness		
	D /nm ^b	D /nm ^c	
4	2.9 ± 0.1	3.1 ± 0.2	1.54 ± 0.01
6	3.8 ± 0.3	3.6 ± 0.5	1.52 ± 0.01
8	4.3 ± 0.4	4.1 ± 0.2	1.52 ± 0.01
10	5.1 ± 0.2	5.2 ± 0.3	1.51 ± 0.01
12	6.1 ± 0.2	6.4 ± 0.2	1.52 ± 0.01
14	6.8 ± 0.2	6.2 ± 0.1	1.52 ± 0.01
16	7.4 ± 0.2	7.1 ± 0.4	1.52 ± 0.01
18	8.0 ± 0.1	8.1 ± 0.1	1.52 ± 0.01
20	9.0 ± 0.1	9.2 ± 0.2	1.51 ± 0.01
22	9.6 ± 0.2	9.8 ± 0.2	1.52 ± 0.01
24	10.6 ± 0.2	10.8 ± 0.3	1.51 ± 0.01
	Average		1.52 ± 0.01
	Approach 2		1.51 ± 0.01

^aOne-standard deviation error bars

^bUtilizing Approach 1

^cUtilizing Approach 2 with ρ data measured in air

Table 5.4. Thickness and refractive index values obtained by MIM ellipsometry for cellulose films regenerated from spincoated TMSC films.^a

wt%	D /nm ^b	n ^b
0.5	7.0 ± 0.1	1.50 ± 0.01
0.6	8.0 ± 0.8	1.51 ± 0.01
0.7	9.1 ± 0.3	1.51 ± 0.01
0.8	10.0 ± 0.1	1.50 ± 0.01
0.9	11.3 ± 0.4	1.52 ± 0.01
1.0	12.2 ± 0.3	1.53 ± 0.02
	Average	1.51 ± 0.01
	Approach 2	1.51 ± 0.01

^aOne-standard deviation error bars

^bUtilizing Approach 1

5.3.4 MIM Ellipsometry Studies of Cellulose Nanocrystal Films

The MIM ellipsometry method is also applicable to thin cellulose nanocrystal films by making measurements in air and hexane. Plots analogous to those in Figure 5.2 in air and hexane are provided in Figure 5.4 for spincoated thin films of cellulose nanocrystals. The refractive index and thickness values deduced for cellulose nanocrystals are summarized in Table 5.5. MIM ellipsometry yields refractive index values for the cellulose nanocrystals that are the same as cellulose films regenerated from TMSC within experimental error. These results may mean that the regenerated cellulose and cellulose nanocrystal films have similar degrees of crystallinity.

Cellulose crystals show birefringence with refractive index values along the direction parallel to the cellulose backbone ($n_{\text{B||}}$) being higher than those perpendicular to the cellulose backbone ($n_{\perp}$)⁴⁰ and similar behavior is expected for cellulose nanocrystals.⁴¹ However, due to the nature of MIM ellipsometry and the TFC CompanionTM software used in this study, estimates of refractive index anisotropy are not possible. Nonetheless, MIM ellipsometry results for cellulose nanocrystals are close to the smaller refractive index reported for $n_{\perp}$.³⁹⁻⁴²

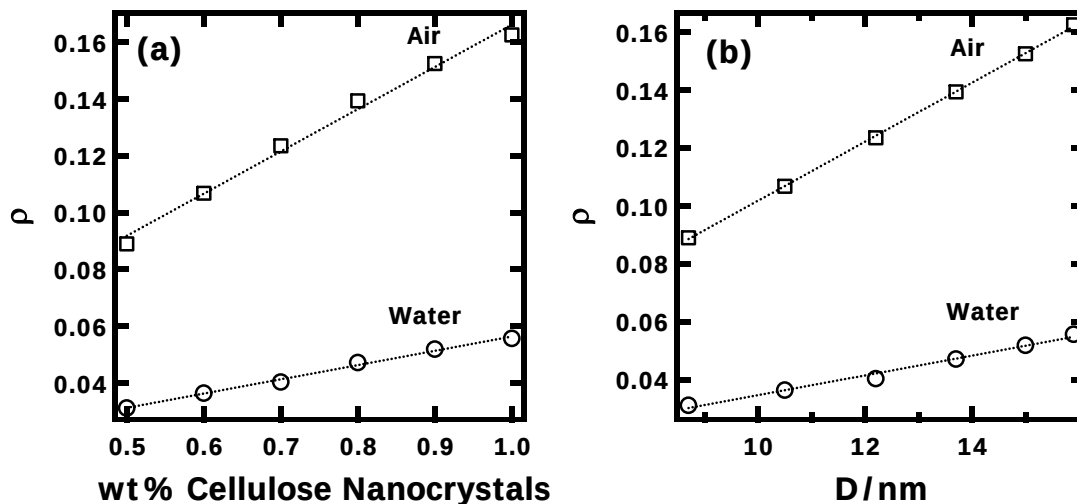


Figure 5.4. (a) ρ vs. wt% concentration of cellulose nanocrystals in the spincoating dispersions and (b) ρ vs. D obtained from MIM ellipsometry data utilizing Approach 1 for spincoated cellulose nanocrystal films. Symbols correspond to measurements in air ($\square$) and hexane ($\circ$) at a wavelength of 632 nm. One standard deviation error bars on ρ are smaller than the size of the symbols used to represent the data.

Table 5.5. Thickness and refractive index values for spincoated films of cellulose nanocrystals deduced from MIM ellipsometry data.^a

wt%	D /nm ^b	n ^b
0.5	8.7 ± 0.1	1.52 ± 0.01
0.6	10.5 ± 0.1	1.51 ± 0.01
0.7	12.2 ± 0.3	1.51 ± 0.01
0.8	13.7 ± 0.1	1.51 ± 0.01
0.9	15.0 ± 0.2	1.51 ± 0.01
1.0	15.9 ± 0.2	1.52 ± 0.01
Average		1.51 ± 0.01
Approach 2		1.51 ± 0.01

^aOne-standard deviation error bars

^bUtilizing Approach 1

5.3.5 MIM Ellipsometry versus SE and MAOI Ellipsometry Measurements

Direct attempts to simultaneously determine the thickness and refractive index values for the TMSC thin films used in this study via SE or MAOI ellipsometry measurements yield estimates with extremely large errors (representative data is provided in Table 5.6). The data in Table 5.6 represents the use of the TFC CompanionTM algorithm without any attempts to constrain D or n . A better approach is to prepare thicker TMSC and regenerated cellulose films and use SE and MAOI ellipsometry to determine the film thickness and refractive index. Once n is known, it serves as a fixed parameter for determining D for the thinner films. Therefore, a thicker spincoated film of TMSC was prepared and measured, and the same film was used to form a regenerated cellulose film. For SE, it is necessary to model $\epsilon(\lambda)$. In this study the CPE material approximation is used. CPE parameters for TMSC and cellulose are provided in Table 5.7. The thicknesses and refractive index values for the thick films are summarized in Table 5.8. As seen in Table 5.8, there is an ~62% reduction in the thickness after cellulose is regenerated from TMSC. The refractive index values as a function of wavelength are also provided through Figure 5.5 and its legend. Using these fixed refractive index values, the thicknesses of the thin films are obtained from SE and MAOI ellipsometry measurements and are summarized in Table 5.9. It is important to note that there are no significant differences for n between the three ellipsometric methods (SE, MIM, and MAOI ellipsometry). Furthermore, D values for thin films deduced from SE and MAOI ellipsometry after n is fixed, yield D values that agree with MIM ellipsometry measurements within experimental error.

Table 5.6. Thickness and refractive index values for representative thin TMSC LB-films from SE and MAOI ellipsometry without any constraints on their values^a

#of Layers	SE (D/nm)	MAOI (D/nm)	n ^b
4	16.0 ± 55.3	14.8 ± 89.1	1.05 ± 2.01
24	47.3 ± 25.1	25.8 ± 11.3	1.22 ± 1.01

^aOne standard deviation error bars

^bMAOI ellipsometry at $\lambda = 632.8$ nm

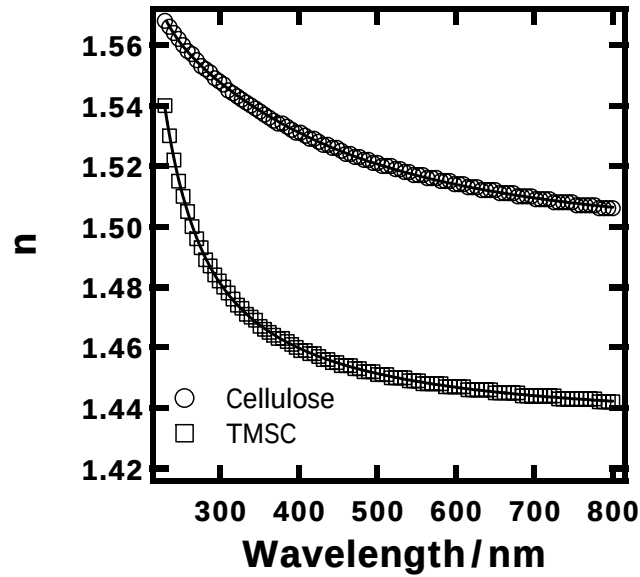


Figure 5.5. n of regenerated cellulose and TMSC films as a function of wavelength obtained via SE ellipsometry. CPE fitting parameters are summarized in Table 7. Solid lines represent empirical fits (according to the Cauchy equations) for $n_{\text{Cellulose}}(\lambda) = 1.4953 + 7628.8/\lambda^2 - 3.5445 \cdot 10^8/\lambda^4 + 8.3012 \cdot 10^{12}/\lambda^6$ and $n_{\text{TMSC}}(\lambda) = 1.436 + 4155.3/\lambda^2 - 1.1466 \cdot 10^8/\lambda^4 + 9.712 \cdot 10^{12}/\lambda^6$. Deviations between the emprical Cauchy equations and the n values obtained from SE ellipsometry are < 0.001 for the wavelength range of $230 \text{ nm} < \lambda < 800 \text{ nm}$.

Table 5.7. CPE parameters for TMSC and regenerated cellulose

Parameters	UV_{term}	A_i	E_{ci}	Γ_i	ϕ_i
TMSC	1.89	-0.74	7.1	-0.038	9.3
Regenerated Cellulose	2.12	-0.86	7.4	0.97	3.0

Table 5.8. Thickness and refractive index values for a thick spincoated film of TMSC and the corresponding regenerated cellulose film^a

	SE (D/nm)	MAOI (D/nm)	n^b
TMSC	228.8 ± 4.1	226.6 ± 1.1	1.45 ± 0.01
Cellulose	86.3 ± 3.6	85.4 ± 0.7	1.52 ± 0.01

^aOne standard deviation error bars^bMAOI ellipsometry at $\lambda = 632.8$ nm**Table 5.9.** Thicknesses for TMSC LB-films obtained from SE and MAOI ellipsometry measurements utilizing the optical constants in Table 5.8 compared to MIM ellipsometry results.^a

#of Layers	D (MIM) ^b /nm	D (SE) /nm	D (MAOI) /nm
4	5.2 ± 0.2	5.5 ± 1.3	5.1 ± 1.1
6	6.9 ± 0.1	6.4 ± 2.4	6.0 ± 0.3
8	9.4 ± 0.3	9.0 ± 1.8	9.8 ± 0.5
10	11.7 ± 0.1	10.9 ± 1.6	11.4 ± 1.2
12	13.8 ± 0.8	14.6 ± 2.8	13.6 ± 0.4
14	14.9 ± 0.3	15.6 ± 2.3	14.0 ± 0.8
16	17.2 ± 0.2	17.9 ± 1.7	18.3 ± 0.6
18	18.7 ± 0.2	19.3 ± 3.1	19.4 ± 0.4
20	20.2 ± 0.3	21.1 ± 1.3	20.1 ± 0.9
22	22.7 ± 0.5	23.2 ± 3.2	22.9 ± 1.2
24	24.2 ± 0.4	25.8 ± 2.3	25.8 ± 0.3

^aOne standard deviation error bars^bUtilizing Approach 1

5.4 Conclusions

Multiple incident media (MIM) ellipsometry provides a rapid (< 5 min for a single film) and unambiguous method for obtaining both film thicknesses and refractive indices of ultrathin films of TMSC, regenerated cellulose, and cellulose nanocrystals. Thickness and refractive index values obtained via the MIM ellipsometry method are in excellent agreement with literature values. Moreover, the MIM ellipsometry results are in quantitative agreement with more traditional ellipsometric techniques (SE and MAOI ellipsometry) within experimental error. Furthermore, it is observed that the value of $n = 1.51 \pm 0.01$ for regenerated cellulose and cellulose nanocrystals via MIM ellipsometry is lower than the parallel component and is consistent with the perpendicular component of the anisotropic refractive index reported for cellulose systems. The fact that there is no difference in n between the regenerated TMSC and cellulose nanocrystal films may indicate that they have similar degrees of crystallinity.

5.5 References

- (1) Richards, G. N.; Blake, J. D. *Carbohydr Res.* **1971**, *18*, 11-21.
- (2) Saake, B.; Kruse, T.; Puls, J. *Bioresource Technol.* **2001**, *80*, 195-204.
- (3) Esker, A.; Becker, U.; Jamin, S. Beppu, S.; Renneckar, S.; Glasser, W. *Hemicelluloses: Science and Technology, ACS, Symp. Ser.* **2004**, *864*, 198-219.
- (4) Gradwell, S. E.; Renneckar, S. Esker A. R.; Heinze, T.; Gatenholm, P.; Vaca-Garcia, C.; Glasser, W. *C. R. Biol.* **2004**, *327*, 945-953.
- (5) Eriksson, J.; Malmsten, M.; Tiberg, F.; Callisen, T. H.; Damhus, T.; Johansen, K. S. *J. Colloid Interface Sci.* **2005**, *285*, 94-99.
- (6) Eriksson, J.; Malmsten, M.; Tiberg, F.; Callisen, T. H.; Damhus, T.; Johansen, K. S. *J. Colloid Interface Sci.* **2005**, *284*, 99-106.
- (7) Freudenberg, U.; Zimmermann, R.; Schmidt, K.; Behrens S. H.; Werner C. J. *Colloid Interface Sci.* **2007**, *309*, 360-365.
- (8) Karlsson, J. O.; Andersson, N.; Berntsson, P.; Chihani, T.; Gatenholm P. *Polymer* **1998**, *39*, 3589-3595.
- (9) Kowalczyk J.; Tritt-Goc, J.; Pislewski N. *Solid State Nucl. Magn. Reson.* **2004**, *25*, 35-41.
- (10) Hardaker, S. S.; Moghazy, S.; Cha, C. Y.; Samuels, R. J. *J. Polym. Sci. Part B: Polym. Phys.* **1993**, *31*, 1951-1963.
- (11) Chiang, K.S.; Cheng S.Y.; Liu, Q.; *J. Lightwave Tech.* **2007**, *25*, 1206-1212.
- (12) Salamon, Z.; Macleod, H. A.; Tollin, G. *Biochim. Biophys. Acta* **1997**, *1331*, 117-129.
- (13) Salamon, Z.; Macleod, H. A.; Tollin, G. *Biophys. J.* **1997**, *73*, 2791-2797.
- (14) Sadik, A. M.; Ramadan, W. A.; Litwin, D. *Meas. Sci. Technol.* **2003**, *14*, 1753-1759.
- (15) Krzyzanowska, H.; Kulik, M.; Zuk, J. *J. Lumin.* **1998**, *80*, 183-186.
- (16) Matsushashi, N.; Okumoto, Y.; Kimura, M.; Akahane, T. *Jpn. J. Appl. Phys. Part I* **2002**, *41*, 4615-4619.
- (17) Cranston, E. D.; Gray, D. G. *Coll. Surf. A* **2008**, In press, Available online.
- (18) Azzam, R. M. A.; Bashara, N. M. *Ellipsometry and Polarized Light*; Elsevier: Amsterdam, 1987.
- (19) Kattner, J.; Hoffmann, H. *J. Phys. Chem. B* **2002**, *106*, 9723-9729.
- (20) Arwin, H.; Aspnes, D. E. *Thin Solid Films* **1986**, *138*, 195-207.
- (21) Irene, E. A. *Solid-State Electron.* **2001**, *45*, 1207-1217.
- (22) Landgren, M.; Jonsson, B. *J. Phys. Chem.* **1993**, *97*, 1656-1664.
- (23) Ayupov, B. M.; Sysoeva, N. P. *Cryst. Res. Technol.* **1981**, *16*, 503-512.
- (24) Mao, M.; Zhang, J. H.; Yoon, R. H.; Ducker, W. A. *Langmuir* **2004**, *20*, 1843-1849.
- (25) McCrackin, F. L.; Passaglia, E.; Stromberg, R. R.; Steinberg, H. L. *J. Res. Natl. Bur. Std.* **1963**, *67*, 363-367.
- (26) Gunnars, S.; Wagberg, L.; Stuart, M. A. C. *Cellulose* **2002**, *9*, 239-249.
- (27) Rosenau, T.; Potthast, A.; Sixta, H.; Kosma, P. *Prog. Polym. Sci.* **2001**, *26*, 1763-1837.

