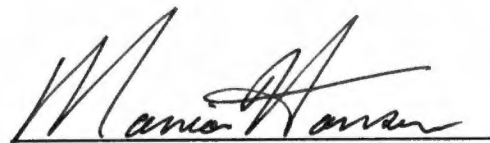


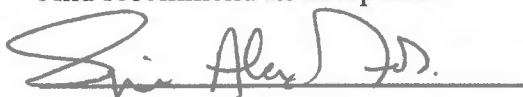
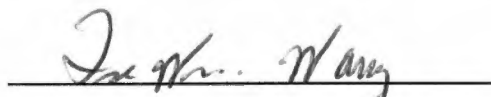
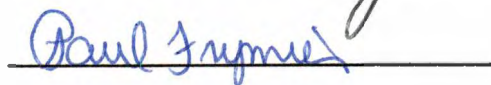
To the Graduate Council:

I am submitting herewith a dissertation written by Bhushan Deshpande entitled "Near-Infrared Spectropolarimetry of Polymers." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemical Engineering.

A handwritten signature in black ink, appearing to read "Marion G. Hansen", written over a horizontal line.

Marion G. Hansen, Major Professor

We have read this dissertation
And recommend its acceptance:

A handwritten signature in black ink, appearing to read "Eric Alex J.D.", written over a horizontal line.A handwritten signature in black ink, appearing to read "Dr. Mr. Wang", written over a horizontal line.A handwritten signature in blue ink, appearing to read "Paul J. Jones", written over a horizontal line.

Accepted for the Council:

A handwritten signature in black ink, appearing to read "L. J. Mink", written over a horizontal line.

Associate Vice Chancellor and
Dean of The Graduate School

SPECTROPOLARIMETRY OF POLYMERS

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

Bhushan Deshpande

May 2000

DEDICATION

This work is dedicated to my parents

ACKNOWLEDGEMENTS

I wish to thank my advisor Dr. Marion G. Hansen, for introducing me to the topic of spectropolarimetry. His support and encouragement is appreciated. I also wish to thank my committee members Dr. S. Alexandratos, Dr. P. D. Frymier, and Dr. T. W. Wang. Dr. R. Benson and Dr. J. E. Spruiell helped by allowing the use of the film stretcher and in interpreting stress data. I wish to thank the Measurement and Control Engineering Center (MCEC) for financial support.

The mechanical components of the spectropolarimeter were built in the machine shop at the University of Tennessee. Doug, Larry, and Ray in the machine shop helped with aspects of design and constructed required components. The personnel at Brimrose Corporation of America were invaluable by letting me use their facilities and expertise. The personnel at the help desk of National Instruments were very helpful with suggestions for LabVIEW programming. I am thankful for Techmer PM for providing me with polymer film samples.

I wish to thank my lab-mates: Srinivas Vedula, Mrunalini Dhamdhere, Jigui Li, Erik Nielsen, and Parag Patil. Other friends at the University of Tennessee and in the city of Knoxville were also very helpful with encouragement and support in my work and free time. Lastly, I wish to thank my family - my parents and my brother and his wife. Without their support this dissertation would not be a reality.

ABSTRACT

A new instrument called the spectropolarimeter was developed in this work. The spectropolarimeter was designed to obtain simultaneously coaxial linear birefringence, linear dichroism, and their coaxial orientation angles.

The instrument was designed to operate in the near-infrared region (1100-2200 nm) of the electromagnetic spectrum. The instrument used an acousto-optic tunable filter as a monochromator. Modulated light was obtained using a photo-elastic modulator. A novel design using a polarizing beam-splitter allowed for simultaneous measurements of six elements of the Mueller matrix of a sample. The instrument was tested using an optical compensator. Linear retardance and its orientation angle were obtained simultaneously over multiple wavelengths.

The instrument was used to obtain composition information through measurements of the isotropic absorbance spectra of polyethylene terephthalate films. Data obtained on a set of low-density polyethylene tube-blown films from the spectropolarimeter were correlated directly to motor torque set value during film manufacture. The spectropolarimeter was used to follow in-line development of linear retardance at 1100 nm during uniaxial film stretching of low-density polyethylene. Simultaneously, stress information was obtained on the films. The stress information was compared with the development of linear retardance during film stretching.

CONTENTS

Chapter	Page
1 Introduction	1
2 Literature review	4
2.1 Introduction	4
2.2 Measurements using polarized light	6
2.3 Photoelastic modulator	9
2.4 Linear birefringence and linear dichroism measurements	11
3 Polarized light	13
3.1 Introduction	13
3.2 Polarization ellipse	14
3.3 Stokes vectors and Jones vectors	17
3.4 Mueller matrices and Jones matrices	20
3.5 Mueller matrices and Jones matrices of common optical elements	23
3.6 Conversion of Jones matrix to Mueller matrix	26
3.7 Linear birefringence and linear dichroism	27
4 Experimental setup	34
4.1 Introduction	34
4.2 Optical components	36
4.3 Electronic components	42
4.4 Mechanical details	50
4.5 Film stretcher	55

5	Experiments on optical compensator	58
	5.1 Introduction	58
	5.2 Experiments at a single wavelength	61
	5.2 Experiments at multiple wavelengths	68
6	Experiments on polymer films	77
	6.1 Introduction	77
	6.2 Isotropic absorbance spectra of polyethylene terephthalate films	77
	6.3 Motor torque set values in low-density polyethylene films	82
	6.4 In-line analysis during uniaxial film stretching	88
7	Conclusions	98
8	Future work	100
	References	102
	Appendices	107
A	Jones and Mueller matrices of optical samples	108
	A.1 Introduction	108
	A.2 Differential propagation Jones matrix	109
	A.3 Jones matrix of the optical sample	112
	A.4 Special forms of the Jones matrix	118
	A.5 Mueller matrix	124
	A.6 Special forms of the Mueller matrix	128
	A.7 Comparison of the Jones and Mueller matrices	

	with published literature	133
B	Operation of the spectropolarimeter	136
	B.1 Mathematics of the optical train	136
	B.2 Mathematical effects of the PEM	141
	B.3 Mathematical analysis for various forms of optical sample	143
	B.4 Alignment of the polarizing beam-splitter	154
	B.5 Alignment procedure for the PEM	156
	B.6 Determination of the calibration constants	158
	B.7 The ratio c_1/c_2	159
Vita		163

LIST OF TABLES

Table	Page
3.1 Differences between Stokes and Jones vectors	21
3.2 Stokes and Jones vectors for various degenerate forms of the polarization ellipse	22
3.3 Mueller matrices and Jones matrices for common optical elements	25
6.1 Conditions for manufacture of tube-blown LDPE film samples	85
A.1 Differential propagation Jones matrices for various optical effects	110

LIST OF FIGURES

Figure		Page
3.1	Representation of linearly horizontally polarized light	16
3.2	Linearly polarized light passing through an optical sample with a complex index of refraction	28
3.3	Effect of linear birefringence (a) and linear dichroism (b)	30
3.4	Vector diagram for the refractive index tensor for an optical sample with non-coaxial linear birefringence and linear dichroism	33
4.1	Spectropolarimetry setup	35
4.2	Details of the AOTF monochromator	37
4.3	Details of the PEM	41
4.4	AOTF control	45
4.5	PEM control	46
4.6	Spectropolarimeter control	48
4.7	Data collection in a lock-in amplifier	51
4.8	Block diagram illustrating the recording of data	52
4.9	Mounting plate for polarizing beam-splitter and sample detectors	54
4.10	Calibration of the load cell	57
5.1	Schematic of a Soleil-Babinet compensator	59
5.2	Raw data for compensator with $\chi = 0^\circ$	62
5.3	Ratios r_1 and r_2 for compensator with $\chi = 0^\circ$	64
5.4	Raw data for compensator with $\mu = 90^\circ$	66
5.5	The ratios R_1 and R_2 for compensator with $\mu = 90^\circ$	67
5.6	Calibration constants as a function of wavelength	70
5.7	Retardance (a) and orientation angle (b) values for	

	various compensator screw settings at $\chi = 0^\circ$	72
5.8	Retardance and orientation angle observed as a function of wavelength when the compensator is set at $\mu = \chi = 0^\circ$	74
5.9	Retardance (a) and orientation angle (b) values for various orientation angles at compensator screw setting 10 mm	76
6.1	Voltage signals V_1 and V_2 from the spectropolarimeter in the absence of PEM and optical sample	80
6.2	Fourier coefficients obtained from detector 1 (a) and detector 2 (b) for the cast PET film	81
6.3	Isotropic absorbance spectra of PET film samples	83
6.4	Film-blowing operation	84
6.5	Raw data for the Fourier coefficient ω from detector 2	87
6.6	Scores plot obtained during PLS regression	89
6.7	PLS regression results	90
6.8	DC and ω Fourier coefficients obtained during film stretching	93
6.9	Real-time stress (a) and linear retardance (b) curves for the same strain rate	95
6.10	Real-time stress (a) and linear retardance (b) curves for the same strain at different strain rates	96
A.1	The parameters a and b . The parameter b is shown for the case of coaxial linear birefringence and linear dichroism	114
A.2	The real part of the elements of the Jones matrix for the case of coaxial linear birefringence and linear dichroism	121
A.3	The imaginary part of the elements of the Jones matrix for the case of coaxial linear birefringence and linear	

	dichroism	122
B.1	PEM amplitude setting	160

NOMENCLATURE

AOTF	Acousto-optic tunable filter
DC	Direct current
GPIB	General purpose interface bus
LDPE	low-density polyethylene
PEM	Photo-elastic modulator
PET	Polyethylene terephthalate
PLS	Partial least squares
RF	Radio frequency
A_e	Isotropic absorbance
c	Speed of light in vacuum
c_i	Proportionality constant in conversion of intensity to voltage at detector number i.
d	Thickness of an optical sample
E_0	Maximum amplitude when E_{0x} and E_{0y} are equal
E_{0x}	Maximum amplitude of E_x
E_{0y}	Maximum amplitude of E_y
E_i	One of three parameters used to convert Jones matrix to Mueller matrix
E_x, E_y	Orthogonal components of the electric field vector along x and y directions
$\mathbf{E}$	Electric field vector
$\mathbf{E}$	Jones vector of light
$\mathbf{E}'$	Jones vector of light emerging from an optical component
F_{ij}	One of three parameters used to convert Jones matrix to Mueller matrix
G_{ij}	One of three parameters used to convert Jones matrix to Mueller matrix
$\mathbf{H}$	Magnetic field vector
$I_0(\lambda)$	The average of the first two Stokes parameters of light emerging from the linear polarizer