- (28) Dawsey, T. R.; McCormick, C. L. *JMS-Rev. Macromol. Chem. Phys.* **1990**, *30*, 405-440.
- (29) Nehl, I. Wagenknecht, W.; Philipp, B. *Cellul. Chem. Technol.* **1995**, *29*, 243.
- (30) Schaub, M.; Wenz, G.; Wegner, G.; Stein, A.; Klemm, D. *Adv. Mater.* **1993**, *5*, 919-922.
- (31) Kontturi, E.; Thune, P. C.; Niemantsverdriet, J. W. *Polymer* **2003**, *44*, 3621-3625.
- (32) Beck-Candanedo, S.; Roman, M.; Gray, D. G. *Biomacromolecules* **2005**, *6*, 1048-1054.
- (33) Holmberg, M.; Berg, J.; Stemme, S.; Odberg, L.; Rasmusson, J.; Claesson, P. *J. Colloid Interface Sci.* **1997**, *186*, 369-381.
- (34) Loscher, F.; Ruckstuhl, T.; Jaworek, T.; Wegner, G.; Seeger, S. *Langmuir* **1998**, *14*, 2786-2789.
- (35) Buchholz, V.; Adler, P.; Backer, M.; Holle, W.; Simon, A.; Wegner, G. *Langmuir* **1997**, *13*, 3206-3209.
- (36) Rehfeldt, F.; Tanaka, M. *Langmuir* **2003**, *19*, 1467-1473.
- (37) Buchholz, V.; Wegner, G.; Stemme, S.; Odberg, L. *Adv. Mater.* **1996**, *8*, 399-402.
- (38) Blodgett, K. B. *J. Am. Chem. Soc.* **1934**, *56*, 495-495.
- (39) Brandrup, J.; Immergut, E. H.; Grulke, E. A. *Polymer Handbook*; John-Wiley: New York, 1999
- (40) Bordel, D.; Putaux, J. L.; Heux, L. *Langmuir* **2006**, *22*, 4899-4901.
- (41) Roman, M.; Gray, D. G. *Langmuir* **2005**, *21*, 5555-5561
- (42) Cranston, E. D.; Gray, D. G. *Biomacromolecules* **2006**, *7*, 2522-2530.

CHAPTER 6

Nanofiller Effects on Glass Transition Temperatures of Ultrathin

Polymer Films and Bulk Systems

6.1 Abstract

Polyhedral oligomeric silsesquioxane (POSS) derivatives, which are hybrid organic/inorganic materials, may be useful in nanocomposite formulations for enhancing the glass transition temperature (T_g) and thermal stability of bulk systems and thin films. Surface T_g is expected to be different from the corresponding bulk value because of greater fractional free volume in thin films and residual stresses that remain from film preparation. As a model system, thin-films of trisilanolphenyl-POSS (TPP) and two different number average molar mass (5 and 23 kg·mol⁻¹) poly(*t*-butyl acrylate) (PtBA) samples were prepared as blends by Y-type Langmuir-Blodgett film deposition. Thermally induced structural changes like surface T_g and the loss of multilayer film architectures were detected by ellipsometry. For comparison, bulk T_g values were obtained by differential scanning calorimetry (DSC) for samples prepared by solution casting. Our observations show that surface T_g increases more than bulk T_g for both high and low molar mass samples upon the addition of TPP nanofiller. The increase in bulk T_g as a function of added TPP for high and low molar mass samples is on the order of $\Delta T_g \sim 10$ °C. Whereas, bulk T_g shows comparable T_g increases for both molar masses ($\Delta T_g \sim 10$ °C), the increase in surface T_g for the higher molar mass PtBA is greater than for lower molar mass PtBA ($\Delta T_g \sim 21$ °C vs. ~ 13 °C, respectively). Nonetheless, the total

enhancement of T_g is complete by the time ~20 wt% TPP is added without further benefit at higher nanofiller loads.

6.2 Introduction

One of the most important thermal parameters for characterizing a polymer as an engineering material is the glass transition temperature, T_g . At very slow heating and cooling rates the glass transition exhibits properties similar to a second order transition according to the Ehrenfest classification of phase transitions.¹⁵ It follows from the Ehrenfest classification that the slopes of the chemical potentials (μ) plotted against the temperature are different on either side of the transition. A transition, in which the first derivative of μ with respect to temperature is discontinuous, is described as a first order phase transition. For T_g , the first derivatives of μ (hence H and V) are continuous but the second derivatives appear to be discontinuous as expected for a second order phase transition. As such, T_g can be determined experimentally by measuring the change in basic thermodynamic properties of a polymer such as volume and enthalpy as a function of temperature.

Ultrathin polymer films can exhibit substantially different polymer properties than they do in the bulk state. Mechanical properties such as translational diffusion coefficients, viscosity, and T_g are influenced by confinement effects and by interfacial interactions.¹⁻¹⁴ The glass transition behavior of a polymer at an interface is not fully understood, prompting new experiments to investigate T_g at surfaces. During the past decade the glass transition phenomenon at surfaces has been studied extensively and many efforts have been made to measure surface T_g . Initial studies focused on detecting changes in the thermal expansion coefficients before and after T_g . Keddie, *et al.* studied

the effect of film thickness on the surface T_g of polymer films supported on hydrogen passivated substrates.¹⁶ A depression of ~ 30 °C in the surface T_g relative to the bulk T_g was observed for a 10 nm polystyrene (PS) film (number average molar mass, $M_n = 120.0$ kg·mol⁻¹; polydispersity index, $M_w/M_n = 1.05$). Keddie, *et al.* also provided an empirical equation for the T_g of PS films of thicknesses less than 40 nm on silicon substrates. (Equation 2.28).¹⁶ Other studies have also reported a depression of surface T_g with decreasing thickness provided there are no specific interactions between the polymer and the substrate.¹⁷⁻¹⁹ On the other hand, the investigation of poly(methyl methacrylate) (PMMA) thin films by ellipsometry reveals the effect of polymer-substrate interactions on the glass transition temperature of thin films. It was observed that upon decreasing PMMA films thickness, the T_g of the films on the native oxide of silicon substrates and on gold substrates increased and decreased, respectively.²⁰ Keddie *et al.* suggested that the increase in T_g for PMMA films supported on SiO₂ substrates is due to hydrogen bonding between surface silanols and PMMA. X-ray reflectivity (XR) studies of polystyrene thin films on hydrogen terminated silicon substrates contrast with the previously published study of Keddie *et al.* on the same surfaces.²¹ Wallace *et al.* argue that the observations by Keddie *et al.* are actually the glass transition behavior of polystyrene on a SiO₂ surfaces because of surface oxidation. Further studies with poly(2-vinyl pyridine) on acid cleaned silicon oxide substrates showed that the surface glass transition temperature increased by up to 50 °C over the bulk T_g .²² This observation is attributed to favorable polar interactions between the substrate and the polymer. Recent studies on the effects of substrate-polymer interactions on surface T_g values reveal that with decreasing film thickness weak polymer/substrate interfacial interactions lead to

lower surface T_g values and strong polymer/substrate interfacial interactions leads to higher surface T_g values relative to the bulk materials.²³⁻²⁸ Both PMMA and poly(2-vinyl pyridine) films on hydrogen terminated silicon highlight the effects of substrate and substrate-polymer interactions whereas, thin film studies by Keddie *et al.* highlight the effect of film confinement effects. Studies by Dutcher *et al.* on free standing films of PS confirmed the previous linear decreases of T_g with decreasing film thickness.^{29,30} Furthermore, they investigated molar mass effects on surface T_g for thin, free standing polystyrene films.^{31,32} Large T_g differences between samples of different molar mass were observed as the film thickness decreased. Detailed investigations showed that reductions in surface T_g for films of high molar mass PS, where chain confinement effects are dominant, was greater than those observed for low molar mass PS where bulk T_g is already depressed by the greater fractional free volume associated with a greater contribution to the polymer properties by the chain ends.³¹

According to most of these studies, deviations from bulk T_g for polymers at interfaces arise from several factors including film structure,³³ film thickness,^{17,18,34} polymer-substrate interactions,²⁰ the chemical structure of the substrate,²² and molar mass.^{31,32} There are also a few reports on the surface T_g of polymeric Langmuir-Blodgett (LB) films, relative to their spincoated analogs.^{33,35} See *et al.* have studied the effects of molecular orientation within the film on surface T_g . When spincoated poly(*tert*-butyl methacrylate) (PtBMA) films on silicon substrates are compared with LB deposited PtBMA films it is seen that the T_g of LB-films are almost independent of the thickness for the first heating cycle.³³ As all facets of surface T_g are not fully understood for LB-films, additional studies of thermal transitions in such films are required.

While much of the reported experimental work has focused on thin homopolymer systems, very little is known about thin multicomponent systems.^{36,37} Furthermore, physical blending of homopolymers with nanofillers could be utilized to control or improve the basic properties of thin films such as surface T_g . Filler content is an essential variable influencing surface T_g and has not been extensively studied.³⁸ Polyhedral oligomeric silsesquioxanes (POSS) acting as nanofillers, have been used to improve the thermal properties of bulk polymeric materials. POSS based materials may play an important role in high temperature applications and space resistant coatings because of their organic-inorganic hybrid structure.³⁹ The organic coronae of POSS allow easy processing and make them compatible with polymeric materials, while the rigid inorganic cores provide mechanical strength and oxidative stability.^{40,41} Furthermore, Li et al. reported enhanced thermal stability for POSS/polymer systems and copolymers.⁴² However, surface T_g of POSS based materials have not been reported elsewhere.

This chapter focuses on surface T_g of a relatively high ($M_n = 23.6 \text{ kg}\cdot\text{mol}^{-1}$) and low ($M_n = 5.0 \text{ kg}\cdot\text{mol}^{-1}$) molar mass poly (t-butyl acrylate) (PtBA), as well as blend films with trisilanolphenyl-POSS (TPP), on hydrophobic silicon surfaces at nominal film thicknesses of $\sim 30 \text{ nm}$. Subsequent comparisons to the corresponding bulk blends are made.

6.3 Results and Discussion

For additional experimental details, please see Chapter 3. In contrast to Chapters 4 and 5, ellipticity values (ρ) are only measured at a single point for thermal expansion curves. Nonetheless, one standard deviation error bars on the points are still smaller than the size of the symbols used to represent the data.

6.3.1 PtBA, TPP, and PtBA/TPP Blend LB-Films: First vs. Second Heating Scans

Temperature scans were used to track thermal expansion from changes in ellipticity. As shown in Figure 6.1 (a) two thermal transitions are observed in the higher molar mass PtBA LB-films during the first thermal annealing scan. The first transition at ~ 13 °C (the intersection of the lines corresponding to the glassy and rubbery states) corresponds to the surface T_g and is weak because PtBA LB-films have a double layer structure with a double layer spacing of ~ 18.8 Å.⁴³ The second transition is attributed to the loss of the double layer structure of the LB layers. Figure 6.2 (a) schematically depicts the double layer structure proposed by Esker *et al.*⁴³ The double layer “melts away” at $T_d \sim 69$ °C for $M_n = 23.6$ kg·mol⁻¹ PtBA LB-films [Figure 6.1 (a)] and at $T_d \sim 72$ °C for $M_n = 5.0$ kg·mol⁻¹ PtBA LB-films as shown in Figure 6.1 (b). At this point, it is important to note that second heating scans only show surface T_g (inset of Figure 6.1), i.e. the double layer is gone. Furthermore, double layer structures are never observed in spincoated PtBA films to be discussed later.

Like PtBA, single component TPP LB-films also show a double layer transition at $T_d \sim 40$ °C during an initial heating scan [Figure 6.1 (c)]. Additional proof for the double layer structure comes from XR studies like the one shown in Figure 6.2 (b). Figure 6.2 (b) contains reflectivity, $R(q)$, as a function of the scattering wave vector q for a 48 layer LB-film of TPP on a passivated silicon (SiH) surface. The Kiessig fringe spacing [Δq on Figure 6.2 (b)] and attenuated intensity of the oscillations with increasing q , are consistent with a TPP total film thickness of $D=42$ nm, and a root-mean-square roughness of $R_p \sim 0.8$ nm. Moreover, the position of the Bragg peak at $q = 0.37$ Å⁻¹ is consistent with a double layer structure with a double layer spacing of ~ 1.7 nm as

depicted in Figure 6.2 (c). Excellent agreement between the total film thickness and the double layer spacing is consistent with quantitative LB-transfer.

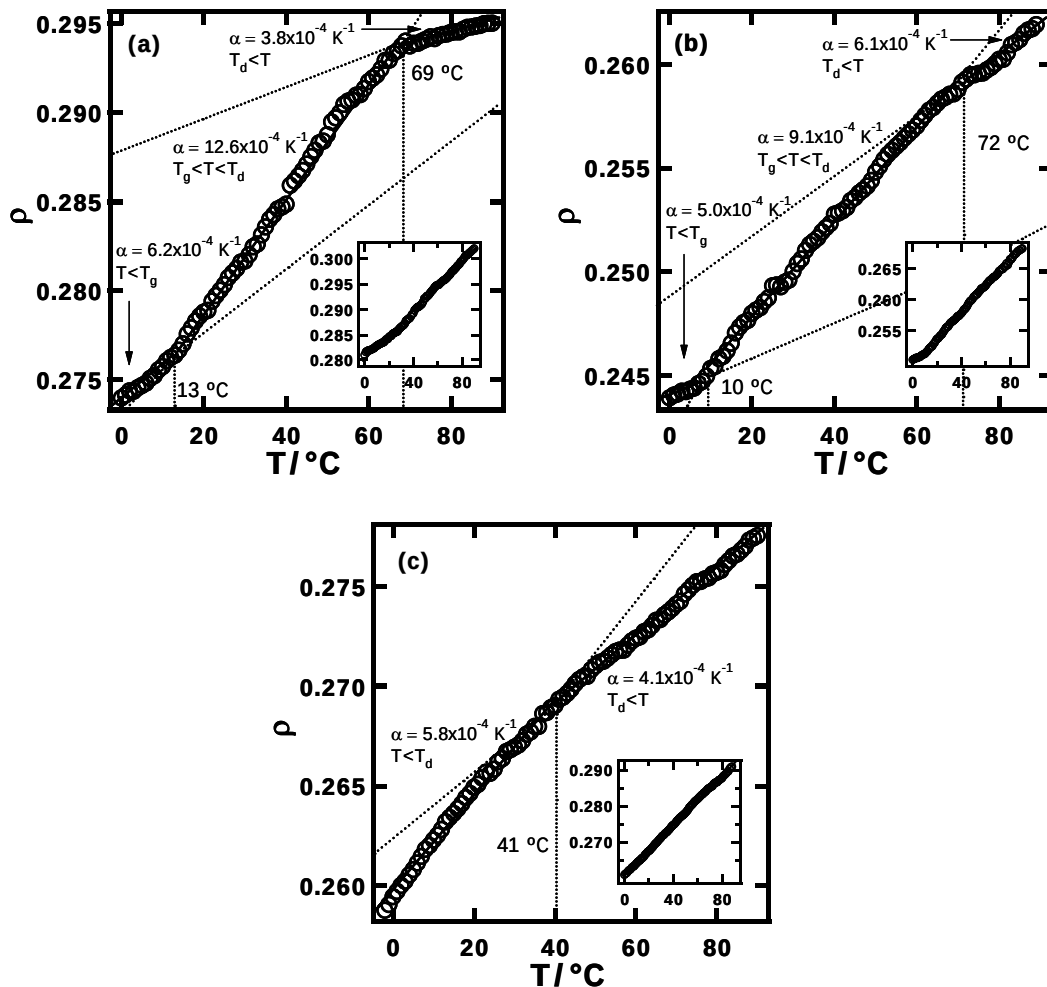


Figure 6.1. Representative first heating scans showing double layer transitions for 30 layer LB-films of (a) $M_n = 23.6 \text{ kg}\cdot\text{mol}^{-1}$ PtBA, (b) $M_n = 5.0 \text{ kg}\cdot\text{mol}^{-1}$ PtBA, and (c) TPP. Insets show the absence of double layer transitions for second heating cycles.

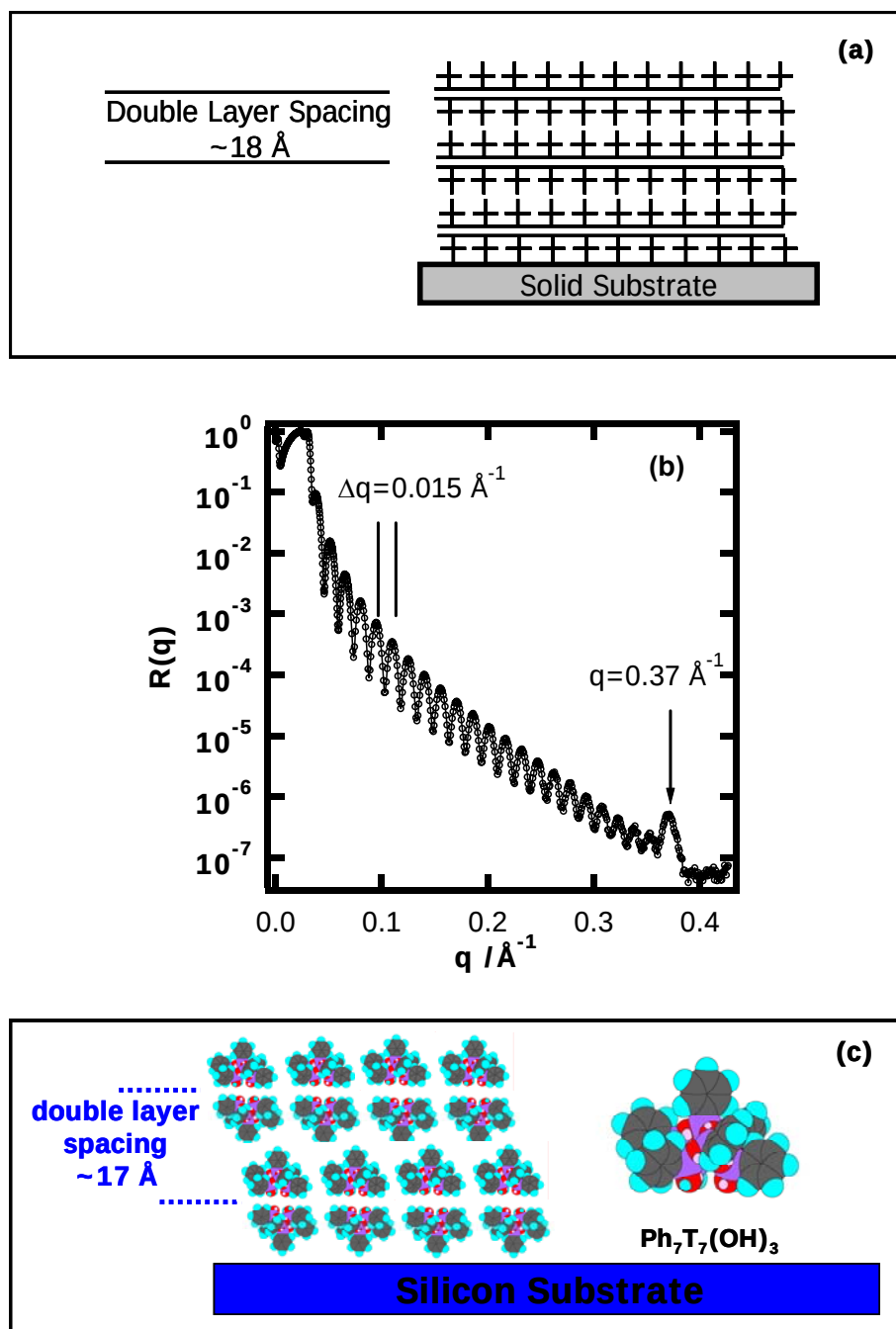


Figure 6.2: (a) A schematic depiction of the double layer structure for PtBA proposed by Esker *et al.*⁴³ (b) A representative X-ray reflectivity profile for a 48 layer LB-film of TPP showing Kiessig fringes and a single Bragg peak. (c) A schematic representation of a double layer structure for TPP molecules on hydrophobic silicon substrates that is consistent with (b).

In addition to studies of single component LB-films, T_d for LB- films of PtBA/TPP blend systems were investigated as a function of TPP content. Analogous plots to Figure 6.1 showing the double layer transition for PtBA/TPP blends of $5.0 \text{ kg}\cdot\text{mol}^{-1}$ PtBA and $23.6 \text{ kg}\cdot\text{mol}^{-1}$ PtBA are provided as Figures 6.3 through 6.6. Figure 6.3 contains thermal expansion curves for 30 layer LB-films of $M_n=5.0 \text{ kg}\cdot\text{mol}^{-1}$ PtBA filled with TPP at low levels wt% (≤ 20 wt% TPP), while Figure 6.4 is the same system filled at high levels (>20 wt% TPP). Likewise, Figure 6.5 contains thermal expansion curves for 30 layer LB-films of $M_n = 23.6 \text{ kg}\cdot\text{mol}^{-1}$ PtBA filled with TPP at low levels (≤ 20 wt% TPP), while Figure 6.6 is the same system filled at high levels (>20 wt% TPP). A summary of T_d values as a function of TPP composition are reported in Table 6.1. T_d for single-component $M_n = 23.6$ and $5.0 \text{ kg}\cdot\text{mol}^{-1}$ PtBA LB-films are 69 and 72 °C, respectively. T_d values for the filled LB-films range between 40 and 50 °C as a function of TPP composition and do not exhibit a discernible molar mass or composition dependence. The most important point of Table 6.1 is that as little as 1 wt% TPP is sufficient to drop the T_d values of PtBA films to essentially the value of a single component TPP film ($T_d = 41$ °C). In essence, the TPP behaves like a plasticizer lowers the energy barrier for reorganization of the Y-type LB-film of PtBA.

Table 6.1: Double layer transition temperatures for 30 layer TPP filled PtBA LB-films.

wt% TPP	$T_d / ^\circ\text{C}$	
	$M_n=5 \text{ kg}\cdot\text{mol}^{-1}$	$23 \text{ kg}\cdot\text{mol}^{-1}$
0	69 ± 1	72 ± 1
1	40 ± 1	44 ± 1
3	43 ± 1	40 ± 1
5	46 ± 1	43 ± 1
20	45 ± 1	45 ± 1
40	46 ± 1	49 ± 1
60	40 ± 1	44 ± 1
90	40 ± 1	45 ± 1
100	41 ± 1	41 ± 1

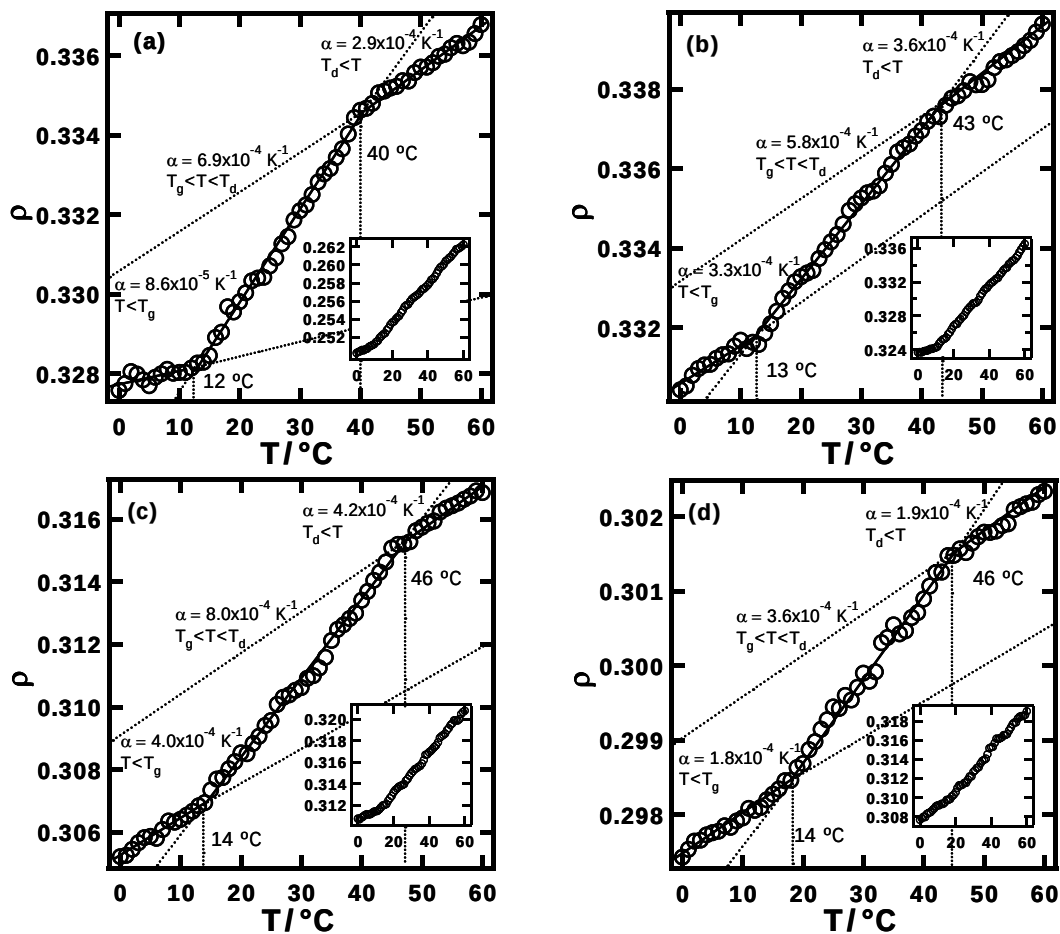


Figure 6.3. Representative first heating scans showing both double layer transitions and surface T_g for 30 layer LB-films of $M_n = 5.0 \text{ kg}\cdot\text{mol}^{-1}$ PtBA filled with (a) 1, (b) 3, (c) 5, and (d) 20 wt% TPP nanofiller. Insets show the absence of a double layer transition for the second heating cycles.

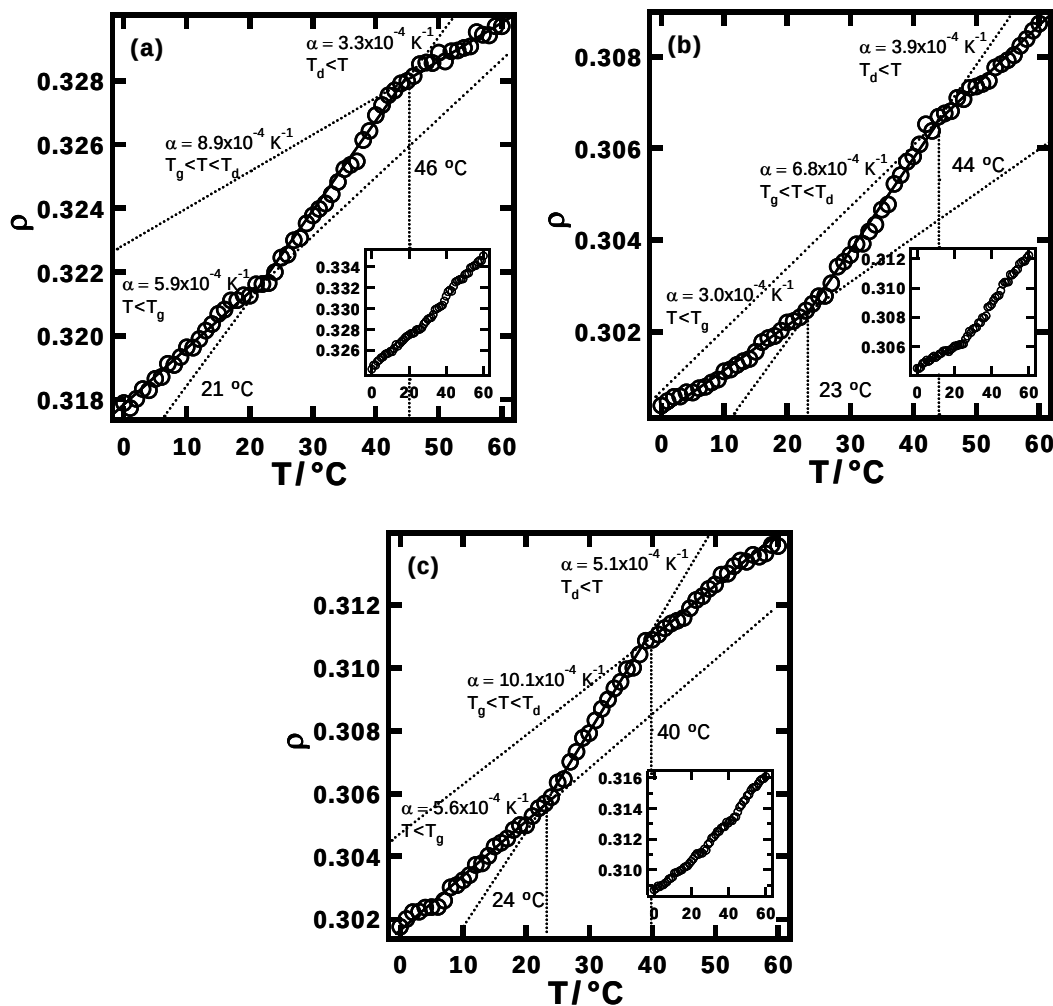


Figure 6.4. Representative first heating scans showing both double layer transitions and surface T_g for 30 layer LB-films of $M_n = 5.0 \text{ kg}\cdot\text{mol}^{-1}$ PtBA filled with (a) 40, (b) 60, and (c) 90 wt% TPP nanofiller. Insets show the absence of a double layer transition for the second heating cycles.