I	Identity matrix
Im	Imaginary part of a complex number
$J_i(\delta_0)$	Bessel function of order i at δ_0
J	Jones matrix
k	Isotropic extinction coefficient
M_{ij}	Element at position i, j of the Mueller matrix
M	Mueller matrix
n_e	Extraordinary refractive index
n_j	Isotropic refractive index
n_o	Ordinary refractive index
n	Complex refractive index
N	Differential propagation Jones matrix
r_1	Ratio of the ω Fourier coefficient with twice the DC Fourier coefficient
r_2	Ratio of the 2ω Fourier coefficient with twice the DC Fourier coefficient
R_1	Ratio of ω Fourier coefficient with twice the DC Fourier coefficient and $J_1(\delta_0)$
R_2	Ratio of 2ω Fourier coefficient with twice DC Fourier coefficient and $J_2(\delta_0)$
Re	Real part of a complex number
S_0	The first Stokes parameter
S_1	The second Stokes parameter
S_2	The third Stokes parameter
S_3	The fourth Stokes parameter
S	Stokes vector of light
S'	Stokes vector of light emerging from an optical component
t	Time
$V_i(\lambda)$	Voltage signal from detector number i at wavelength λ
$V_i^{DC}(\lambda)$	The DC Fourier coefficient from detector number i at wavelength λ
$V_i^{\omega}(\lambda)$	The ω Fourier coefficient from detector number i at wavelength λ
$V_i^{2\omega}(\lambda)$	The 2ω Fourier coefficient from detector number i at wavelength λ

x	Direction along the X-axis in a Cartesian coordinate system
y	Direction along the Y-axis in a Cartesian coordinate system
z	Direction along the Z-axis in a Cartesian coordinate system
χ	Orientation angle for linear birefringence, angle made by a linear retarder
δ	Difference in the phase shifts $\delta_y - \delta_x$
δ_0	Maximum amplitude setting in the PEM
δ_x	Phase shift of E_x
δ_y	Phase shift of E_y
$\Delta n'$	Linear birefringence
$\Delta n''$	Linear dichroism
Δn_{CB}	Circular birefringence
Δn_{CD}	Circular dichroism
ϕ_d	Orientation angle for linear dichroism
λ	Wavelength of light
μ	Linear retardance, phase shift of a linear retarder
μ_{PEM}	Retardance of the PEM
θ	Coaxial orientation angle for linear birefringence and linear dichroism
θ_{LP}	Alignment angle of a linear polarizer
ν	Relative absorption coefficient
ω	Frequency of operation of the PEM
$\omega t - k_z z$	Propagator of the electric field vector

CHAPTER 1

INTRODUCTION

Polymers are marketed on certain performance criteria. The criteria are usually a measure of strength (modulus or yield point) or a rheological property (melt index). For the same polymer, a large variation in properties can be realized by manipulating its molecular weight distribution. Within the same molecular weight distribution, modifying crystal morphology alters polymer properties. We can thus observe a range of mechanical properties - ductile, brittle, and elastic for the same polymeric material. An understanding of crystal morphology will lead us to valuable information about macroscopic properties of the polymer. Different techniques can be used for the characterization of crystalline polymer structure. Optical techniques were chosen in this work to probe polymer morphology. Specifically, linear birefringence and linear dichroism were used.

Measurements of linear birefringence and linear dichroism lead to valuable insights in the structure, morphology, and rheology of a polymer. Linear birefringence is related to orientation functions in polymer films and fibers. In polymer melts linear birefringence is linearly related to stresses in the polymer. It is thus used to obtain a measure of rheological properties of the melt. Linear dichroism can be used to probe orientation of polymer chain constituents in polymer crystals and melts.

In this work, a *spectropolarimeter* was designed to probe optical properties in oriented polymers. Data were obtained in the wavelength range 1100 and 2200 nm and correlated to macroscopic polymer film production or film properties - motor torque set value and stress-strain behavior. The spectropolarimeter was also used, for composition of polymers through measurements of isotropic absorbance spectra.

The spectropolarimeter is based on measurements of modulating polarized light. Instruments based on similar principles were studied to ascertain if they could be used to probe optical properties of polymer samples. The instruments in use were found to have various drawbacks especially in the operating wavelength range and in the manner of producing a modulated signal. These drawbacks are discussed in greater detail in the literature review chapter. A new instrument was thus designed that would operate in the entire near-infrared wavelength region without any mechanically moving parts.

There are various advantages of operating in the near-infrared region of the electromagnetic spectrum. Common polymers show spectral information in the near-infrared region. This information is weaker than the fundamental bands that appear in the infrared. This is an advantage as it allows for the use of thicker samples with lesser sample preparation. There are fewer interference effects from impurities and additives in the polymer. Remote sensing through the use of fiber-optic cables is also possible.

The spectropolarimeter was analyzed mathematically using Mueller matrix and Stokes vector calculus. Mueller matrices for optical samples containing various anisotropies were derived. Based on these matrices, theoretical predictions for spectropolarimeter results using various optical samples were derived. Methods of analysis for the data to obtain optical properties at different wavelengths were derived. The spectropolarimeter could analyze samples containing simultaneously coaxial linear birefringence and linear dichroism. Components were procured and integrated into a single system. Computer codes were written for instrument control and data analysis.

The spectropolarimeter was analyzed using a standard sample - an optical compensator. Theoretical predictions were compared with experimental values to check the working of the spectropolarimeter. It was then used to analyze polymer films. Isotropic absorption spectra were obtained for polyethylene terephthalate (PET) film samples. Spectropolarimetry data were correlated directly with motor torque set values in a series of low-density polyethylene (LDPE) blown film samples. Spectropolarimetry data were obtained in-line during uniaxial film stretching operation. Simultaneously, stress-strain information was obtained on the films. The stress behavior was compared with the spectropolarimetry results.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In a melt, polymer chain conformations are changing continuously. However, in the absence of external stresses, average end-to-end polymer chain distance remains a constant. The chains are in a form known as "random coil structure" in which there is no preferential order in the polymer chains. When external stresses are applied to the melt, for example to generate flow, the chains are preferentially stretched. This orients polymer chains in a particular direction. The direction and extent of orientation depends on external stresses and molecular weight distribution (MWD) of the chains. When external stresses applied on the same polymer are equal, extent of orientation is a function of the MWD. On the other hand, MWD influences rheological properties of a polymer. Thus, a measure of the extent of orientation could lead us to a measure of the rheological properties.

Hansen and Vedula [1, 2] have monitored rheological properties of molten flowing polymers using in-line isotropic near-infrared (NIR) spectroscopy. In their work, melt index and complex viscosity values of a series of ethylene vinyl acetate (EVA) copolymers were predicted from their isotropic NIR spectra. The authors collected isotropic NIR spectra of flowing molten polymers, and correlated the data to rheological properties using partial least squares regression techniques. This however

had several drawbacks. In their system of study rheological properties are influenced by two factors: vinyl acetate (VA) content in the copolymer and MWD of the particular copolymer. Isotropic NIR spectroscopic data is influenced by VA content. However, the effect of VA content on NIR spectra and rheological properties is not necessarily linear. Changes in MWD for the same VA content do not influence isotropic NIR spectra. Thus, samples with similar VA content but large differences in MWD (and hence rheological properties) have similar isotropic NIR spectra. Successful correlation of NIR spectra for such samples with rheological properties is thus difficult to justify physically. The authors relied on regression techniques to develop successful mathematical correlations between isotropic NIR spectra and rheological properties. It was however difficult to interpret these results and to predict results for new systems. This is especially true for homopolymer systems in which the only change is in MWD.

Preferential orientation of polymer chains leads to development of linear birefringence and linear dichroism. These properties are probed with measurements using polarized light. They are dependent on the wavelength of light used. Linear birefringence is correlated to stresses in molten flowing polymers [3] and through the stress to other rheological properties. It is also correlated to molecular orientation functions in polymer films [4]. Linear dichroism can be used to probe orientation of chain constituents in the polymer crystal [5, 6]. Measurements of linear birefringence

and linear dichroism lead us to an important understanding of polymer structure and its rheological properties.

2.2 Measurements using polarized light

As explained by Collett [7], the polarization state of light is completely described by four real numbers arranged along a 4×1 column vector called Stokes vector. Changes in the polarization state of light as it passes through an optical sample are expressed in a linear relation, given in equation 2.1, between the incident Stokes vector S and the Stokes vector, S' , of light emerging from the sample.

$$S' = M \cdot S \quad 2.1$$

In equation 2.1, M is a 4×4 matrix called the Mueller matrix of the sample. Elements of the Mueller matrix are related to physical and optical properties (such as linear birefringence and linear dichroism) of the sample.

Polarimetry is the study of polarization state of light or of changes in the polarization state during propagation of light through a sample. Polarimetric measurements are carried out at a single wavelength. Spectropolarimetry is an extension of polarimetry to multiple wavelengths over a given spectral band.

Polarimetric studies can be divided into two categories: Stokes vector polarimetry and Mueller matrix polarimetry. In Stokes vector polarimetry some or all elements of the Stokes vector are measured. Stokes vector polarimetry is useful in

characterization of light sources, astronomical measurements, and the measurement of changes in the state of polarization. Hauge [8] has reviewed different techniques in Stokes vector polarimetry. Fymat [9] and Birich *et al.* [10] discuss the extension of Stokes vector polarimetry to multiple wavelengths. Mueller matrix polarimetry involves the measurement of some or all elements of the Mueller matrix of the optical sample. Mueller matrix polarimetry is useful in characterizing optical properties of a sample. A Mueller matrix spectropolarimeter has been developed in the present work.