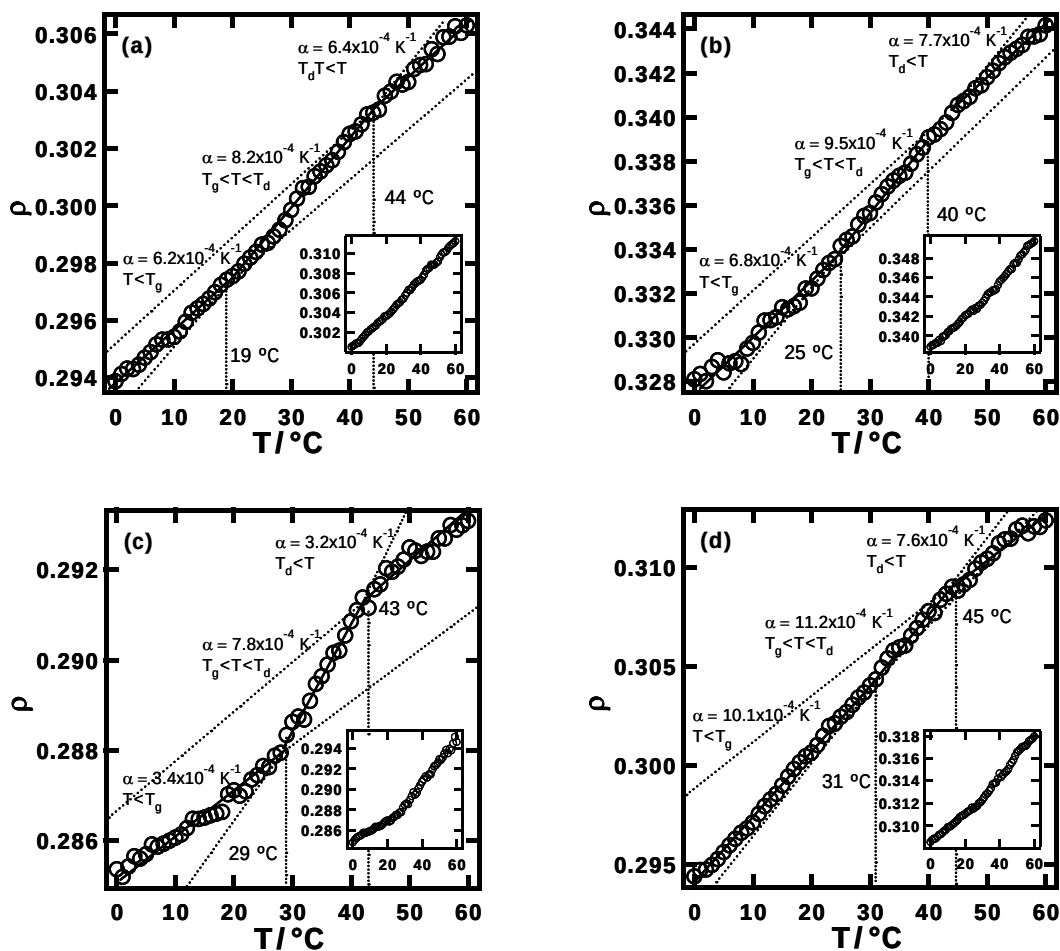


Figure 6.5. Representative first heating scans showing both double layer transitions and surface T_g for 30 layer LB-films of $M_n = 23.6 \text{ kg}\cdot\text{mol}^{-1}$ PtBA filled with (a) 1, (b) 3, (c) 5, and (d) 20 wt% TPP nanofiller. Insets show the absence of a double layer transition for the second heating cycles.

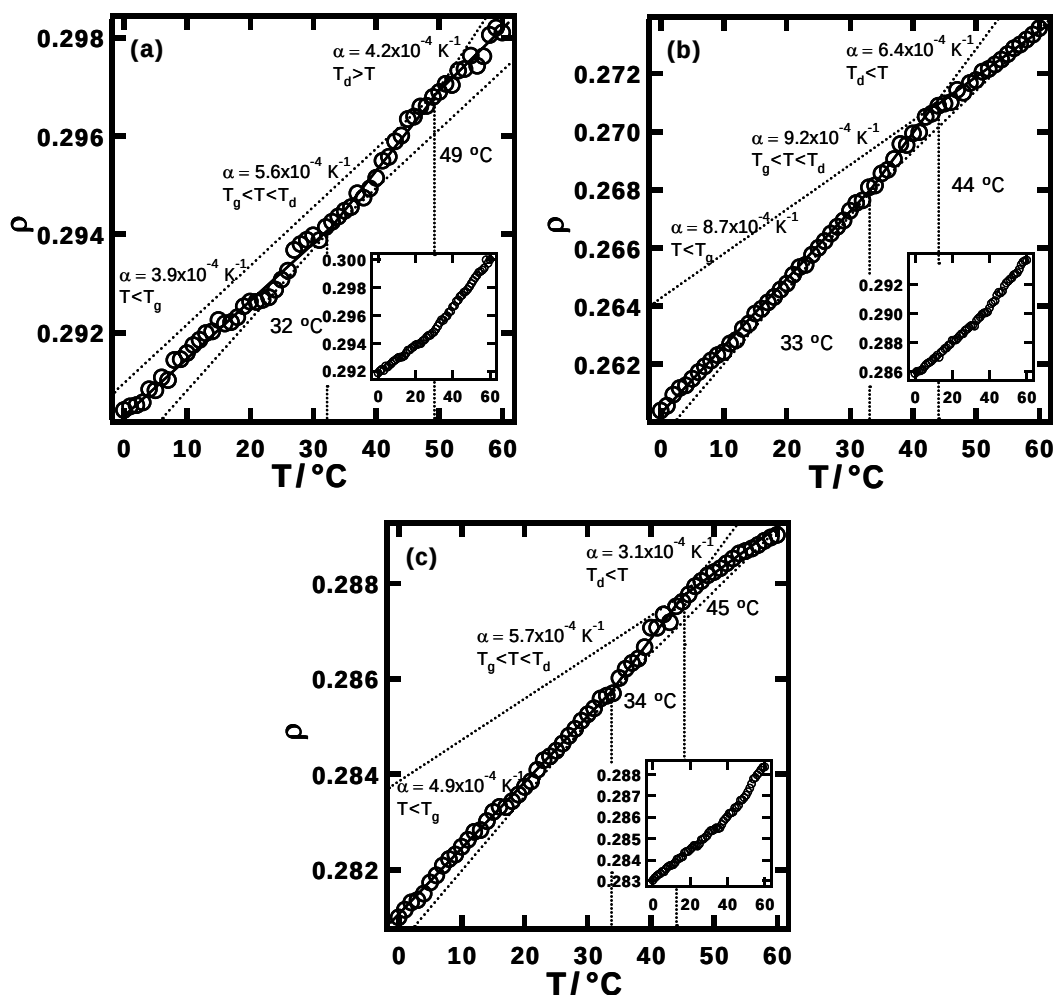


Figure 6.6. Representative first heating scans showing both double layer transitions and surface T_g for 30 layer LB-films of $M_n = 23.6 \text{ kg}\cdot\text{mol}^{-1}$ PtBA filled with (a) 40, (b) 60, and (c) 90 wt% TPP nanofiller. Insets show the absence of a double layer transition for the second heating cycles.

6.3.2 LB vs. Spincoated Films of PtBA

Figure 6.7 shows plots of ellipticity versus temperature, for second heating scans of a spincoated [Figure 6.7 (a)] and LB [Figure 6.7 (b)] film of $M_n = 23.6 \text{ kg}\cdot\text{mol}^{-1}$ PtBA with comparable thicknesses ($\sim 30 \text{ nm}$). The surface T_g of the $M_n = 23.6 \text{ kg}\cdot\text{mol}^{-1}$ PtBA LB

and spincoated films are determined from the intersection of the thermal expansion curves corresponding to the glassy and rubbery states. From Figure 6.7, the surface T_g values are estimated to be 13 and 15 °C for LB and spincoated films, respectively. As observed in Figure 6.7 (a) and (b), the slopes before and after T_g are quite different for LB-films compared to spincoated films of similar thicknesses. This behavior is attributed to differences in residual stresses in the LB and spincoated films arising from sample preparation. To test this hypothesis, both LB and spincoated $M_n = 5.0 \text{ kg}\cdot\text{mol}^{-1}$ PtBA films were annealed overnight under vacuum at 90 °C. After overnight annealing the surface T_g (~ 14 °C) and α values in both the glassy ($\alpha = 3.4 \times 10^{-4} \text{ K}^{-1}$) and rubbery states ($\alpha_G = 6.1 \times 10^{-4} \text{ K}^{-1}$), for the spincoated film [Figure 6.7 (c), first scan] are comparable to the T_g (~ 15 °C) and α values in both the glassy ($\alpha_R = 3.5 \times 10^{-4} \text{ K}^{-1}$) and rubbery states ($\alpha = 6.7 \times 10^{-4} \text{ K}^{-1}$) of the LB-film [Figure 6.7 (d), first scan]. It is worth noting that after preannealing at 90 °C for 16 h, T_g and α values do not change between the first and second heating scans, and the double layer transition is absent during the first heating scan as shown in the insets of Figure 6.7 (c) and Figure 6.7 (d).

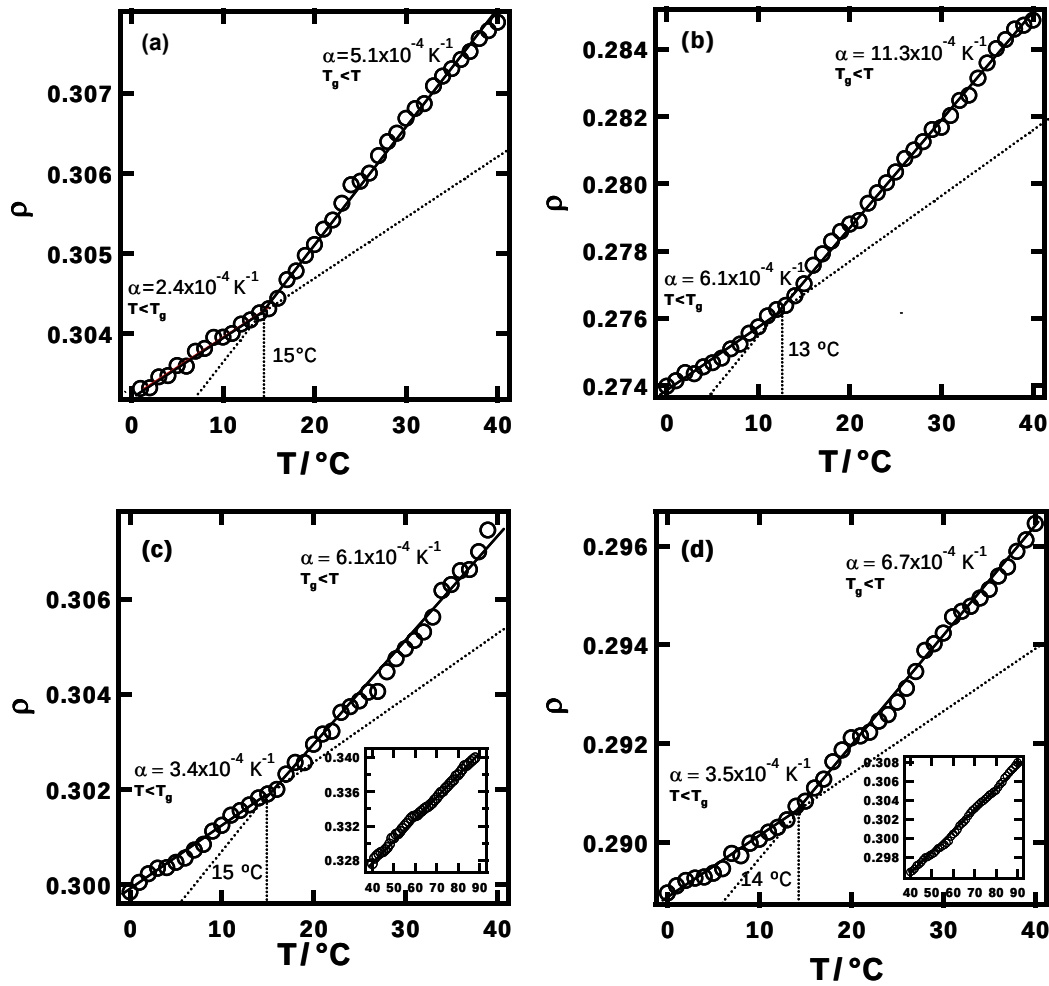


Figure 6.7. Thermal expansion curves for $M_n = 23.6 \text{ kg}\cdot\text{mol}^{-1}$ PtBA films. (a) and (b) contain second heating scans for (a) $\sim 30 \text{ nm}$ spincoated and (b) $\sim 28 \text{ nm}$ LB films without first subjecting the films to overnight annealing. (c) and (d) contain first heating scans for (c) $\sim 30 \text{ nm}$ spincoated and (d) $\sim 28 \text{ nm}$ LB films after annealing at 90°C for 16 h. The insets show the entire heating scan range in (c) and (d).

Overnight annealing experiments (90°C , 16 h) were also performed for $M_n = 5.0 \text{ kg}\cdot\text{mol}^{-1}$ PtBA samples. The behavior of the $M_n = 5.0 \text{ kg}\cdot\text{mol}^{-1}$ sample is similar to the

$M_n = 23.6 \text{ kg}\cdot\text{mol}^{-1}$ samples with respect to annealing the samples for 16 h. Analogous plots to Figure 6.7 (c) and (d) are provided in Figure 6.8. As seen in Figure 6.8, spincoated and LB-films of $M_n = 5.0 \text{ kg}\cdot\text{mol}^{-1}$ PtBA exhibit thermal behavior around the glass transition that is similar to spincoated films after overnight annealing. The key parameters are $T_g = 11 \text{ }^\circ\text{C}$, $\alpha_G = 5.3 \times 10^{-4} \text{ K}^{-1}$ (glassy) and $\alpha_R = 7.2 \times 10^{-4} \text{ K}^{-1}$ (rubbery) for spincoated samples and $T_g = 10 \text{ }^\circ\text{C}$ and $\alpha_G = 5.1 \times 10^{-4} \text{ K}^{-1}$ (glassy), and $\alpha_R = 7.6 \times 10^{-4} \text{ K}^{-1}$ (rubbery) for LB-films. Furthermore, no double layer transition is observed for the $M_n = 5.0 \text{ kg}\cdot\text{mol}^{-1}$ PtBA LB-films after overnight annealing (insets of Figure 6.8). This result is consistent with similar studies for $M_n = 23.6 \text{ kg}\cdot\text{mol}^{-1}$ PtBA LB-films.

On the basis of Figures 6.7 and 6.8, it is clear that differences in thermal expansion coefficient between as prepared LB and spincoated PtBA films during first and second heating scans primarily arise from residual stresses, double layer structures in LB films, that are less important in spincoated films. Nonetheless, the spincoated films also have residual stresses. Annealing spincoated PtBA films for 16h at $90 \text{ }^\circ\text{C}$ led to changes in the thermal expansion coefficients. As expected, the changes in the thermal expansion coefficients for the spincoated films are smaller than those for LB-films, a reflection of the greater residual stresses in LB-films.

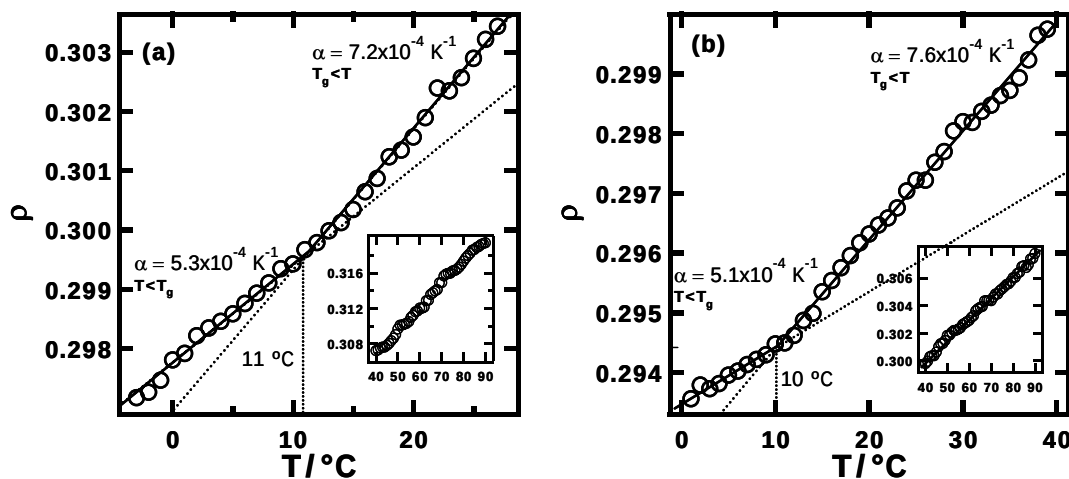


Figure 6.8. Thermal expansion curves for $M_n = 5.0 \text{ kg}\cdot\text{mol}^{-1}$ PtBA films after first annealing the films for 16h at 90 °C under vacuum. First heating scans for (a) an ~30 nm thick spincoated film and (b) an ~28 thick LB-film.