Mueller matrix polarimetry was introduced by Thompson *et al.* [11]. The authors developed an instrument that allowed for direct measurement of all sixteen elements in the Mueller matrix. This was accomplished with the use of four electro-optic modulators (EOM). EOM's are devices that produce a linear retardance that is proportional to an applied voltage. The instrument operated at 632.8 nm using a He-Ne laser. The instrument was used [12] to measure light scattering properties of several samples of phytoplankton in water. Mueller matrices for various scattering angles between 8° and 168° were directly presented as the light scattering property of the sample without further analysis. It was also used [13] to measure the Mueller matrices of common optical components - linear polarizer and quarter wave plate retarder. However, this instrument has several drawbacks. EOM devices are expensive. Alignment problems and losses are compounded with the use of four EOM devices. Each EOM device has to operate at a unique fundamental frequency to minimize interference effects. The signal obtained is in the form of a Fourier series

with sixteen coefficients (direct current and various multiples of the four fundamental frequencies) that have to be measured simultaneously.

Azzam [14] proposed a method for measuring all sixteen elements of the Mueller matrix using two linear polarizers and two linear retarders. The linear retarders were rotated at unique frequencies. Again, the voltage signal obtained was in a form of a Fourier series and its coefficients could be related to elements of the Mueller matrix of the sample. The instrument however, was never built, only the theoretical analysis was presented. Such a device would however have several drawbacks. Moving components (rotating linear retarders) can cause mechanical and alignment problems. Linear retarders need careful optical alignment and even the best linear retarders have errors in their retardance. The operating range of linear retarders is usually limited to a single wavelength.

Delplancke [15] designed an instrument to measure all sixteen Mueller matrix elements. The instrument used two photoelastic modulators (PEM) that modulated the polarization state of light. The two PEM devices operate at unique fundamental frequencies. Light emerging from the sample was split into four beams using three non-polarizing beam-splitters. Non-polarizing beam-splitters are beam-splitters that split the incident light beam without changing its polarization state. The four light beams are incident on four light detectors. As in other instruments, the signals from the four detectors are in a form of a Fourier series whose coefficients were related to

the elements of the Mueller matrix of the sample. The instrument was tested by obtaining the Mueller matrix of a linear polarizer and used to study reflections from films and rough surfaces [16, 17]. Delplancke *et al.* [18] used the instrument to study scattering from suspensions of polystyrene beads in chiral solutions. These instruments operated at 632.8 nm using a He-Ne laser and are difficult to modify for other wavelengths because of wavelength restrictions of the non-polarizing beam-splitters.

Chenault and Chipman [19] modified a Fourier transform (FT) spectrometer to obtain elements of the Mueller matrix. The instrument had an operating range of 2500-25000 nm (2.5 to 25 μm). However, the instrument required obtaining a series of sixteen spectra to obtain all of the elements in the Mueller matrix. The instrument was similar to that proposed by Azzam [14] and used two rotating quarter wave plate retarders. The same authors modified the instrument [20] using a rotating sample between two fixed polarizers. Again, a series of spectra had to be collected to obtain the elements of the Mueller matrix. The modified instrument was used [21] to obtain linear birefringence of cadmium sulfide and cadmium selenide between 2500 nm and 16500 nm.

2.3 Photoelastic modulator

Stokes vector or Mueller matrix polarimetry requires the generation of a modulating polarization state of light. The modulation is usually sinusoidal. Earlier

devices [11, 12, and 13] used electro-optic modulators (EOM) for generation of modulated light. An alternative was the use of a rotating linear retarder [14, 19] or the use of a rotating sample [20]. Kemp [22] introduced a new method, the photoelastic modulator (PEM), for modulating light. Operation of the PEM is based on photoelastic effect, in which a mechanically stressed isotropic material exhibits birefringence proportional to the resulting strain. When the material is stressed sinusoidally, the result is a sinusoidally varying birefringence that modulates light propagating through the material. The PEM has several advantages over other methods of modulating light. It does not have mechanically moving parts. The angular aperture of the PEM is greater (up to 25° versus $1\text{-}2^\circ$ in EOM) than other devices. This results in fewer restrictions during positioning and alignment of the PEM. The spectral range of a PEM can be large, and is only limited by any absorption bands of the PEM material.

Jensen *et al.* [23] have analyzed the use of PEM devices in Mueller matrix polarimeters. They derived mathematically, signals produced from different instruments configurations using PEM devices. Possible artifacts from instruments and their solutions were also analyzed. Hipps and Crosby [24] built an instrument based on a PEM device. The instrument obtained linear dichroism data in the wavelength range 550-750 nm. Shindo [25] has reviewed earlier work on instruments using PEM devices. Detailed analysis of instruments and their components was presented. Elements of the Mueller matrix obtained from various instruments were correlated with physical properties of the sample.

2.4 Linear birefringence and linear dichroism measurements

Numerical values of elements of Mueller matrices by themselves are helpful in determining the output Stokes vector when a known Stokes vector is incident on the material. To be of greater use, these numerical values have to be correlated to physical properties of the material. Jensen *et al.* [23] have correlated the elements to physical properties of a sample - isotropic absorbance, isotropic retardance, linear birefringence, linear dichroism, circular birefringence, and circular dichroism. Schellman and Jensen [26] have reviewed Mueller matrices in a similar fashion. They have also provided molecular interpretations for the physical properties in a sample. They reviewed the requirements of instruments needed to measure different physical properties.

Frattoni and Fuller [27] built an instrument to measure linear birefringence at 632.8 nm using a He-Ne laser. The device used a single PEM and a single detector. Only a few elements of the Mueller matrix were measured, but these elements could yield linear birefringence. The instrument was modified and used [28] to measure linear dichroism in the absence of linear birefringence. Linear dichroism data of a dilute suspension of nonabsorbing spheroid's subjected to a shear field was obtained. Further modifications using a beam-splitter [29] allowed for the measurement of more elements in the Mueller matrix of the sample. The elements could then be correlated simultaneously to coaxial linear birefringence and linear dichroism. The instrument was used to obtain data on dilute colloidal suspensions in shear flow. Abetz and Fuller

[30] have addressed the problem of determining correctly linear birefringence in samples with multiple orders of retardation. Their instrument used two laser sources: a He-Ne laser at 632.8 nm and an Argon laser at 514 nm. Data obtained with two lasers was compared to obtain the correct order of retardation. Fuller [31] provides a review of the different instruments, their analysis and their use for obtaining data on polymer melts. More recently, Kalogrianitis and vanEgmond [32] have built an instrument to simultaneously obtain linear birefringence in three directions. This leads to the determination of the complete stress tensor. Their instrument essentially put together three separate instruments for measurements of linear birefringence.

Ghaneh-Fard *et al.* [33] measured linear birefringence during the process of film blowing. They analyzed the effect of light beams that are not perpendicular to the film sample. They used [34] the instrument to obtain linear birefringence information on linear low-density polyethylene film blowing process. Linear birefringence values were obtained along the length of the bubble. Ajji *et al.* [35] have introduced an instrument to obtain linear birefringence values on films in the wavelength range 550-700 nm. They used the instrument to obtain linear birefringence values on polypropylene (PP) and polyethylene terephthalate (PET) films. Ajji and Guevremont [36] have described the instrument in greater detail in their patent.

CHAPTER 3

POLARIZED LIGHT

3.1 Introduction

Near-infrared light is a form of electromagnetic energy, other forms of which include radio waves, infrared radiation, visible spectrum, ultraviolet radiation, X-rays, and gamma radiation. In vacuum, electromagnetic radiation is completely specified by two vectors, the electric field vector $\mathbf{E}$, and the magnetic field vector $\mathbf{H}$. These vectors are functions of time and position in space. Any function of time can be written as a Fourier series. Electromagnetic radiation is termed monochromatic if the Fourier transform of the field vectors consist of a single discrete frequency component. If multiple frequency components are present, electromagnetic radiation is termed as polychromatic. Unless otherwise stated, mathematical equations in this chapter pertain to monochromatic light.

The behavior with time of the electric field vector at a fixed position in space is referred to as polarization of light. Polarization leads to information on amplitude, phase, and orientation of the electric field vector. In turn, this information leads to a physical understanding of the nature of light. It also provides us with a mathematical tool for interpreting interactions of light with matter.

3.2 Polarization Ellipse

The electric field vector is oriented in a plane orthogonal to the direction of propagation of light. Thus, for light propagating in the z direction orthogonal components $E_x(z, t)$ and $E_y(z, t)$ of the electric field vector are expressed in equation 3.1

$$\begin{aligned} E_x(z, t) &= E_{0x} \cos(\omega t - k_z z + \delta_x) \\ E_y(z, t) &= E_{0y} \cos(\omega t - k_z z + \delta_y) \end{aligned} \quad 3.1$$

In equation 3.1, $(\omega t - k_z z)$ is called the propagator, E_{0x} and E_{0y} are maximum amplitudes, and δ_x and δ_y are phase shifts associated with the orthogonal components E_x and E_y respectively. As the electric field propagates through space and time $E_x(z, t)$ and $E_y(z, t)$ give rise to a resultant vector. This vector describes a locus of points in space. Collett [7] has derived the equation for the loci given here in equation 3.2.

$$\begin{aligned} \frac{E_x^2}{E_{0x}^2} + \frac{E_y^2}{E_{0y}^2} - 2 \frac{E_x}{E_{0x}} \frac{E_y}{E_{0y}} \cos \delta &= \sin^2 \delta \\ \text{where } \delta &= \delta_y - \delta_x \end{aligned} \quad 3.2$$

Equation 3.2 is the equation of an ellipse and known as the polarization ellipse. The polarization ellipse represents the most general form of polarized light. The ellipse degenerates to special forms for specific values of E_{0x} , E_{0y} and δ . These forms are described below

1) $E_{0y} = 0$: In this case $E_y(z, t)$ is zero and equation 3.1 reduces to equation 3.3.

$$\begin{aligned} E_x(z, t) &= E_{0x} \cos(\omega t - k_z z + \delta_x) \\ E_y(z, t) &= 0 \end{aligned} \quad 3.3$$

Here we have oscillations of the electric field vector in x direction only. Such a light beam is said to be *linearly horizontally polarized light*. Figure 3.1 shows the representation of such a light beam as it propagates along the z -axis (wave representation) and at a point (linear representation). Similarly, if $E_{0x} = 0$, we have oscillations in y direction only. The light is then called *linearly vertically polarized light*.

2) $\delta = 0^\circ$ or 180° : In this case equation 3.2 reduces to equation 3.4.

$$\begin{aligned} \frac{E_x^2}{E_{0x}^2} + \frac{E_y^2}{E_{0y}^2} \pm 2 \frac{E_x}{E_{0x}} \frac{E_y}{E_{0y}} &= 0 \text{ as } \delta = 0 \text{ or } \pi \\ \left(\frac{E_x}{E_{0x}} \pm \frac{E_y}{E_{0y}} \right)^2 &= 0 \\ E_y &= \pm \left(\frac{E_{0y}}{E_{0x}} \right) E_x \end{aligned} \quad 3.4$$

Equation 3.4 is the equation of a straight line with a slope $\pm(E_{0y}/E_{0x})$ and a zero intercept. If $E_{0y} = E_{0x}$ we have $E_y = \pm E_x$. The positive value is said to represent *linear $+45^\circ$ polarized light* and the negative value is said to represent *linear -45° polarized light*.

3) $E_{0y} = E_{0x} = E_0$ and $\delta = 90^\circ$ or 270° : Under these conditions equation 3.2 reduces to equation 3.5.

$$\frac{E_x^2}{E_0^2} + \frac{E_y^2}{E_0^2} = 1 \quad 3.5$$

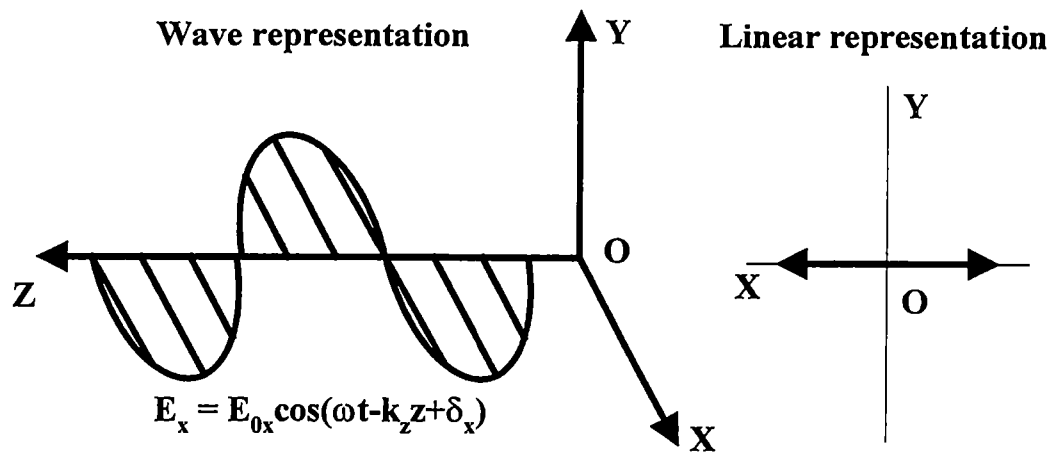


Figure 3.1 Representation of linearly horizontally polarized light

Equation 3.5 is the equation of a circle and the light it represents is called *circularly polarized light*. The light may be right circularly polarized (for $\delta = 90^\circ$) or left circularly polarized (for $\delta = 270^\circ$). Equation 3.5 does not include sufficient information for us to determine if the light is right or left circularly polarized. For that, we need some other independent information about the nature of light.

Thus, we can have three important forms of polarized light: linearly polarized, circularly polarized or elliptically polarized. Linearly polarized light can be linearly polarized at an angle to the coordinate system. In general, linearly polarized light and circularly polarized light are degenerate forms of elliptically polarized light.

3.3 Stokes vectors and Jones vectors

Equations 3.1 and 3.2 include all the polarization state information for light. However, these equations are in an amplitude formulation of the optical field that cannot be measured or observed. Optical detectors in use measure time averages of the squares of the optical field amplitudes (intensities). Stokes [37] discovered that the polarization state of an optical beam could be expressed in terms of intensities rather than amplitudes using four parameters. These parameters are known as the Stokes polarization parameters. The Stokes polarization parameters for a plane wave represented by equations 3.1 and 3.2 are given in equation 3.6.

$$\begin{aligned}
S_0 &= E_{0x}^2 + E_{0y}^2 \\
S_1 &= E_{0x}^2 - E_{0y}^2 \\
S_2 &= 2E_{0x}E_{0y} \cos \delta \\
S_3 &= 2E_{0x}E_{0y} \sin \delta
\end{aligned} \tag{3.6}$$

The parameter δ was defined in equation 3.2. Stokes parameters are real quantities that can be measured using optical detectors and have physical meaning. The first parameter S_0 is the total intensity of the optical beam, S_1 is the preference of linearly horizontally polarized light over linearly vertically polarized light, S_2 is the preference of linear $+45^\circ$ polarized light over linear -45° polarized light, and S_3 is the preference of right circularly polarized light over left circularly polarized light. The Stokes parameters describe the polarization state of any optical beam regardless of its state of polarization, from completely polarized light to unpolarized light. The four Stokes parameters can be arranged as shown in equation 3.7.

$$\mathbf{S} = \begin{bmatrix} S_0 \\ S_1 \\ S_2 \\ S_3 \end{bmatrix} = \begin{bmatrix} E_{0x}^2 + E_{0y}^2 \\ E_{0x}^2 - E_{0y}^2 \\ 2E_{0x}E_{0y} \cos \delta \\ 2E_{0x}E_{0y} \sin \delta \end{bmatrix} \tag{3.7}$$

By custom, this arrangement is known as the Stokes vector of light. Stokes vectors for various degenerate forms of polarized light can be derived from equation 3.7.

An alternative method of representation of equation 3.1, introduced by Jones [38, 39], is shown in equation 3.8.

$$\begin{aligned} E_x(z,t) &= E_{0x} \exp[i(\omega t - k_z z + \delta_x)] \\ E_y(z,t) &= E_{0y} \exp[i(\omega t - k_z z + \delta_y)] \end{aligned} \quad 3.8$$

Equation 3.8 is used with the understanding that the real part of the equation represents the actual physical property. Equation 3.9 is a vector formulation of equation 3.8 in which the propagator $(\omega t - k_z z)$ is suppressed for ease of mathematical manipulation.

$$\mathbf{E} = \begin{bmatrix} E_x \\ E_y \end{bmatrix} = \begin{bmatrix} E_{0x} \exp(i\delta_x) \\ E_{0y} \exp(i\delta_y) \end{bmatrix} \quad 3.9$$

Equation 3.9 is the Jones vector representation of light. It is customary to normalize the Jones vector using equation 3.10.

$$E_{0x}^2 + E_{0y}^2 = E_0^2 = 1 \quad 3.10$$

Jones vectors for various degenerate forms of the polarization ellipse can be obtained using equations 3.9 and 3.10. The Jones vector for linearly horizontally polarized light is determined below. For linearly horizontally polarized light we have $E_{0y} = 0$. Substituting in equation 3.9 we get equation 3.11.

$$\mathbf{E} = \begin{bmatrix} E_{0x} \exp(i\delta_x) \\ 0 \end{bmatrix} \quad 3.11$$

From the normalization condition in equation 3.10 we get $E_{0x}^2 = 1$, that is $E_{0x} = 1$. Substituting in equation 3.11 and suppressing $\exp(i\delta_x)$ the Jones vector for linearly horizontally polarized light is given by equation 3.12.

$$\mathbf{E} = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \quad 3.12$$

Jones vectors are in terms of optical amplitudes, which as noted earlier are difficult to measure physically. However, the advantage of using Jones vectors is that they are smaller and hence easier to manipulate. Table 3.1 gives the differences between the Stokes and Jones vectors.

Stokes and Jones vectors express the same quantities in different mathematical formulations. They are used alternatively based on the nature of the problem being tackled. Table 3.2 gives the Stokes and Jones vectors for various degenerate forms of the polarization ellipse.

3.4 Mueller matrices and Jones matrices

Consider a case when an incident beam with the Stokes vector S interacts with an element that changes the state of polarization of the beam. Let the Stokes vector of the emerging beam be S' . If we assume that the interactions are linear, we can express the Stokes parameters of the emerging beam as a linear combination of the Stokes parameters of the incident beam. This is expressed mathematically in equation 3.13.

$$S' = M \cdot S \quad 3.13$$

The 4×4 matrix M is known as the Mueller matrix of the interacting optical element. It represents the changes that occur in the polarization state of the incident beam due to linear interactions with the optical element. Since Stokes parameters are real numbers, the elements of the Mueller matrix are real numbers. Similarly, if we are working with

Table 3.1 Differences between Stokes and Jones vectors

Stokes Vectors	Jones Vectors
They are expressed in terms of light intensities. Optical detectors can measure their components.	They are expressed in terms of light amplitudes. Optical detectors cannot measure their components.
Expressed in terms of real numbers.	Expressed in terms of complex numbers with the understanding that the real part of the complex number represents the actual physical quantity.
Stokes vectors can be used to express any polarization state of light from unpolarized to completely polarized light.	Jones vectors can only be used with completely polarized light.
Not normalized.	Usually normalized before use.

Table 3.2 Stokes and Jones vectors for various degenerate forms of the polarization ellipse

Polarization state	Mathematical explanation	Stokes Vector	Jones Vector
Linearly horizontally polarized light	$E_{0y} = 0$	$S = E_0^2 \begin{bmatrix} 1 \\ 1 \\ 0 \\ 0 \end{bmatrix}$	$E = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$
Linearly vertically polarized light	$E_{0x} = 0$	$S = E_0^2 \begin{bmatrix} 1 \\ -1 \\ 0 \\ 0 \end{bmatrix}$	$E = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$
Linearly +45° polarized light	$E_{0x} = E_{0y} = E_0$ $\delta = 0^\circ$	$S = E_0^2 \begin{bmatrix} 1 \\ 0 \\ 1 \\ 0 \end{bmatrix}$	$E = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 1 \end{bmatrix}$
Linearly -45° polarized light	$E_{0x} = E_{0y} = E_0$ $\delta = 180^\circ$	$S = E_0^2 \begin{bmatrix} 1 \\ 0 \\ -1 \\ 0 \end{bmatrix}$	$E = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -1 \end{bmatrix}$
Right circularly polarized light	$E_{0x} = E_{0y} = E_0$ $\delta = 90^\circ$	$S = E_0^2 \begin{bmatrix} 1 \\ 0 \\ 0 \\ 1 \end{bmatrix}$	$E = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ i \end{bmatrix}$
Left circularly polarized light	$E_{0x} = E_{0y} = E_0$ $\delta = 270^\circ$	$S = E_0^2 \begin{bmatrix} 1 \\ 0 \\ 0 \\ -1 \end{bmatrix}$	$E = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -i \end{bmatrix}$

Jones matrices we express the changes between the incident beam, E , and the emerging beam, E' , through the Jones matrix as given in equation 3.14.

$$E' = J \cdot E \quad 3.14$$

The 2×2 matrix J is known as the Jones matrix of the interacting optical element. The elements of Jones matrix are complex numbers.