6.3.3 LB-films vs. Bulk PtBA/TPP Blends

In this section the effect nanofillers have on surface T_g is investigated. Figure 6.9 (a) contains the same thermal expansion curve as Figure 6.7 (b) for a second heating scan of an ~28 nm LB-film of $M_n = 23.6 \text{ kg}\cdot\text{mol}^{-1}$ PtBA, while Figure 6.9 (b) contains an analogous thermal expansion curve for an ~28 nm LB-film of $M_n = 23.6 \text{ kg}\cdot\text{mol}^{-1}$ PtBA with 5 wt% TPP. As seen in Figure 6.9, 5 wt% TPP increases surface T_g by ~15 °C.

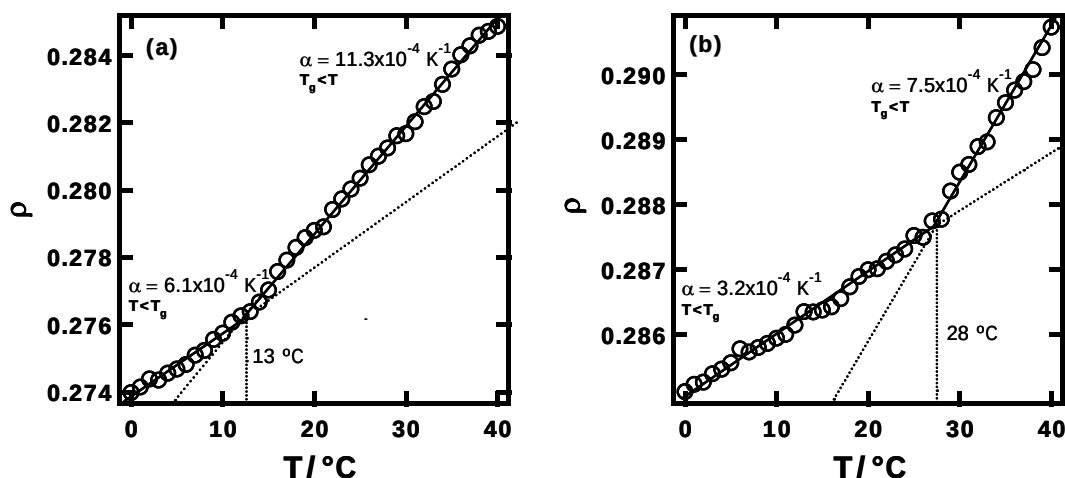


Figure 6.9: Thermal expansion curves (second heating scans) for ~ 28 nm thick films of $M_n = 23.6 \text{ kg}\cdot\text{mol}^{-1}$ PtBA LB-films (a) without and (b) with 5 wt% TPP.

On the basis of the significant effect TPP had on surface T_g in PtBA LB-films, the effect of TPP composition on surface T_g was also examined. Figure 6.10 contains thermal expansion curves (second heating scans) for ~ 28 nm LB-films of $M_n = 23.6 \text{ kg}\cdot\text{mol}^{-1}$ PtBA containing 1 to 90 wt% TPP, while Figures 6.11 (low wt% TPP) and 6.12 (high wt% TPP) contain analogous data for the $M_n = 5.0 \text{ kg}\cdot\text{mol}^{-1}$ PtBA/TPP system. Both systems show a systematic increase in surface T_g with increasing TPP that saturates for high enough levels of TPP. Rather than provide a discussion of each graph sequentially, the key trends are summarized in the next paragraph.

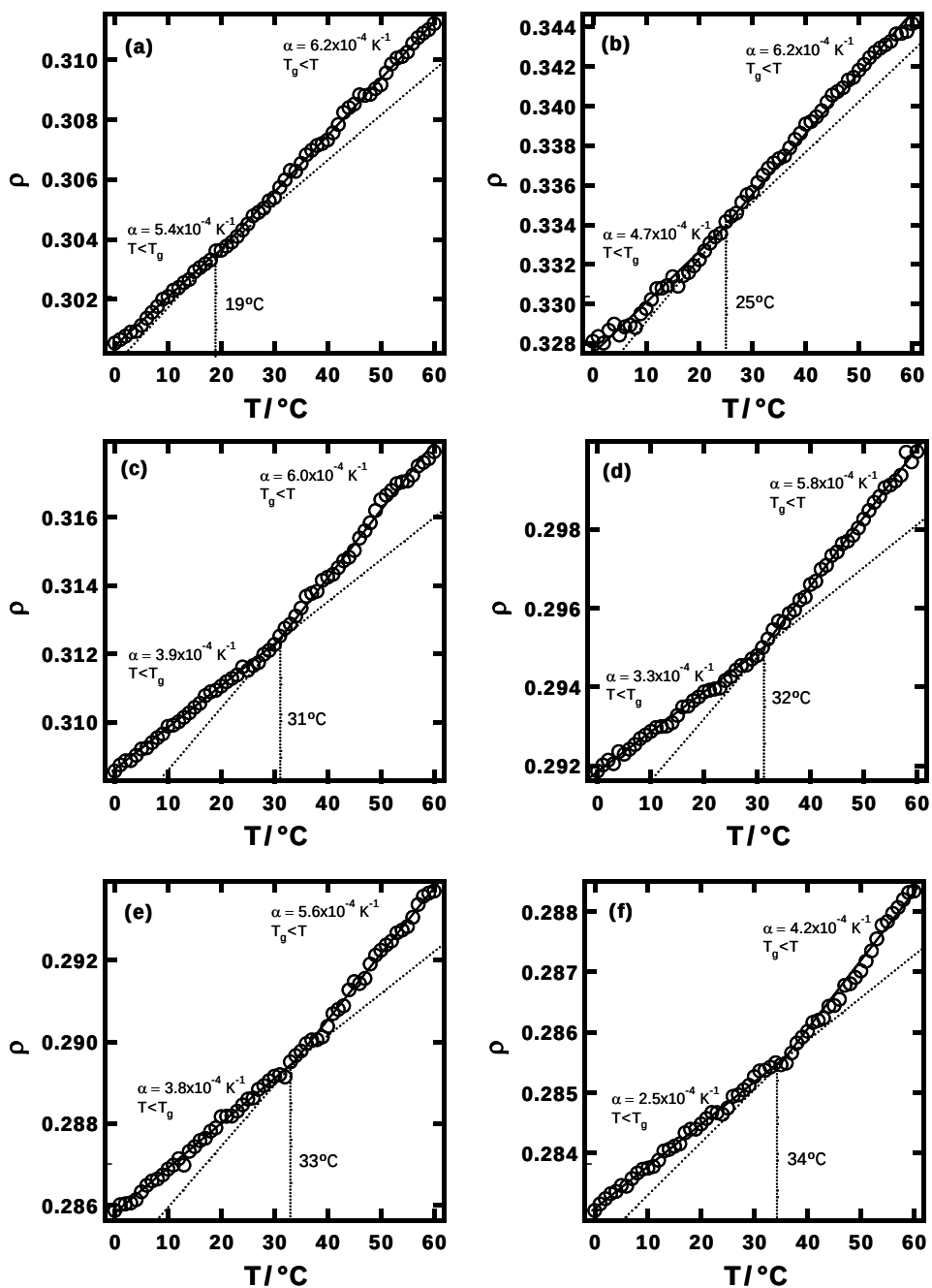


Figure 6.10: Thermal expansion curves for second heating scans of ~ 28 nm $M_n = 23.6$ kg $\cdot$ mol $^{-1}$ PtBA LB-films containing (a) 1, (b) 3, (c) 20, (d) 40, (e) 60, and (f) 90 wt% TPP.

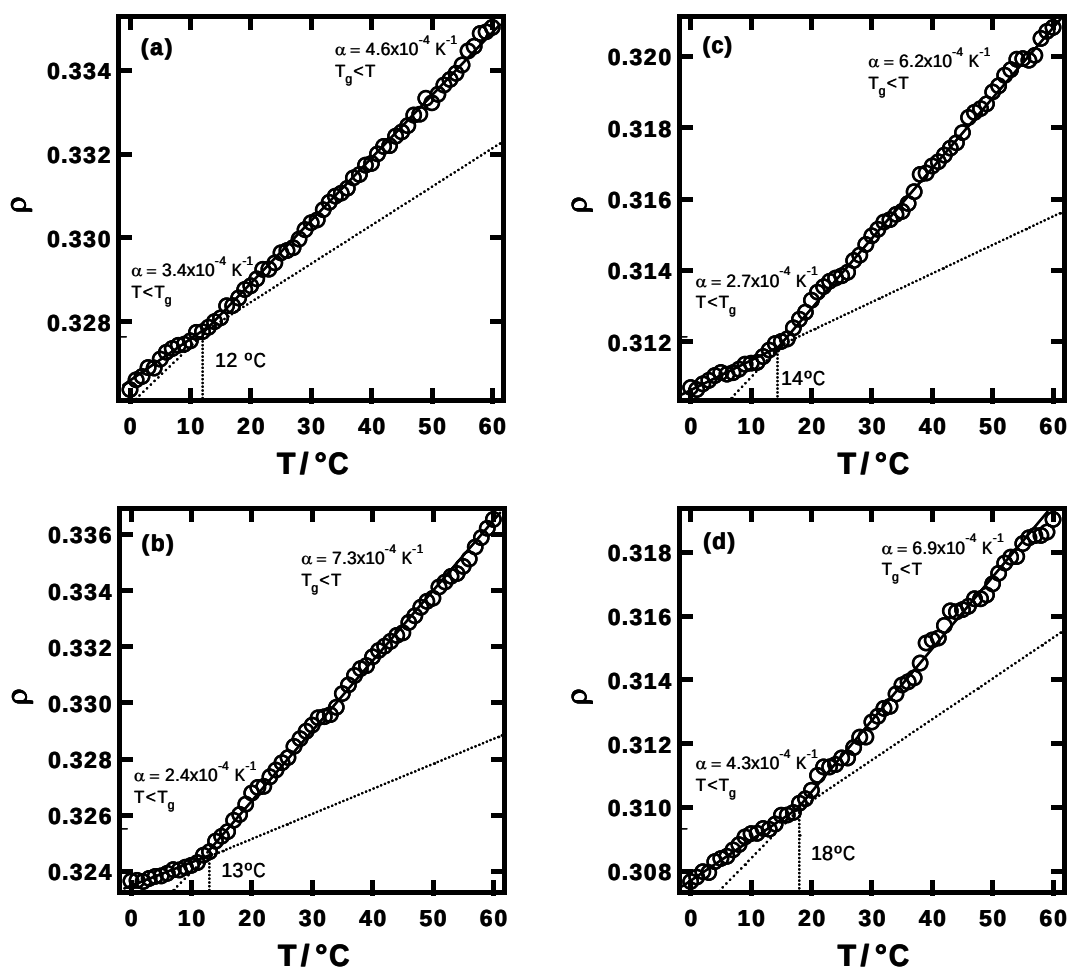


Figure 6.11: Thermal expansion curves for second heating scans of ~ 28 nm $M_n = 5.0$ $\text{kg}\cdot\text{mol}^{-1}$ PtBA LB-films containing (a) 1, (b) 3, (c) 5, and (d) 20 wt% TPP.

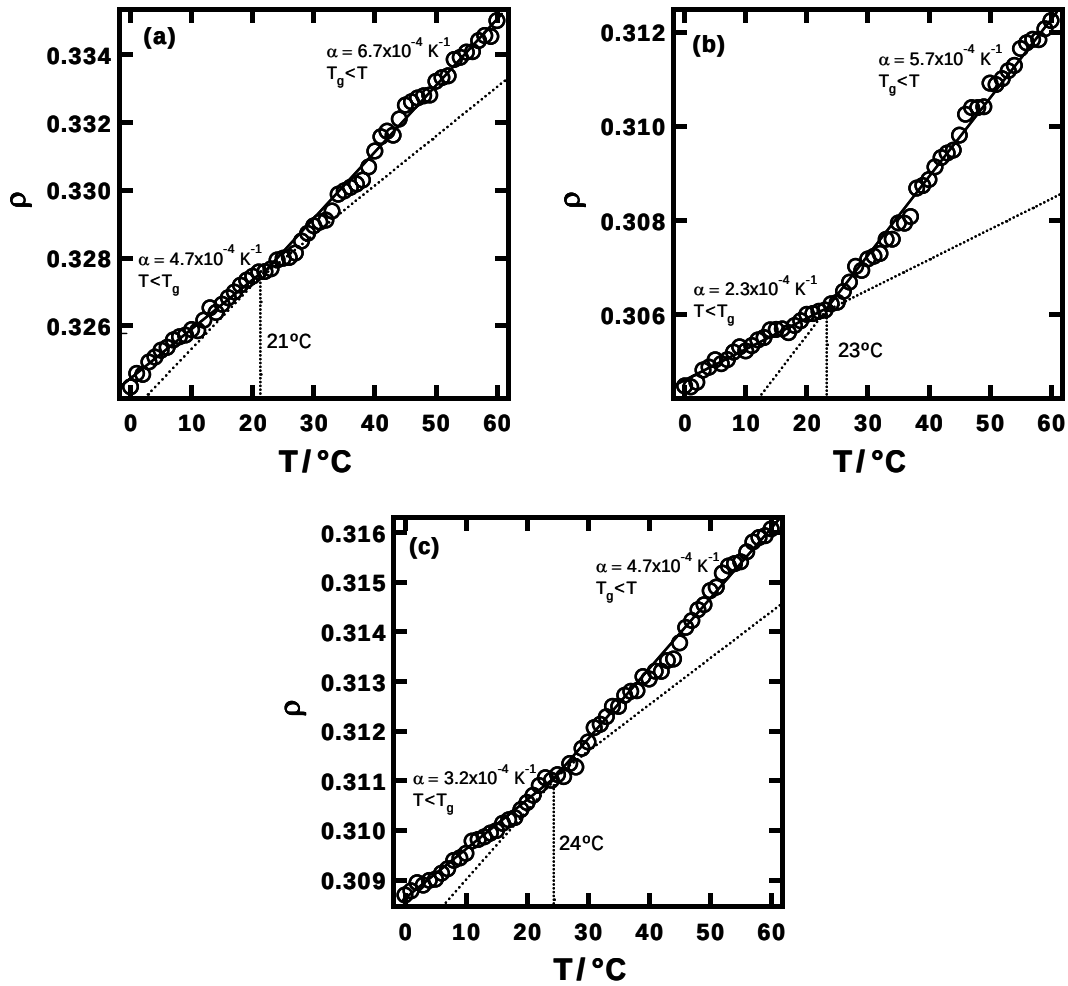


Figure 6.12: Thermal expansion curves for second heating scans of ~ 28 nm, $M_n = 5.0$ $\text{kg}\cdot\text{mol}^{-1}$ PtBA LB-films containing (a) 40, (b) 60, and (c) 90 wt% TPP.