The advantage of using Mueller or Jones matrices is in their use to examine a series of optical elements in an experimental design. If the series contains n optical elements and the Stokes vector of light incident on the series is S_0 , then the Stokes vector of light, S_n , emerging from the series is given by equation 3.15.

$$S_n = M_n \cdot M_{n-1} \cdots M_2 \cdot M_1 \cdot S_0 \quad 3.15$$

In equation 3.15, M_i is the Mueller matrix of the i^{th} optical element in the series. Similarly, equation 3.16 represents the change in the incident Jones vector E_0 as it passes through a series of optical elements.

$$E_n = J_n \cdot J_{n-1} \cdots J_2 \cdot J_1 \cdot E_0 \quad 3.16$$

In equation 3.16, J_i is the Jones matrix of the i^{th} optical element in the series.

3.5 Mueller matrices and Jones matrices of common optical elements

Various optical elements; such as polarizers and retarders are in common use. This section explains their action along with their respective Mueller and Jones matrices.

- 1) Ideal linear polarizer aligned at an angle θ_{LP} : A linear polarizer attenuates unequally amplitudes of the orthogonal components of the electric field vector. If E_x and E_y represent orthogonal components of the electric field vector incident on a linear polarizer, then components of the emerging beam are expressed in equation 3.17.

$$\begin{aligned} E'_x &= p_x E_x \text{ where } 0 \leq p_x \leq 1 \\ E'_y &= p_y E_y \text{ where } 0 \leq p_y \leq 1 \end{aligned} \quad 3.17$$

An ideal linear polarizer has 100% transmission along one axis and no transmission along the other axis. Equation 3.17 is valid when the components of the electric field vector of incident light align with the axes of the polarizer. Collett [7] has considered the changes that occur when they are not aligned. The angle between components of the electric field vector and the axes of the linear polarizer is θ_{LP}° . Table 3.3 gives the Jones and Mueller matrices for an ideal linear polarizer aligned at such an angle.

- 2) Linear retarder aligned at an angle χ : A linear retarder is an element that changes the phase of the optical beam. If E_x and E_y represent orthogonal components of the electric field vector incident on a retarder, then components of the emerging beam are given in equation 3.18.

$$\begin{aligned} E'_x &= \exp\left(+i\frac{\mu}{2}\right)E_x \\ E'_y &= \exp\left(-i\frac{\mu}{2}\right)E_y \end{aligned} \quad 3.18$$

Table 3.3 Mueller matrices and Jones matrices for common optical elements

Ideal linear polarizer aligned at an angle θ_{LP}°	
Mueller matrix	$M = \begin{bmatrix} 1 & \cos 2\theta_{LP} & \sin 2\theta_{LP} & 0 \\ \cos 2\theta_{LP} & \cos^2 2\theta_{LP} & \sin 2\theta_{LP} \cos 2\theta_{LP} & 0 \\ \sin 2\theta_{LP} & \sin 2\theta_{LP} \cos 2\theta_{LP} & \sin^2 2\theta_{LP} & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$
Jones matrix	$J = \begin{bmatrix} \cos^2 \theta_{LP} & \sin \theta_{LP} \cos \theta_{LP} \\ \sin \theta_{LP} \cos \theta_{LP} & \sin^2 \theta_{LP} \end{bmatrix}$
Retarder aligned at an angle χ° causing a phase shift μ	
Mueller matrix	$M = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos^2 2\chi + \cos \mu \sin^2 2\chi & (1 - \cos \mu) \sin 2\chi \cos 2\chi & \sin \mu \sin 2\chi \\ 0 & (1 - \cos \mu) \sin 2\chi \cos 2\chi & \sin^2 2\chi + \cos \mu \cos^2 2\chi & -\sin \mu \cos 2\chi \\ 0 & -\sin \mu \sin 2\chi & \sin \mu \cos 2\chi & \cos \mu \end{bmatrix}$
Jones matrix	$J = \begin{bmatrix} \cos \frac{\mu}{2} + i \sin \frac{\mu}{2} \cos 2\chi & i \sin \frac{\mu}{2} \sin 2\chi \\ i \sin \frac{\mu}{2} \sin 2\chi & \cos \frac{\mu}{2} - i \sin \frac{\mu}{2} \cos 2\chi \end{bmatrix}$

The phase shift caused by the retarder in orthogonal components of the incident beam is μ . Again, equation 3.18 is valid when the components of the electric field vector align with the axes of the retarder. Collett [7] has examined the non-coaxial effects. Table 3.3 gives the Jones and Mueller matrices for a retarder aligned at an angle χ° .

3.6 Conversion of Jones matrix to Mueller matrix

The Mueller matrix of an optical element can be obtained from the corresponding Jones matrix. Such a conversion is often necessary, as it is easier to derive the Jones matrix of an optical element. Once the Jones matrix of the element has been derived from first principles we can easily obtain its Mueller matrix following a procedure described by Azzam and Bashara [40].

Let equation 3.19 represent the Jones matrix of an optical element.

$$J = \begin{bmatrix} J_1 & J_3 \\ J_4 & J_2 \end{bmatrix} \quad 3.19$$

Then its corresponding Mueller matrix is given by equation 3.20.

$$M = \begin{bmatrix} \frac{1}{2}(E_1 + E_2 + E_3 + E_4) & \frac{1}{2}(E_1 - E_2 - E_3 + E_4) & F_{13} + F_{42} & -G_{13} - G_{42} \\ \frac{1}{2}(E_1 - E_2 + E_3 - E_4) & \frac{1}{2}(E_1 + E_2 - E_3 - E_4) & F_{13} - F_{42} & -G_{13} + G_{42} \\ F_{14} + F_{32} & F_{14} - F_{32} & F_{12} + F_{34} & -G_{12} + G_{34} \\ G_{14} + G_{32} & G_{14} - G_{32} & G_{12} + G_{34} & F_{12} - F_{34} \end{bmatrix} \quad 3.20$$

Where

$$\begin{aligned}
E_i &= J_i J_i^* = |J_i|^2 \\
F_{ij} &= F_{ji} = \text{Re}(J_i J_j^*) \\
G_{ij} &= -G_{ji} = \text{Im}(J_i^* J_j)
\end{aligned} \tag{3.21}$$

In equation 3.21, the symbol * represents the complex conjugate of the quantity under consideration. We can use equations 3.20 and 3.21 to obtain the Mueller matrix of any Jones matrix represented by equation 3.19.

3.7 Linear birefringence and linear dichroism

Consider a light beam propagating through an isotropic optical sample as shown in figure 3.2. If the sample is both isotropically refracting and isotropically absorbing, the light beam is retarded and attenuated. For isotropic optical samples retardation and attenuation is independent of the direction of propagation or state of polarization of the incident light beam. It is only dependent on the thickness of the isotropic samples. The sample is said to have a complex index of refraction $(n_j - ik)$, where n_j is the usual refractive index, k the extinction coefficient of the sample and $i = \sqrt{-1}$.

Many samples are however not isotropic. Retardation and attenuation observed in such samples are dependent on the direction of propagation and polarization state of the incident beam. These samples are characterized by a complex refractive index tensor shown in equation 3.22.