Figure 6.13 summarizes surface T_g values deduced from Figures 6.9 through 6.12. Bulk T_g values obtained by differential scanning calorimetry (DSC) for blends prepared by solution casting from a common solution are also provided on Figure 6.13. Both surface and bulk T_g values increase with TPP for filler contents < 20 wt% TPP, before exhibiting a plateau at higher wt% TPP. Surface T_g increases more than bulk T_g for both $M_n = 23.6$ and $M_n = 5.0$ $\text{kg}\cdot\text{mol}^{-1}$ PtBA systems as TPP is added. The maximum increase

in bulk T_g for $M_n = 23.6 \text{ kg}\cdot\text{mol}^{-1}$) and $M_n = 5.0 \text{ kg}\cdot\text{mol}^{-1}$ PtBA are on the order of $\Delta T_g \sim 10 \text{ }^\circ\text{C}$. In contrast, the maximum increase in surface T_g for $M_n=23.6 \text{ kg}\cdot\text{mol}^{-1}$ PtBA ($\Delta T_g \sim 21 \text{ }^\circ\text{C}$) is greater than $M_n = 5.0 \text{ kg}\cdot\text{mol}^{-1}$ PtBA ($\Delta T_g \sim 14 \text{ }^\circ\text{C}$). Nonetheless, the total enhancement for T_g for all PtBA systems (bulk vs. surface, $M_n = 5.0$ vs. $23.6 \text{ kg}\cdot\text{mol}^{-1}$) is complete by the time 20 wt% TPP is added without further benefit at higher nanofiller loads. A speculative mechanism for the observed behavior in Figure 6.13 is that the aggregation of TPP particles pins PtBA chains leading to lower chain mobility. It is interesting to note that investigations by Dutcher *et al.* show reductions in T_g in films of high molar mass PS where chain confinement effects are dominant are greater than those observed for low molar mass PS.³¹ Our observations also show that the T_g depression for the $M_n = 23.6 \text{ kg}\cdot\text{mol}^{-1}$ PtBA sample is greater than for the $M_n = 5.0 \text{ kg}\cdot\text{mol}^{-1}$ PtBA sample. Upon adding nanofiller, surface T_g values increase towards, but do not reach, bulk T_g values. For both $M_n = 5.0 \text{ kg}\cdot\text{mol}^{-1}$ and $M_n = 23.6 \text{ kg}\cdot\text{mol}^{-1}$ PtBA the depression of surface T_g is $\sim 12 \text{ }^\circ\text{C}$ relative to bulk T_g even at the highest TPP levels. Whether or not it is possible to completely recover bulk T_g values by adding nanofillers to ultrathin polymer films is still an open question.

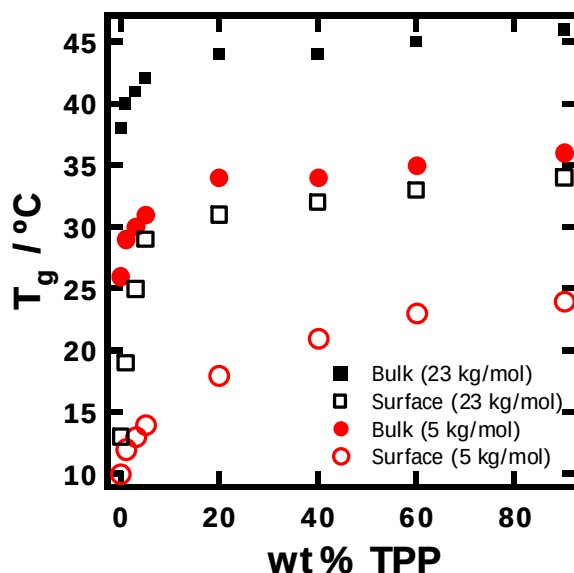


Figure 6.13. Plots of surface and bulk T_g as a function of TPP content for ~ 28 nm LB-films of $M_n = 23.6 \text{ kg}\cdot\text{mol}^{-1}$ and $M_n = 5.0 \text{ kg}\cdot\text{mol}^{-1}$ PtBA. Surface and bulk T_g values are obtained from second heating scans by ellipsometry and DSC, respectively.

6.4 Conclusions

Spincoated and LB-films of $M_n = 23.6 \text{ kg}\cdot\text{mol}^{-1}$ and $M_n = 5.0 \text{ kg}\cdot\text{mol}^{-1}$ PtBA on passivated silicon (SiH) substrates exhibit depressed T_g values compared to their corresponding bulk values. This observation is consistent with greater local free volume at surfaces and interfaces leading to greater chain mobility near the surface. Surface T_g values for LB-films are similar to those for spincoated films, leading to the conclusion that T_g behavior is independent of the interlayer architecture. However, this study clearly shows that residual stresses present in LB-films lead to different thermal properties relative to spincoated films, especially during initial heating scans. These differences can be eliminated by annealing the samples overnight above the double layer transition

temperatures for the LB-films. Furthermore, the addition of TPP to PtBA leads to an enhancement of both bulk and surface T_g . The decreases in T_g associated with the confinement of PtBA to thin films are partially recovered by adding TPP as a nanofiller

6.5 References

- (1) Haramina, T.; Kircheim, R.; Tibrewala, A.; Peiner, E. *Polymer*, **2008**, *49*, 2115-2118.
- (2) Shalaev, E. Y.; Steponkus, P. L. *Langmuir* **2001**, *17*, 5137-5140.
- (3) Zhang, J.; Liu, G.; Jonas, J. J. *Phys. Chem.* **1992**, *96*, 3478-3480.
- (3) Papaleo, R. M.; Leal, R.; Carreira, W. H.; Barbosa, L. G.; Bulla, A.; Bello, I. *Phys. Rev.* **2006**, *74*, 094203.
- (4) Tsui, O. K. C.; Zhang, H. F. *Macromolecules* **2001**, *34*, 9139-9142.
- (5) Mundra, M. K.; Donthu, S. K.; Dravid, V. P.; Torkelson, J. M. *Nano Lett.* **2007**, *7*, 713-718.
- (6) Dutcher, J. R.; Ediger, M. D. *Science*, **2008**, *319*, 577-578.
- (7) Bliznyuk, V. N.; Assender, H. E.; Briggs, G. A. D. *Macromolecules* **2002**, *35*, 6613-6622.
- (8) Lee, J. Y.; Su, K. E.; Edwin, P. C.; Zhang, Q.; Emrick, T.; Crosby, A. J. *Macromolecules*, **2007**, *40*, 7755-7757.
- (9) Hall, D. B.; Torkelson, J. M. *Macromolecules* **1998**, *31*, 8817-8825.
- (10) Fakhraai, Z.; Forrest, J. A. *Science*, **2008**, *319*, 600-604.
- (11) Pu, Y.; White, H.; Rafailovich, M. H.; Sokolov, J.; Patel, A.; White, C.; Wu, W.-L.; Zaitsev, V.; Schwarz, S. A. *Macromolecules* **2001**, *34*, 8518-8522.
- (12) Li, C.; Koga, T.; Li, C.; Jiang, J.; Sharma, S.; Narayanan, S.; Lurio, L. B.; Hu, X.; Jiao, X.; Sinha, S. K.; Billet, S.; Sosnowik, D.; Kim, H.; Sokolov, J. C.; Rafailovich, M. H. *Macromolecules* **2005**, *38*, 5144-5151.
- (13) Horn, R. G.; Israelachvili, J. N. *Macromolecules* **1988**, *21*, 2836-2841.
- (14) Svanberg, C. *Macromolecules* **2007**, *40*, 312-315.
- (15) Sperling, L. H. *Introduction to Physical Polymer Science*, John Wiley: New York, NY, 2001.
- (16) Keddie, J.; Jones, R. A. L.; Cory, R. A. *Europys. Lett.* **1994**, *27*, 59-64.
- (17) Kim, H. J.; Jang, J.; Zin, W. *Langmuir* **2001**, *17*, 2703-2710.
- (18) Kim, H. J.; Jang, J.; Zin, W. *Langmuir* **2000**, *16*, 4064-6047
- (19) Kim, H. J.; Jang, J.; Zin, W.; Lee D. *Macromolecules* **2002** *35*, 311-313
- (20) Keddie, J.; Jones, R. A. L.; Cory, R. A. *Faraday Discussions* **1995**, *98*, 219-230.
- (21) Wallace, W. E.; Zanten, J. H.; Wu, W. L. *Physical Review E* **1995**, *52*, 3329-3332.
- (22) Wallace, W. E.; Zanten, J. H.; Wu, W. L. *Physical Review E*, **1996**, *53*, 2053-2056.
- (23) D'Amour, J. N.; Okoroanyanwu, U.; Frank, W. C. *Microelectronic Engineering*, **2004** *74*, 209-217.
- (24) Fryer, S. D.; Peters, D. R.; Kim, J. E.; Tomaszewski, E. J.; Pablo, J. J.; Nealey, F. P. *Macromolecules* **2001**, *34*, 5627-5634.
- (25) Mundra, M. K.; Ellison, J. C.; Behling, R. E.; Torkelson, J. M. *Polymer*, **2006**, *47*, 7747-7759.
- (26) Weber, R.; Grotkopp, I.; Stettner, J.; Tolan, M.; Press, W. *Macromolecules* **2003**, *36*, 9100-9106.

- (27) Priestley, R. D.; Broadbelt, L. J.; Ellison, C. J.; Torkelson J. M.; *Macromolecules*, **2005**, *38*, 654-657.
- (28) Gilcreest, V. P.; Carroll, W. M.; Rochev, Y. A.; Blute, I.; Dawson, K. A.; Gorelov, A. V. *Langmuir* **2004**, *20*, 10138-10145
- (29) Forrest, J. A.; Veress-Dalnoki, K.; Stevens, J. R.; Dutcher, J.R. *Phys. Rev. Lett.* **1996**, *77*, 2002-2005.
- (30) Dutcher, J. R.; Roth, C. B. *Eur. Phys. J. D* **2003**, *12*, 103-107.
- (31) Dutcher, J. R.; Veress-Dalnoki, K.; Forrest, J. A.; Murray, C.; Gigault, C. *Phys. Rev. E* **2001**, *63*, 1-10.
- (32) Dutcher, J. R.; Veress-Dalnoki, K.; Forrest, J. A. *Phys. Rev. E* **1997**, *56*, 5705-5715.
- (33) Vogt, B. D.; Campbell, C. G. *Polymer*, **2007**, 7169-7175.
- (34) Schlossman, M. L.; Schwartz, D. K.; Kawamoto, E. H.; Kellogg, G. J.; Pershan, S.; M. W. Kim, M. W.; Chung, T. C. *J. Phys. Chem.* **1991**, *95*, 6628-6632.
- (35) Prucker, O.; Christian, S.; Bock, H.; Ruhe, J.; Frank, C. W.; Knoll, W. *Macromol. Chem. Phys.* **1998**, *199*, 1435-1444.
- (36) Hamon, L.; Grohens, Y.; Holl, Y. *Langmuir* **2003**, *19*, 10399-10402.
- (37) Kim, J. H.; Jang, J.; Lee, D. Y.; Zin, W. C. *Macromolecules* **2002**, *25*, 311-313.
- (38) Zhang, Z.; Liang, G.; Wang, X. *Polym. Bull.* **2007**, *58*, 1013-1020.
- (39) Wright, M. E.; Petteys B. J.; Guenther, A. J.; Fallis, S.; Yandek, G. R.; Tomczak, S. J.; Minton, T. K.; Brunsvold, A. *Macromolecules* **2006**, *39*, 4710-4718.
- (40) Pittman, C. U. Jr.; Li, G-Z.; Ni, H. *Macromol. Symposium* **2003**, *196*, 301-325.
- (41) Markovic, E; Clarke, S.; Matisons, J.; Simon, G. P. *Macromolecules* **2008**, *41*, 1685-1692.
- (42) Li, M.; Wang, L.; Ni, H.; Pittman, C. U. J. *Inorg. Organomet. P.* **2001**, *11*, 123-154.
- (43) Esker, A. R.; Mengel, C; Wegner, G. *Science* **1998**, *280*, 892-895.

CHAPTER 7

Conclusions and Suggestions for Future Work

7.1 Overall Conclusions

7.1.1. Applications of Multiple Incident Media (MIM) Ellipsometry

Ellipsometry is a well established and straight forward technique for determining the film thickness and refractive index of a film supported on a solid substrate. The technique operates on the principle of detecting the change in the polarization state of light upon reflection from a surface. Drude derived the governing equations for ellipsometry in the 1800s, and equations are still used today.^{1,2} The application of these equations is greatly simplified for measurements made at Brewster's angle, the most sensitive condition for ellipsometry measurements. The measurement for a simple incident medium/thin film/substrate system yields the ellipticity, a quantity that depends on the angle of incidence, wavelength of the source, thickness of the film, and the dielectric constants of the different layers. Of these, the incident angle, wavelength of the source, and the dielectric constants for medium and substrate are usually known, while the thickness and dielectric constant of the film are normally the quantities of interest. However, the thickness and dielectric constant of the film are coupled parameters. Therefore, two independent equations are required for simultaneous determinations of a film's thickness and refractive index. Changing the wavelength of the source or the incident angle results in two linearly dependent equations, where simultaneous solutions for thickness and refractive index are still not possible. One possible way to obtain two

independent equations is utilizing a two different ambient media. This technique has been previously applied to SiO₂/Si substrates with relatively thick (~30 nm) native oxide films.^{3,4} However, the method has not previously been utilized for the determination of film thicknesses and refractive indices for polymeric materials as done in this thesis.

Utilizing single wavelength ellipsometry measurements at Brewster's angle and conducting the experiments in different ambient media, simultaneous determinations of a film's thickness and refractive index are possible. Poly(tert-butyl acrylate) (PtBA) Langmuir-Blodgett (LB) films served as a model system for the simultaneous determination of thickness and refractive index. LB-films were particularly useful because of the linear dependence between film thickness and the number of deposited layers.⁵ After showing MIM ellipsometry results agreed with X-ray reflectivity (XR) studies, it was possible to apply the method to spincoated systems of PtBA and other common polymer systems. All results were consistent with previously published findings.⁶ Furthermore, multiple incident media (MIM) ellipsometry was also utilized to optically characterize thin films of trimethylsilylcellulose (TMSC), regenerated cellulose, and cellulose nanocrystals. Results from these systems were also consistent with previous studies.⁷ In general, MIM ellipsometry provides a rapid and unambiguous method for obtaining both film thicknesses and refractive indices of ultrathin films that lack anisotropic refractive indices. Thickness values agree with results from X-ray reflectivity to less than ± 1 nm, i.e. $\pm$ the surface roughness, and refractive index values are in excellent agreement with the literature values. The results are also in quantitative agreement with traditional ellipsometric techniques, spectroscopic ellipsometry (SE) and

multiple angle of incidence ellipsometry (MAOI), without the need for prior assumptions about the value of the refractive index.

7.1.2 Effect of Nanofillers on Surface Glass Transition Temperatures

Thermal properties of PtBA films containing a polyhedral oligomeric silsesquioxane (POSS) derivative, trisilanolphenyl-POSS (TPP), were investigated via ellipsometry. Single component PtBA films exhibit a surface glass transition temperature (T_g) that is depressed in comparison to bulk values. These observations are consistent with an increase in the local free volume and chain mobility near the surface and relatively weak polymer/substrate interactions for PtBA on passivated silicon (SiH) substrates. As a consequence, surface T_g is smaller than bulk T_g . The depression of surface T_g for films lacking strong substrate/polymer interactions is greater for high molar mass than low molar mass samples as demonstrated for the PtBA system. These observations were unaffected by the method used to prepare the PtBA thin films. PtBA LB-films on silicon wafers exhibit surface T_g values similar to those of spincoated films leading to the conclusion that T_g behavior is independent of the interlayer architecture. This result is consistent with the conclusion of Prucker *et al.* in a less controlled system.⁸ Nonetheless, this study clearly shows that residual stresses present in LB-films lead to different thermal expansion coefficients relative to spincoated films. These differences can be eliminated by annealing the samples overnight above the double layer transition temperatures for the LB-film. Furthermore, the addition of TPP to PtBA leads to an enhancement of both bulk and surface T_g . The decreases in T_g associated with the confinement of PtBA to thin films were lessened by adding nanofiller.