$$n = n' + in'' \tag{3.22}$$

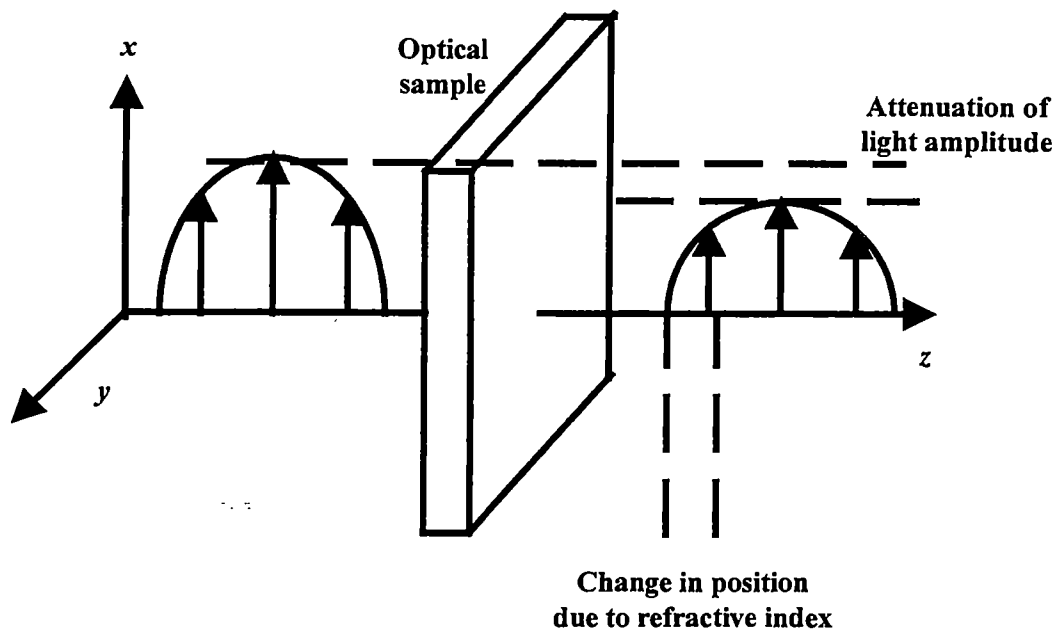


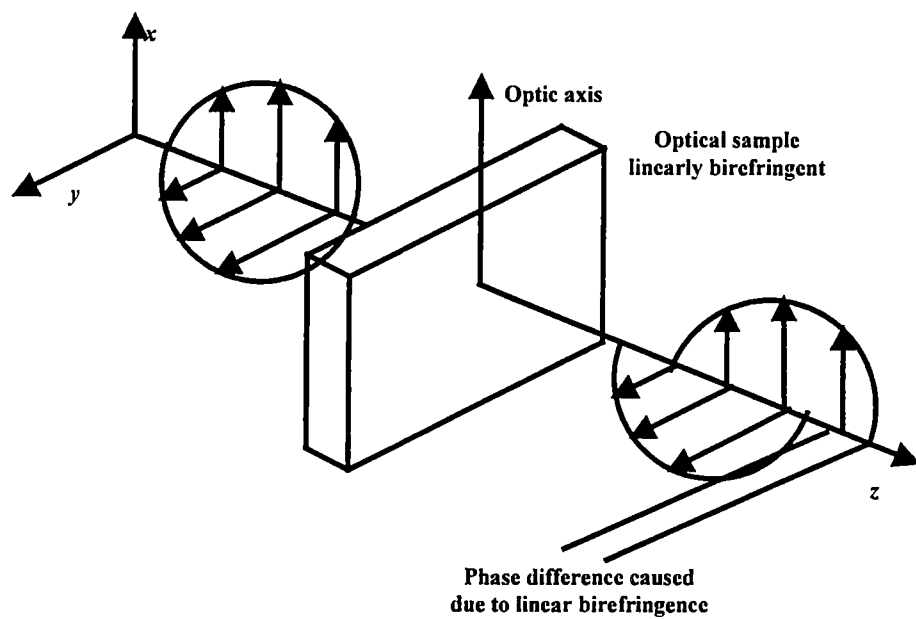
Figure 3.2 Linearly polarized light passing through an optical sample with a complex index of refraction

In equation 3.22, $\mathbf{n}'$ represents the real part of the refractive index tensor. Physically, this part describes retardation changes for linearly polarized light propagating in different directions. Similarly, $\mathbf{n}''$ represents the imaginary part of the refractive index tensor and describes the attenuation for linearly polarized light propagating in different directions.

If an optical sample is uniaxially linearly birefringent, we observe two unequal refractive index values in the real part of the refractive index tensor. These values are known as the extraordinary (n_e) and ordinary (n_o) refractive indices. The extraordinary refractive index is along the optic axis of the sample and the ordinary refractive index is along directions perpendicular to the optic axis. Light polarized linearly along the optic axis of the sample travels at a speed of c/n_e , where c is the speed of light in vacuum. Similarly, light polarized linearly in directions perpendicular to the optic axis travels at a speed of c/n_o . This is illustrated in figure 3.3. In general components of the electric field vector of incident light in directions parallel and perpendicular to the optic axis are retarded by the amounts $2\pi n_e d / \lambda$ and $2\pi n_o d / \lambda$, respectively. The thickness of the optical samples is d and λ is the wavelength of light. The quantity $\Delta n' = n_e - n_o$ is known as linear birefringence of the optical sample and linear retardance is defined by equation 3.23.

$$\mu = -\frac{2\pi\Delta n' d}{\lambda} \quad 3.23$$

a)



b)

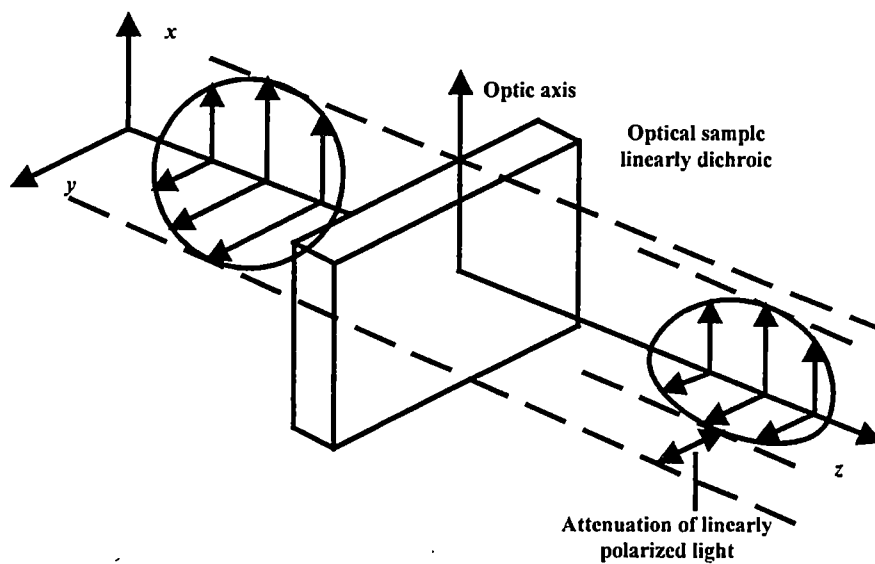


Figure 3.3 Effect of linear birefringence (a) and linear dichroism (b)

Some authors define linear retardance without the negative sign given in equation 3.23. Mathematically, this sign difference causes a change in sign of elements that involve the *sine* function of linear retardance in Jones and Mueller matrices.

Similarly, if the optical sample is uniaxially linearly dichroic, we observe two unequal extinction coefficient values in the imaginary part of the refractive index tensor. Light polarized linearly along the optic axis of the sample experiences a specific extinction coefficient k_e and is attenuated according to $I(z) = I(0) \exp\left(-\frac{2\pi k_e}{\lambda} d\right)$ where $I(0)$ is the intensity of light incident on the surface.

Similarly, light polarized linearly in a direction perpendicular to the optic axis experiences a specific extinction coefficient k_o and is attenuated accordingly. This is illustrated in figure 3.3. The quantity $\Delta n'' = k_e - k_o$ is known as the linear dichroism of the material and the relative absorption coefficient of the optical sample is defined as follows

$$\nu = \frac{2\pi \Delta n'' d}{\lambda} \quad 3.24$$

In many samples we observe both linear birefringence and linear dichroism. In such samples, the two anisotropies may have the same or independent optic axes. If the optic axes are same, the sample is said to have coaxial linear birefringence and linear dichroism, else the two anisotropies are noncoaxial. The optic axes of the

anisotropy need not be in the same direction as the components of the electric field vector of incident light. The angle made by the optic axes of the anisotropy with the axes of the electric field vector is known as the orientation angle of the anisotropy. χ represents the orientation angle for linear birefringence and ϕ_d represents the orientation angle for linear dichroism. The optical sample is said to have noncoaxial linear birefringence and linear dichroism if $\chi \neq \phi_d$ and coaxial linear birefringence and linear dichroism if $\chi = \phi_d$. Figure 3.4 shows the optic axes and axes of the electric field vector are for noncoaxial linear birefringence and linear dichroism.

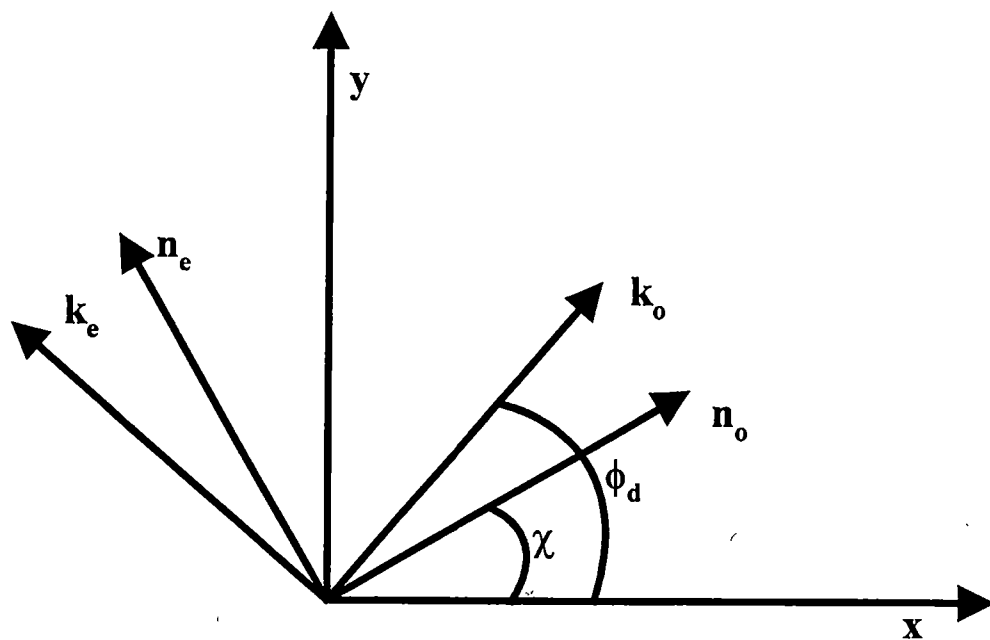


Figure 3.4 Vector diagram for the refractive index tensor for an optical sample with non-coaxial linear birefringence and linear dichroism

CHAPTER 4

EXPERIMENTAL SETUP

4.1 Introduction

Polymer films are usually uniaxially or biaxially stretched. Film stretching can be carried out at various temperatures, strains, and strain rates. Stretching changes the morphology and orientation of polymer chains that make up the film. Appropriate morphology and orientation, not the amount of polymer or thickness of the film, leads to desired film properties. Manufacturers desire to minimize costs by imparting appropriate morphology to the films with minimum amount of polymer.

It is thus desired to follow in-line changes in morphology and orientation during uniaxial and biaxial film stretching. Changes in morphology and orientation lead to changes in linear birefringence and linear dichroism of the film. In this work, these changes are observed in-line using a technique called spectropolarimetry. A new instrument called *spectropolarimeter* was designed for this purpose.

The components (optical, electronic, and mechanical) that make up the spectropolarimeter are discussed in this chapter. Figure 4.1 shows the spectropolarimetry setup. The Mueller matrices for various samples are derived in appendix A. Mathematical analysis of the setup using Stokes vectors and Mueller matrices is provided in appendix B.