7.2 Suggestions for Future Work

Studies of optical constants for polymeric materials by multiple angle of incidence ellipsometry and our temperature dependent experiments provided us with an understanding of how to optimally apply characterization techniques for surface properties of polymers and polymer/nanofiller systems. As such, this dissertation serves as a starting point for the future studies of optical or thermal properties of polymeric thin film systems. Here, some of the suggestions for future work are provided.

7.2.1 Applications of Multiple Incident Media (MIM) Ellipsometry

As discussed in detail in Chapters 4 and 5, the MIM ellipsometry is suitable for determining optical constants for polymeric materials. At this stage, future studies could focus on POSS systems and PtBA/POSS blends. PtBA, TPP, and PtBA/TPP blends have been found to form well defined LB-films. Thus, the LB-technique can be used to prepare films of controlled thicknesses. Refractive indices of POSS based materials have not been extensively studied in literature. Therefore, optical properties of POSS systems would be interesting. Our preliminary results for TPP films obtained via MIM ellipsometry are comparable to XR results, once again validating MIM ellipsometry as a reliable method for studying the properties of thin films. Figure 7.1 shows a representative X-ray reflectivity profile for different LB-films of TPP. For $q > q_c$, the reflectivity, $R(q)$, exhibits periodic oscillations, Kiessig fringes, which arise from interference between X-rays reflected from the silicon/TPP and TPP/air interfaces. The spacing of the maxima or minima are related to the film's thickness through Bragg's Law.⁹ The reflectivity profiles in Figure 7.1 were also fit using a multilayer algorithm^{10,11} and the film thickness, D and roughness values at the TPP/air interface, σ_p ,

and silicon/TPP interface, σ_s were deduced. These parameters are summarized in Table 7.1 for all TPP LB-films. XR results of TPP and ellipsometry results are in excellent agreement.

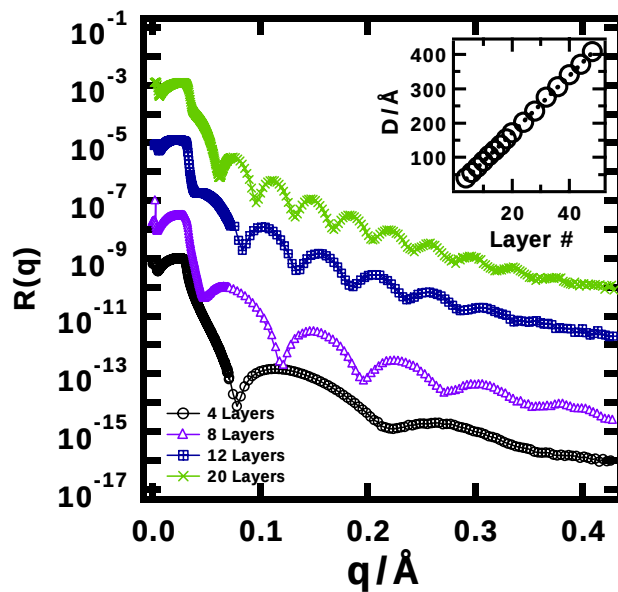


Figure 7.1. Representative XR profiles for TPP LB-films. The inset shows D vs. the number of LB-layers (layer #) for each film. The slope of the inset yields the thickness per layer, $d = 0.84 \pm 0.01$ nm.

Table 7.1. X-Ray reflectivity and ellipsometry data for TPP LB-films.

#of Layers	X-Ray Reflectivity		
	Thickness	Roughness ^a	
	D /nm ^a	σ_p /nm	σ_s /nm
4	4.0	0.89	0.50
6	5.6	0.74	0.52
8	7.2	0.81	0.53
10	8.9	0.86	0.55
12	10.4	0.85	0.51
14	12.0	0.92	0.48
16	13.5	0.87	0.49
18	15.3	0.73	0.46
20	17.2	0.82	0.45

#of Layers	Ellipsometry		
	Thickness		
	D /nm ^b	D /nm ^c	n ^c
4	4.4	4.3	1.58
6	6.1	6.1	1.57
8	7.7	7.4	1.56
10	9.2	9.3	1.55
12	10.9	11.1	1.54
14	12.4	12.7	1.54
16	13.7	14.0	1.55
18	15.3	15.6	1.56
20	17.0	17.2	1.56
		Average ^d	1.56±0.01
		Approach 2 ^d	1.57±0.01

^aFit utilizing a multilayer algorithm; ^bUtilizing Approach 1;

^cUtilizing Approach 2; ^dOne-standard deviation error bars

Figure 7.2 shows the ellipticity, ρ , measured in air along with ρ data measured in water plotted as a function of the number of LB-layers. Figure 7.2 clearly shows that there is a linear relationship between ρ and the number of layers transferred for films measured in air and water. The analysis of the multiple incident media (MIM) data proceeded using Approach 1 and Approach 2 discussed in Chapters 4 and 5. The refractive index and thickness of each film is determined according to Equations 3.4 and

3.6 (Approach 1); or the slope of each curve in Figure 7.2 is used to obtain $\rho^{\text{air}}/\text{layer}$ and $\rho^{\text{water}}/\text{layer}$ (Approach 2). These values are then used to determine the refractive index and thickness, d , per layer through Equations 3.4 and 3.6 ($d = 0.80 \pm 0.01$ nm).

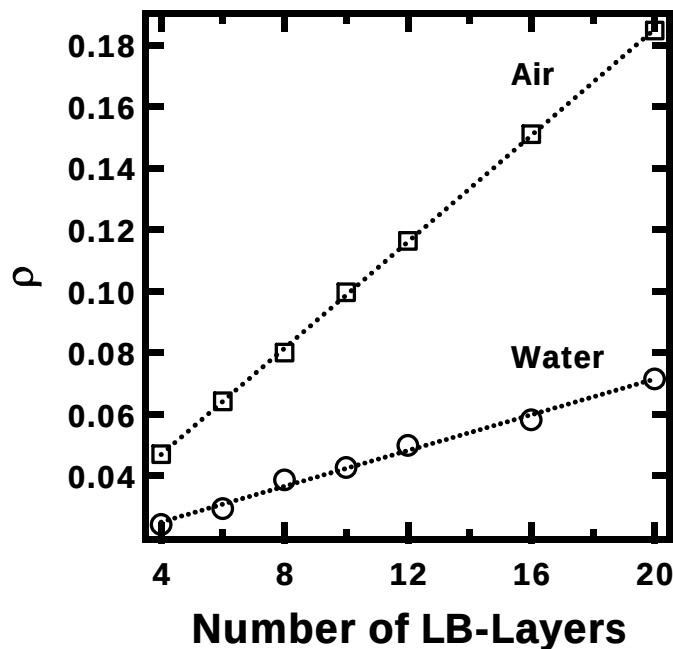


Figure 7.2. MIM ellipsometry data for TPP LB-films in air ($\square$) and in water ($\circ$) at a wavelength of 632 nm.

In addition to data obtained via XR for TPP LB-films, Table 7.1 also contains the thickness and refractive index values for each film obtained from measurements made in air and water. As shown in Table 7.1, the agreement between the XR data and the ellipsometry data is excellent with less than 1 nm deviation, i.e. the deviation is essentially the surface roughness. Table 7.1 also shows that n values are largely independent of the number of layers transferred, with an average value of $n = 1.56 \pm 0.01$ using Approach 1. This value is in excellent agreement with the result obtained via Approach 2 ($n = 1.57 \pm 0.01$). As was the case for PtBA films in Chapter 4, the largest

deviation is observed for the thinnest films. The deviation is not surprising. As previously discussed for PtBA in Chapter 4 and cellulose systems in Chapter 5, TPP/substrate and TPP/air or TPP/water interfacial roughnesses also make the largest contributions to the observed ρ values from ellipsometry on a percentage basis for the thinnest films. The MIM ellipsometry values provide model independent values of film thickness that agree with XR with subnanometer deviation. The conclusion is clear, this method can also be applied to the TPP/PtBA blends in Chapter 6 to determine how n changes with composition for the blends. Obviously samples having different thicknesses with different compositions should be analyzed in order to obtain the change in the refractive index of the PtBA as a function of TPP content. Such information may allow us to detect the formation of adsorption or depletion of layers if segregation occurs. MIM ellipsometry could also be utilized to characterize different polymer systems with different nanofillers. Finally, MIM ellipsometry could be applied to understand swelling behavior of cellulose and cellulose derivatives.

7.2.2 Temperature Dependent Ellipsometry Experiments

The most important variables that can be manipulated when investigating thermal properties such as the surface T_g , loss of double layer transition, and thermal expansion coefficients of PtBA/TPP blend system are annealing history, film preparation method, polymer molar mass, thicknesses of the PtBA/TPP layers, and structure of the nanofiller (i.e. different POSS nanofillers). Furthermore, chemically different repeating units (different polymers and copolymers) and chain ends, the chemical nature of the substrate, specific and non-specific interactions between substrates and polymers could also be altered to study how these variables influence surface T_g . Our temperature dependent

experiments provide an important first step towards addressing how these variables influence the thermal properties of thin films. Clearly, the incorporation of TPP as nanofillers into polymers is attractive for high temperature applications.¹²⁻¹⁵

As a starting point, I would suggest temperature dependent ellipsometry experiments to address how composition affects the thermal expansion coefficients (α) for TPP/PtBA blends above and below T_g . As shown in Figure 7.3, preliminary results indicate that the thermal expansion coefficient, α , for both $M_n = 5.0$ and $M_n = 23.0$ kg.mol⁻¹ PtBA samples in the glassy and rubbery state decrease upon the addition of TPP. As discussed in the experimental section all the blends were prepared at different surface pressures because the surface pressure area per monomer isotherms exhibit composition dependent collapse pressures. Thus, different blend compositions may have different residual stresses. Section 6.3.3 explains that long annealing times remove residual stresses arising from thin film deposition. Therefore, annealing LB films of the blends overnight or even longer times under vacuum at ~40 - 50 °C (below 60 °C to avoid phase separation)¹⁶ may yield stress-free films. Then the effect of TPP on the thermal expansion coefficients as well as any composition dependent features should be more readily apparent.

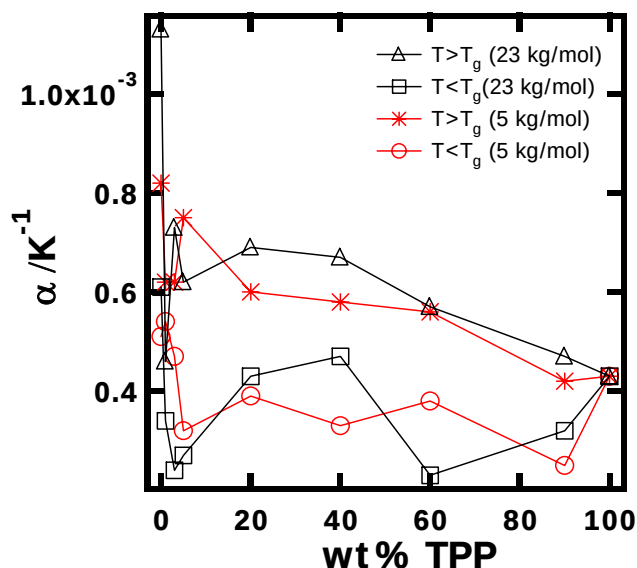


Figure 7.3. α for ~ 28 nm LB-films of $M_n = 5$ and $23.6 \text{ kg}\cdot\text{mol}^{-1}$ PtBA/TPP blends obtained from second heating scans.

Keddie *et al.* described the thickness dependence of polystyrene T_g via an empirical equation,^{17,18} discussed in Chapter 2 (Equation 2.28). As we have already noted, LB film deposition provides unique control over film thickness. PtBA films with different numbers of layers should be tested to determine the applicability of Keddie *et al.*'s equation to LB-films. The empirical parameters, adjustable parameter A, and degree of T_g depression δ for PtBA thin films can then be calculated. The critical thickness where the depressed T_g approaches bulk values could also be obtained. These results should be compared to studies of spincoated PtBA films. In addition, the effect of nanofillers on the empirical parameters could easily be deduced from detailed investigations of blend films with different compositions and thicknesses.

Dutcher *et al.* investigated the molar mass dependence of the surface glass transition temperature of thin polystyrene films.^{19,20} They observed large surface T_g differences for various molar mass polystyrenes as the film thickness was reduced. They reported that reductions in surface T_g for films of high molar mass PS, where chain confinement effects are dominant, was greater than for low molar mass PS. Our observations also indicate that the depression of T_g for the higher molar mass PtBA sample is greater ($\Delta T_g \sim 25^\circ\text{C}$) than for lower molar mass PtBA sample ($\Delta T_g \sim 14^\circ\text{C}$). However, other molar mass samples should be investigated to deduce the functional dependence of surface T_g on molar mass.

To take advantage of the unique and enhanced properties of nanoparticle/polymer blend systems the nanofillers must be well dispersed within the polymer matrix.^{21,22} In our studies, TPP nanoparticles act as monodisperse nanoparticles. Although the chemical structures and groups of the nanoparticle could be very important in the enhancement of surface T_g , we focused on the impact of the PtBA/TPP composition. One explanation for the observed enhancement is that favorable TPP-TPP interactions lead to TPP aggregate formation within the system that pin the polymer chains leading to lower chain mobility and consequently higher T_g . In order to gain insight into the physical mechanism that controls the enhancement of T_g , different POSS systems should be studied. Different amphiphilic POSS materials such as trisilanoethyl-, trisilanolisobutyl-, trisilanolisooctyl-, and trisilanolcyclohexyl-POSS are commercially available and could be utilized to investigate the study the effects POSS materials have on surface T_g . In our studies with TPP we have not observed a diluent role of TPP which could be observed for other POSS/polymer blends. Xu *et al.* proposed that the greatest

contribution to the enhancement of T_g in materials containing POSS derivatives arises from POSS-POSS interactions rather than the dipole-dipole interactions between POSS and polymer.²³ Thus, strong POSS-POSS interactions might provide a better enhancement of surface T_g . The first choice of different POSS derivatives should be trisilanolcyclohexyl-POSS since it has been shown by Deng *et al.* that trisilanolcyclohexyl-POSS amphiphilics form hydrophobic aggregates in their multilayer films.²⁴ The authors attributed the formation of these stable and hydrophobic structures to the strong tendency of trisilanolcyclohexyl-POSS systems to form intermolecular hydrogen bonds. Therefore, the incorporation of trisilanolcyclohexyl-POSS into PtBA polymer matrix might yield a greater enhancement of surface T_g .