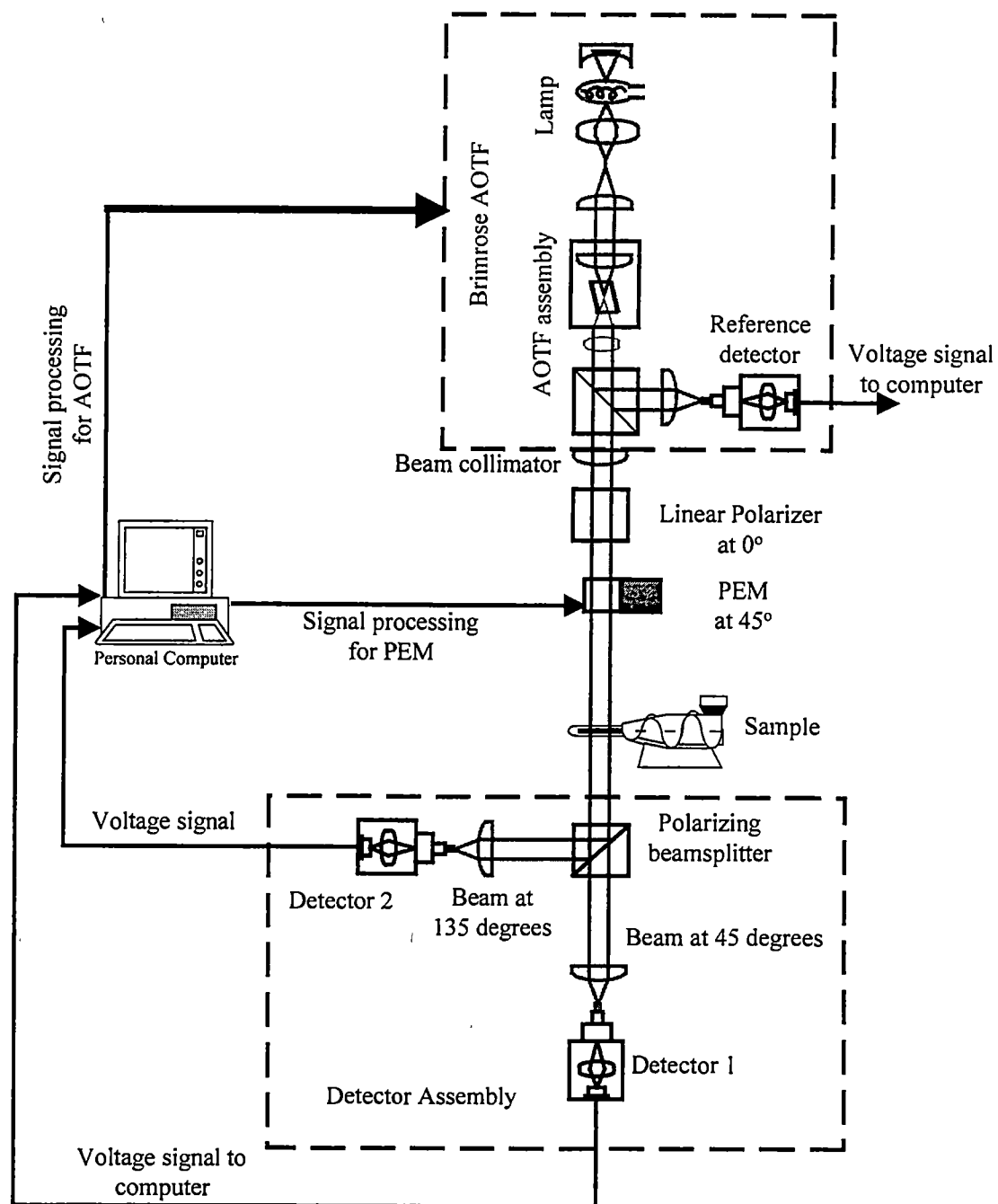


Figure 4.1 Spectropolarimetry setup

4.2 Optical components

4.2.1 Acousto-optic tunable filter (AOTF) monochromator

Successful application of spectropolarimetry necessitates recording data at a number of different but known wavelengths. Some form of monochromator is thus an essential component in the system. The AOTF monochromator was chosen over other available devices because of several advantages. The AOTF monochromator does not have any mechanically moving parts (common in Fourier transform devices or scanning devices) and does not need precise geometrical arrangements (common in fixed grating or detector arrays). It is also easier to apply at high resolutions over multiple wavelength ranges.

Brimrose Corporation of America manufactures the AOTF monochromator used in this work [41]. Details of the device are explained by Wang *et al.* [42]. Essentially an AOTF acts as a spectral bandpass filter. This filter can be tuned electronically to a desired wavelength. It consists of a piezoelectric transducer bonded to a birefringent material as shown in figure 4.2. When the transducer is excited by an applied radio frequency (RF) signal, acoustic waves are generated in the medium. The propagating acoustic wave produces a periodic modulation of the crystal's optical index of refraction. This modulation acts as a grating that diffracts only certain wavelengths of incident light. The diffracted beam emerges from the AOTF and other beams are blocked using a beam stop. Changing the RF frequency applied to the crystal changes the wavelength of the diffracted beam. The AOTF in use had a crystal

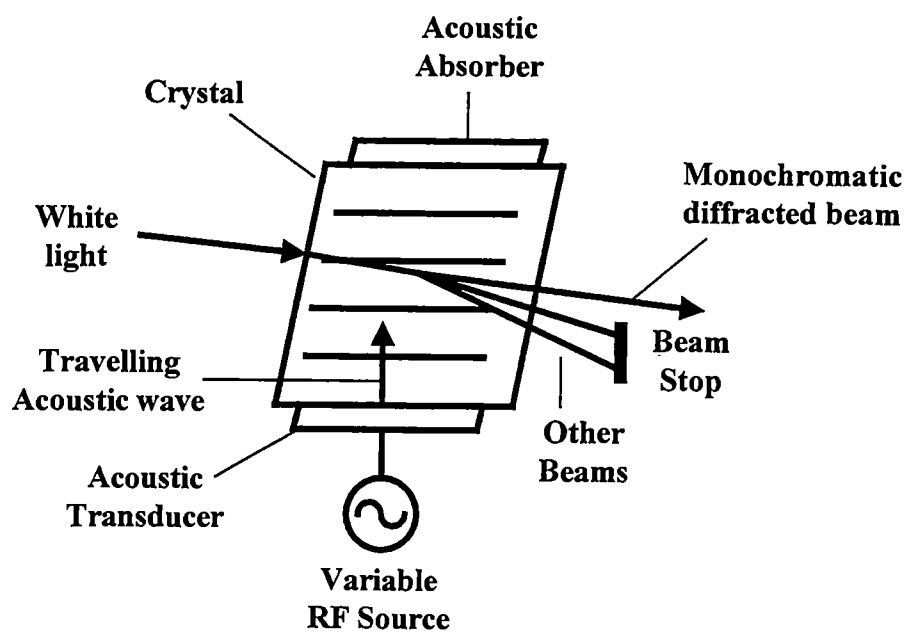


Figure 4.2 Details of the AOTF monochromator. Source: Wang [42]

of Tellurium dioxide (TeO_2). It had a spectral resolution (actual spectral bandwidth at any operating wavelength) of less than 20 nm. The operating range was 1100-2200 nm.

In this spectropolarimeter, the output of a quartz halogen lamp was directed into the TeO_2 AOTF that operated in the near-infrared region. The lamp intensity was maximized to compensate for intensity losses in the AOTF device. The AOTF was controlled by a tunable RF source that consisted of two pieces of hardware: direct digital synthesizer (DDS) and RF control board. The DDS generated a low frequency RF with the appropriate amplitude. The output frequency from the DDS was increased in the RF board and then amplified to the RF power level required by the AOTF. Brimrose Corporation of America provided calibration data (RF versus wavelength curve) for the AOTF in use. RF frequency information was provided to the DDS via serial port communication from the personal computer.

The output of the AOTF was linearly polarized monochromatic light of a known wavelength. This light was directed into the linear polarizer at 0° using a collimating lens.

4.2.2 Linear Polarizer

Light emerging from the AOTF passed through a linear polarizer where it was completely linearly polarized. The light incident on the linear polarizer was already

partially linearly polarized. However, its extinction ratio (1×10^{-2}) was not as good as desired and was improved to 1×10^{-5} using a Calcite linear polarizer. This linear polarizer had to be oriented such that it was parallel to the orientation of linearly polarized light emerging from the AOTF. This maximized the intensity of light emerging from the linear polarizer. The orientation could be achieved by rotating the linear polarizer till output intensity of light was maximized. The linear polarizer in use was obtained from CASIX [43].

4.2.3 Photo-elastic modulator (PEM)

A PEM modulates the polarization state of light at a fixed frequency. The principle of operation, explained by Kemp [22], is based on the photoelastic effect, in which a mechanically stressed sample exhibits birefringence proportional to the resulting strain. PEM's are resonant devices in which an oscillating birefringence is produced at a fixed frequency. Light passing through the PEM experiences the oscillating birefringence, modulating the polarization state of light at the frequency of oscillations. In the simplest form, the PEM consists of a rectangular bar of a suitable transparent material attached to a piezoelectric transducer. The bar resonantly vibrates along its long dimension at a frequency determined by its length and the speed of a longitudinal sound wave in the optical element material. The transducer is tuned to the same frequency and is driven by an electronic circuit that controls the amplitude of vibration.

The PEM used in the present setup was a model II/FS42 Hinds Instruments, Inc. [44] device. The optical element was made of fused silica in an octagonal shape. The element was bonded to a quartz piezoelectric transducer. Figure 4.3 shows details of the PEM. The device had an operating range of 180-2400 nm. Maximum retardance produced at a wavelength was user controlled to any value between zero and half-wave retardance. Maximum retardance was established and stabilized by a driver circuit that controlled vibrations in the optical element. The frequency of vibrations was around 42 kHz and was a weak function of wavelength, temperature and actual device. It was continuously adjusted by a control mechanism in the driver circuit so as to maintain the optical element in resonance with the piezoelectric transducer. The PEM could be set for any wavelength and maximum retardance via serial port communication from the personal computer.

Light emerging from the AOTF was linearly polarized in the linear polarizer and then incident on the PEM. The wavelength of light was determined by the AOTF. The PEM was operated at the same wavelength. Maximum retardance setting of the PEM was dependent on the experiment and is explained in greater detail in appendix B. The polarization state of light emerging from the PEM was modulating at a frequency 42 kHz. This light was incident on the optical sample. The optical sample could have various forms - standard samples in the form of a compensator and polymer films were used in this work.