7.3 References

- (1) Drude, P. *Ann. Phys.* **1887**, 32, 584-625.
- (2) Drude P., *Ann. Phys.* **1888**, 34, 489.
- (3) Landgren, M.; Joensson, B. *J. Phys. Chem.* **1993**, 97, 1656-1664.
- (4) Kattner, J.; Hoffmann, H. *J. Phys. Chem. B* **2002**, 106, 9723-9729.
- (5) Schaub, M.; Wenz, G.; Wegner, G.; Stein, A.; Klemm, D. *Adv. Mater.* **1993**, 5, 919-922.
- (6) Esker, A. R.; Mengel, C.; Wegner, G. *Science* **1998**, 280, 892-895.
- (7) Buchholz, V.; Adler, P.; Backer, M.; Holle, W.; Simon, A.; Wegner, G. *Langmuir* **1997**, 13, 3206-3209.
- (8) Prucker, O.; Christian, S.; Bock, H.; Ruhe, J.; Frank, C. W.; Knoll, W. *Macromol. Chem. Phys.* **1998**, 199, 1435-1444.
- (9) Tippmann-Krayer, P.; Moehwald, H.; Yu M. L. *Langmuir* **1991**, 7, 2298-2302.
- (10) Esker, A. R.; Grüll, H.; Satija, S. K.; Han, C. C. *J. Polym. Sci., Part B* . **2004**, 42, 3248-3257.
- (11) Welp, K. A.; Co, C.; Wool, R. P. *J. Neutron Res.* **1999**, 8, 37-46.
- (12) Gonzalez, R. I.; Phillips, S. H.; Hoflund, G. B. *J. Spacecr. Rockets.* **2000**, 37, 463-464
- (13) Zhang, C.; Babbonneau, F.; Bonhomme, C.; Laine, R. M.; Soles, C. L.; Hristov, H. A.; Yee, A. F. *J. Am. Chem. Soc.* **1998**, 120, 8380-8391.
- (14) Gupta, S. K.; Schwab, J. J.; Lee, A.; Fu, B. X.; Hsiao, B. S.; Soles, C. L. *Int. SAMPE Symp. Exhib.* **2002**, 47, 1517-1526.
- (15) Blanski, R.; Leland, J.; Viers, B.; Phillips, S. H. *Int. SAMPE Symp. Exhib.* **2002**, 47, 1503-1507.
- (16) Paul, R.; Karabiyik, U.; Swift, M. C.; Esker, A. R. *Langmuir* **2008**, 24, 5079-5090.
- (17) Keddie, J. L.; Jones, R. A.; Cory, R. A. *Faraday Discuss.* **1994**, 98, 219-230.
- (18) Keddie, J. L.; Jones, R. A.; Cory, R. A. *Europhys. Lett.* **1994**, 27, 59-64.
- (19) Dutcher, J. R.; Veress-Dalnoki, K.; Forrest, J. A.; Murray, C.; Gigault, C. *Phys. Rev. E* **2001**, 63, 1-10.
- (20) Dutcher, J. R.; Ediger, M. D. *Science* **2008**, 319, 577-578.
- (21) Jordan, J.; Jacob, K. I.; Tannenbaum, R.; Sharaf, M. A.; Jasiuk, I. *Mater. Sci. Eng., A* **2005**, 393, 1-11.
- (22) Thostenson, E. T.; Li, C. Y.; Chou, T. W. *Compos. Sci. Technol.* **2005**, 65, 491-516.
- (23) Xu, H.; Kuo, S.-W.; Lee, J.-S.; Chang, F.-C. *Macromolecules* **2002**, 35, 8788-8793.
- (24) Deng, J.; Farmer-Creely, C. E.; Viers, B. D.; Esker, A. R. *Langmuir* **2004**, 20, 2527-2530.

APPENDIX

Error Estimates for D and n

Equations A1 and A2 are the same as Equations 3.6 and 3.4, respectively.

$$\varepsilon = \frac{\rho^A \sqrt{\varepsilon_1^B + \varepsilon_2} (\varepsilon_1^A - \varepsilon_2) (\varepsilon_1^B) - \rho^B \sqrt{\varepsilon_1^A + \varepsilon_2} (\varepsilon_1^B - \varepsilon_2) (\varepsilon_1^A)}{\rho^A \sqrt{\varepsilon_1^B + \varepsilon_2} (\varepsilon_1^A - \varepsilon_2) - \rho^B \sqrt{\varepsilon_1^A + \varepsilon_2} (\varepsilon_1^B - \varepsilon_2)} \quad (\text{A1})$$

$$D = \frac{\rho}{\frac{\pi (\varepsilon_1 + \varepsilon_2)^{1/2}}{\lambda (\varepsilon_1 - \varepsilon_2)} \frac{(\varepsilon - \varepsilon_1)(\varepsilon - \varepsilon_2)}{\varepsilon}} \quad (\text{A2})$$

Variances for ε and D, obtained from propagation of error calculations, are provided as Equations A3 and A4:

$$\sigma_\varepsilon^2 = \left(\frac{\partial \varepsilon}{\partial \rho_A} \right)^2 \sigma_{\rho_A}^2 + \left(\frac{\partial \varepsilon}{\partial \varepsilon_1^B} \right)^2 \sigma_{\varepsilon_1^B}^2 + \left(\frac{\partial \varepsilon}{\partial \varepsilon_2} \right)^2 \sigma_{\varepsilon_2}^2 + \left(\frac{\partial \varepsilon}{\partial \varepsilon_1^A} \right)^2 \sigma_{\varepsilon_1^A}^2 + \left(\frac{\partial \varepsilon}{\partial \rho_B} \right)^2 \sigma_{\rho_B}^2 \quad (\text{A3})$$

$$\sigma_D^2 = \left(\frac{\partial D}{\partial \rho} \right)^2 \sigma_\rho^2 + \left(\frac{\partial D}{\partial \varepsilon_1} \right)^2 \sigma_{\varepsilon_1}^2 + \left(\frac{\partial D}{\partial \varepsilon_2} \right)^2 \sigma_{\varepsilon_2}^2 + \left(\frac{\partial D}{\partial \varepsilon} \right)^2 \sigma_\varepsilon^2 \quad (\text{A4})$$

The derivatives in Equations A3 and A4 are provided in Equations A5 through A13.

$$\left(\frac{\partial \varepsilon}{\partial \rho_A}\right) = \frac{\varepsilon_1^B (\varepsilon_1^A - \varepsilon_2) \sqrt{\varepsilon_1^B + \varepsilon_2}}{(\varepsilon_1^A + \varepsilon_2) \rho^A \sqrt{\varepsilon_1^B + \varepsilon_2} - (\varepsilon_1^B - \varepsilon_2) \rho^B \sqrt{\varepsilon_1^A + \varepsilon_2}} - \frac{(\varepsilon_1^A - \varepsilon_2) \sqrt{\varepsilon_1^B + \varepsilon_2} \left(\varepsilon_1^B (\varepsilon_1^A - \varepsilon_2) \rho^A \sqrt{\varepsilon_1^B + \varepsilon_2} - \varepsilon_1^A (\varepsilon_1^B - \varepsilon_2) \rho^B \sqrt{\varepsilon_1^A + \varepsilon_2} \right)}{\left((\varepsilon_1^A - \varepsilon_2) \rho^A \sqrt{\varepsilon_1^B + \varepsilon_2} - (\varepsilon_1^B - \varepsilon_2) \rho^B \sqrt{\varepsilon_1^A + \varepsilon_2} \right)^2} \quad (\text{A5})$$

$$\left(\frac{\partial \varepsilon}{\partial \varepsilon_1^B}\right) = \frac{\rho^A \varepsilon_1^B (\varepsilon_1^A - \varepsilon_2) / 2 \sqrt{\varepsilon_1^B + \varepsilon_2} + (\varepsilon_1^A - \varepsilon_2) \rho^A \sqrt{\varepsilon_1^B + \varepsilon_2} - \varepsilon_1^A \rho^B \sqrt{\varepsilon_1^A + \varepsilon_2}}{(\varepsilon_1^A + \varepsilon_2) \rho^A \sqrt{\varepsilon_1^B + \varepsilon_2} - (\varepsilon_1^B - \varepsilon_2) \rho^B \sqrt{\varepsilon_1^A + \varepsilon_2}} - \frac{\left(\varepsilon_1^B ((\varepsilon_1^A - \varepsilon_2) \rho^A \sqrt{\varepsilon_1^B + \varepsilon_2} - \varepsilon_1^A (\varepsilon_1^B - \varepsilon_2) \rho^B \sqrt{\varepsilon_1^A + \varepsilon_2}) \right)}{\left((\varepsilon_1^A - \varepsilon_2) \rho^A \sqrt{\varepsilon_1^B + \varepsilon_2} - (\varepsilon_1^B - \varepsilon_2) \rho^B \sqrt{\varepsilon_1^A + \varepsilon_2} \right)^2} \times \left((\varepsilon_1^A - \varepsilon_2) \rho^A / 2 \sqrt{\varepsilon_1^B + \varepsilon_2} - \rho^B \sqrt{\varepsilon_1^A + \varepsilon_2} \right) \quad (\text{A6})$$

$$\left(\frac{\partial \varepsilon}{\partial \varepsilon_2}\right) = \frac{(\varepsilon_1^B (\varepsilon_1^A - \varepsilon_2) \rho^A / 2 \sqrt{\varepsilon_1^B + \varepsilon_2}) - \varepsilon_1^B \rho^A \sqrt{\varepsilon_1^B + \varepsilon_2}}{(\varepsilon_1^A - \varepsilon_2) \rho^A \sqrt{\varepsilon_1^B + \varepsilon_2} - (\varepsilon_1^B - \varepsilon_2) \rho^B \sqrt{\varepsilon_1^A + \varepsilon_2}} - \frac{\varepsilon_1^A \rho^B (\varepsilon_1^B - \varepsilon_2) / 2 \sqrt{\varepsilon_1^A + \varepsilon_2} + \varepsilon_1^A \rho^B \sqrt{\varepsilon_1^A + \varepsilon_2}}{(\varepsilon_1^A - \varepsilon_2) \rho^A \sqrt{\varepsilon_1^B + \varepsilon_2} - (\varepsilon_1^B - \varepsilon_2) \rho^B \sqrt{\varepsilon_1^A + \varepsilon_2}} - \frac{\left(\varepsilon_1^B (\varepsilon_1^A - \varepsilon_2) \rho^A \sqrt{\varepsilon_1^B + \varepsilon_2} - \varepsilon_1^A (\varepsilon_1^B - \varepsilon_2) \rho^B \sqrt{\varepsilon_1^A + \varepsilon_2} \right)}{\left((\varepsilon_1^A - \varepsilon_2) \rho^A \sqrt{\varepsilon_1^B + \varepsilon_2} - (\varepsilon_1^B - \varepsilon_2) \rho^B \sqrt{\varepsilon_1^A + \varepsilon_2} \right)^2} \times \left((\varepsilon_1^A - \varepsilon_2) \rho^A / 2 \sqrt{\varepsilon_1^B + \varepsilon_2} - \rho^A \sqrt{\varepsilon_1^B + \varepsilon_2} - \varepsilon_1^B - \varepsilon_2 \right) \rho^B / 2 \sqrt{\varepsilon_1^A + \varepsilon_2} + \rho^B \sqrt{\varepsilon_1^A + \varepsilon_2} \quad (\text{A7})$$

$$\begin{aligned}
\left(\frac{\partial \varepsilon}{\partial \varepsilon_1^A} \right) &= \frac{\varepsilon_1^B \rho^A (\varepsilon_1^B - \varepsilon_2) - \varepsilon_1^A (\varepsilon_1^B - \varepsilon_2) \rho^B / 2 \sqrt{\varepsilon_1^A + \varepsilon_2} - (\varepsilon_1^B - \varepsilon_2) \rho^B \sqrt{\varepsilon_1^A + \varepsilon_2}}{(\varepsilon_1^A - \varepsilon_2) \rho^A \sqrt{\varepsilon_1^B + \varepsilon_2} - (\varepsilon_1^B - \varepsilon_2) \rho^B \sqrt{\varepsilon_1^A + \varepsilon_2}} - \\
&\frac{(\varepsilon_1^B \rho^A (\varepsilon_1^A - \varepsilon_2) \sqrt{\varepsilon_1^B + \varepsilon_2} - \varepsilon_1^A (\varepsilon_1^B - \varepsilon_2) \rho^B \sqrt{\varepsilon_1^A + \varepsilon_2})}{\left((\varepsilon_1^A + \varepsilon_2) \rho^A \sqrt{\varepsilon_1^B + \varepsilon_2} - (\varepsilon_1^B - \varepsilon_2) \rho^B \sqrt{\varepsilon_1^A + \varepsilon_2} \right)^2} \times \\
&(\rho^A \sqrt{\varepsilon_1^B + \varepsilon_2} - \rho^B (\varepsilon_1^B - \varepsilon_2) / 2 \sqrt{\varepsilon_1^A + \varepsilon_2})
\end{aligned} \tag{A8}$$

$$\begin{aligned}
\left(\frac{\partial \varepsilon}{\partial \rho_B} \right) &= \frac{-\varepsilon_1^A (\varepsilon_1^B - \varepsilon_2) \sqrt{\varepsilon_1^A + \varepsilon_2}}{(\varepsilon_1^A - \varepsilon_2) \rho^A \sqrt{\varepsilon_1^B + \varepsilon_2} - (\varepsilon_1^B - \varepsilon_2) \rho^B \sqrt{\varepsilon_1^A + \varepsilon_2}} - \\
&\frac{(\varepsilon_1^B - \varepsilon_2) \sqrt{\varepsilon_1^A + \varepsilon_2} \left(\varepsilon_1^B (\varepsilon_1^A - \varepsilon_2) \rho^A \sqrt{\varepsilon_1^B + \varepsilon_2} - \varepsilon_1^A (\varepsilon_1^B - \varepsilon_2) \rho^B \sqrt{\varepsilon_1^A + \varepsilon_2} \right)}{\left((\varepsilon_1^A - \varepsilon_2) \rho^A \sqrt{\varepsilon_1^B + \varepsilon_2} - (\varepsilon_1^B - \varepsilon_2) \rho^B \sqrt{\varepsilon_1^A + \varepsilon_2} \right)^2}
\end{aligned} \tag{A9}$$

$$\left(\frac{\partial D}{\partial \rho} \right) = \frac{\varepsilon \lambda (\varepsilon_1 - \varepsilon_2)}{\pi (\varepsilon - \varepsilon_1) (\varepsilon - \varepsilon_2) \sqrt{\varepsilon_1 + \varepsilon_2}} \tag{A10}$$

$$\begin{aligned}
\left(\frac{\partial D}{\partial \varepsilon_1} \right) &= \frac{\rho \varepsilon \lambda (\varepsilon_1 - \varepsilon_2)}{\pi (\varepsilon - \varepsilon_1) (\varepsilon - \varepsilon_2) \sqrt{\varepsilon_1 + \varepsilon_2}} - \\
&\frac{\rho \varepsilon \lambda (\varepsilon_1 - \varepsilon_2)}{2 \pi (\varepsilon - \varepsilon_1) (\varepsilon - \varepsilon_2) (\varepsilon_1 + \varepsilon_2)^{3/2}} + \frac{\rho \varepsilon \lambda}{\pi (\varepsilon - \varepsilon_1) (\varepsilon - \varepsilon_2) \sqrt{\varepsilon_1 + \varepsilon_2}}
\end{aligned} \tag{A11}$$

$$\begin{aligned}
\left(\frac{\partial D}{\partial \varepsilon_2} \right) &= \frac{\rho \varepsilon \lambda (\varepsilon_1 - \varepsilon_2)}{\pi (\varepsilon - \varepsilon_1) (\varepsilon - \varepsilon_2)^2 \sqrt{\varepsilon_1 + \varepsilon_2}} - \\
&\frac{\rho \varepsilon \lambda (\varepsilon_1 - \varepsilon_2)}{2 \pi (\varepsilon - \varepsilon_1) (\varepsilon - \varepsilon_2) (\varepsilon_1 + \varepsilon_2)^{3/2}} + \frac{\rho \varepsilon \lambda}{\pi (\varepsilon - \varepsilon_1) (\varepsilon - \varepsilon_2) \sqrt{\varepsilon_1 + \varepsilon_2}}
\end{aligned} \tag{A12}$$

$$\begin{aligned}
\left(\frac{\partial D}{\partial \varepsilon}\right) = & \frac{\rho \varepsilon \lambda(\varepsilon_1 - \varepsilon_2)}{\pi(\varepsilon - \varepsilon_1)(\varepsilon - \varepsilon_2)^2 \sqrt{\varepsilon_1 + \varepsilon_2}} - \\
& \frac{\rho \varepsilon \lambda(\varepsilon_1 - \varepsilon_2)}{\pi(\varepsilon - \varepsilon_1)^2(\varepsilon - \varepsilon_2) \sqrt{\varepsilon_1 + \varepsilon_2}} + \frac{\rho \varepsilon \lambda(\varepsilon_1 - \varepsilon_2)}{\pi(\varepsilon - \varepsilon_1)(\varepsilon - \varepsilon_2) \sqrt{\varepsilon_1 + \varepsilon_2}}
\end{aligned} \tag{A13}$$