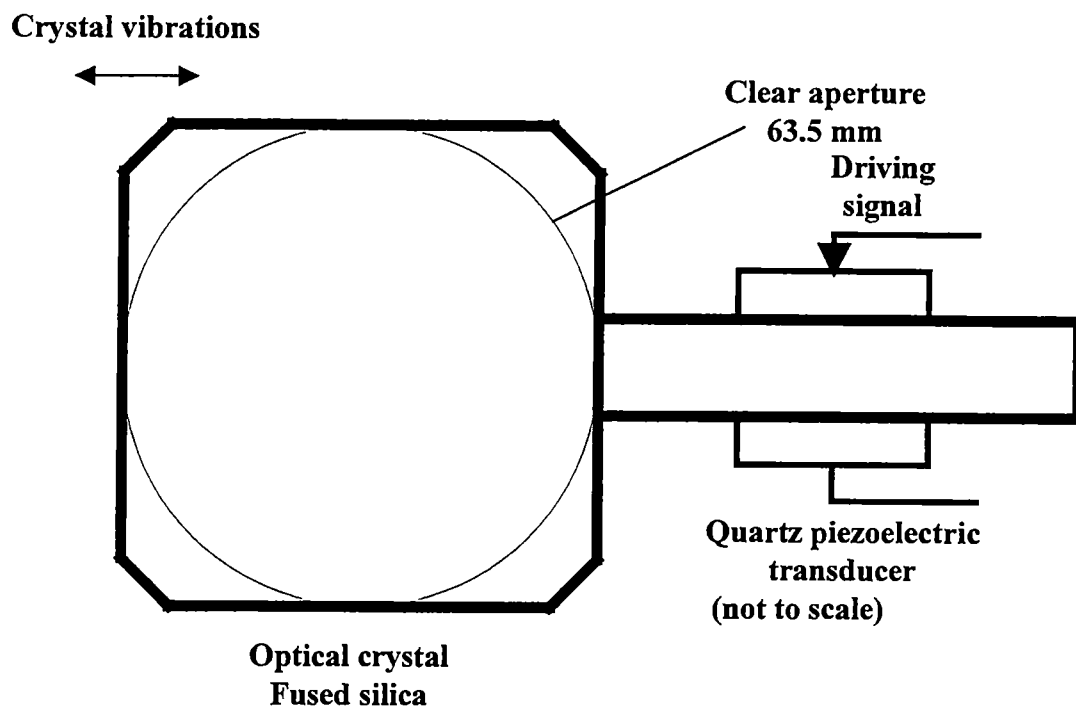


Figure 4.3 Details of the PEM

4.2.4 Polarizing beam-splitter

Light emerging from the sample passed through a Glan-Thompson polarizing beam-splitter. A conventional linear polarizer eliminates the totally reflected ordinary beam by absorption at a blackened side wall. A polarizing beam-splitter makes use of this beam by incorporating a third polished face that is perpendicular to the ordinary beam direction. In this work a model MSBTA-10-45 polarizing beam splitter from Karl Lambrecht corporation [45] was used. The polarizing beam-splitter had a working range of 350-2200 nm. The straight through beam extinction ratio was 1×10^{-5} and the deviated beam extinction ratio was 5×10^{-5} . The deviated beam emerged at an angle of $45^\circ \pm 1^\circ$ for all wavelengths. The clear aperture was 10 mm.

4.3 Electronic components

Electronic components include the detectors, various computer cards for instrument control and data analysis, and peripheral equipment. Optical detectors convert light intensity signals to voltage signals. The signals were then analyzed to obtain elements of the Mueller matrix of the optical sample.

4.3.1 Optical detectors

There were three optical detectors in the spectropolarimetry setup: a reference detector and two sample detectors. Part of the light emerging from the AOTF was split off and focussed on the reference detector. The reference detector produced a voltage response in which voltage was proportional to the intensity of light incident on the

face of the detector. The reference detector was used if needed; to monitor time changes of light intensity emerging from the AOTF. It could thus be used to compensate for any lamp stability problems. The two light beams emerging from the polarizing beam-splitter were focussed on two sample detectors. Again, the voltage response of the sample detectors was proportional to the intensity of light incident on the face of the detector. As explained in appendix B, the useful polarization state of light incident on the sample detectors is modulating at a maximum frequency that is twice the modulation frequency of the PEM. The modulation frequency of the PEM was 42 kHz and thus the detectors have to capture the response at 84 kHz. We were also interested in the direct current (DC) component of the signal. The frequency bandwidth of the sample detectors had to be from DC to several times the modulation frequency of the PEM.

The reference detector is a model ETX-1000-GR-2.5-TE detector from Epitaxx, Inc [46]. The detector was a thermoelectrically cooled InGaAs detector with a 1-mm active area. The two sample detectors were model J18TE1-37S-R01M-2.6-BRIMROSE detectors from EG&G Judson [47]. They were one-stage thermoelectrically cooled extended InGaAs detectors with a 1-mm active diameter. Their operating range was 1000-2400 nm. The cutoff frequency is 3 MHz. Brimrose Corporation of America [41] incorporated all the detectors in the setup with appropriate pre-amplifiers.

4.3.2 Instrument control and data collection

Various components in the system had to be controlled simultaneously and data had to be collected at the same time. Instrument control and data recording was achieved through programs written in the platform LabVIEW (version 5.1) obtained from National Instruments [48]. LabVIEW is a graphical programming environment with in-built hardware and software libraries. LabVIEW programs based on these libraries were written for all aspects of instrument control and data recording.

The AOTF is controlled through serial port communication from the personal computer. Figure 4.4 shows a schematic for AOTF control. The desired wavelength was first converted to RF frequency using the wavelength-frequency calibration information provided. The numerical value of frequency was converted to a format acceptable to the AOTF. This was transferred to the AOTF using the libraries for communication using serial port in LabVIEW. A check was then performed to ascertain if the frequency information was understood by the AOTF and the desired wavelength was obtained. The PEM was similarly controlled using serial port communications. Figure 4.5 shows a schematic for PEM control. Maximum retardance in the PEM was not changed, only the wavelength of operation was changed. The PEM modulates sinusoidally polarization state of light. Retardance is related to linear birefringence and wavelength through equation 3.23 reproduced here as equation 4.1.

$$\mu = -\frac{2\pi\Delta n' d}{\lambda} \quad 4.1$$

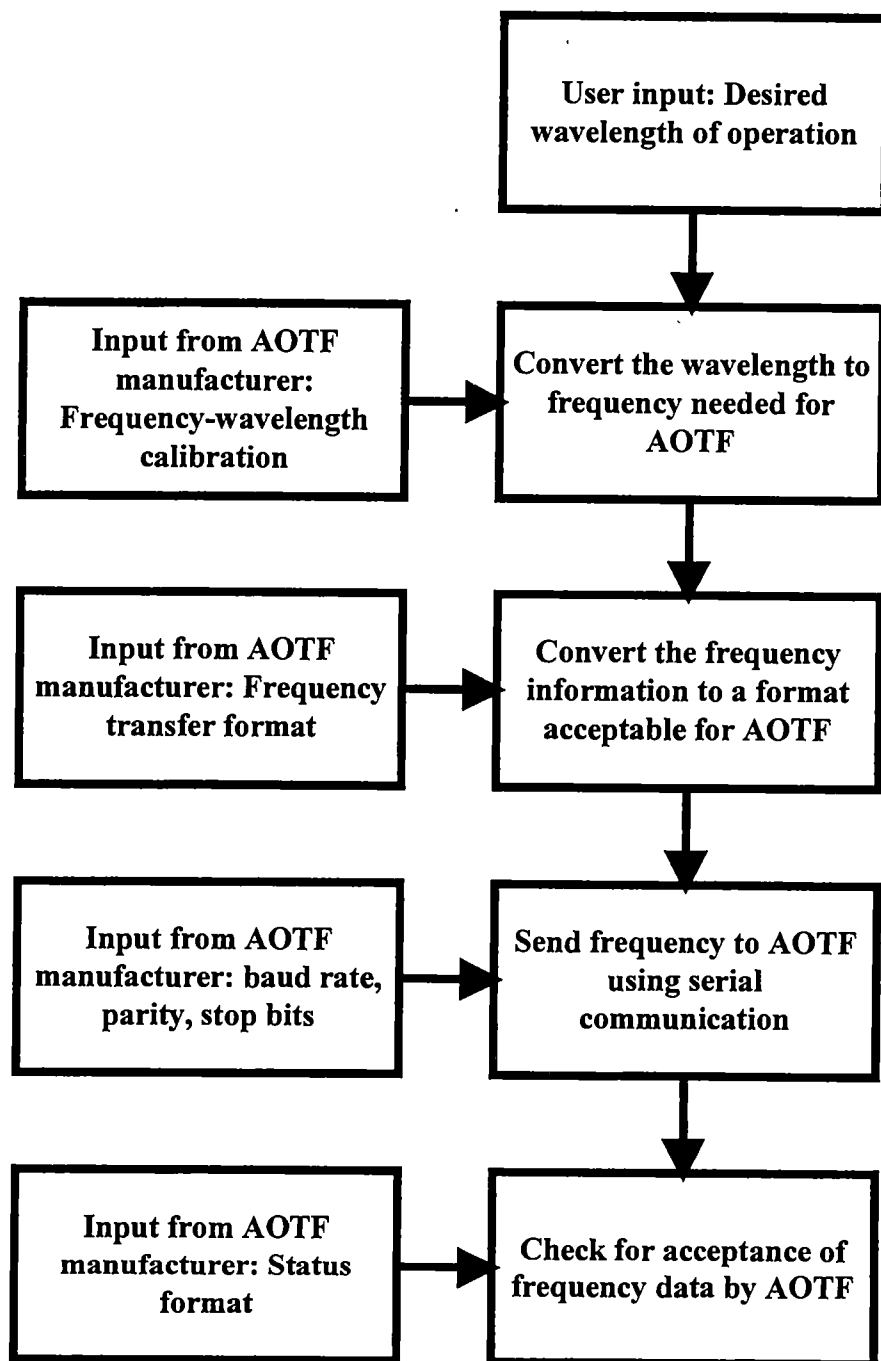


Figure 4.4 AOTF Control

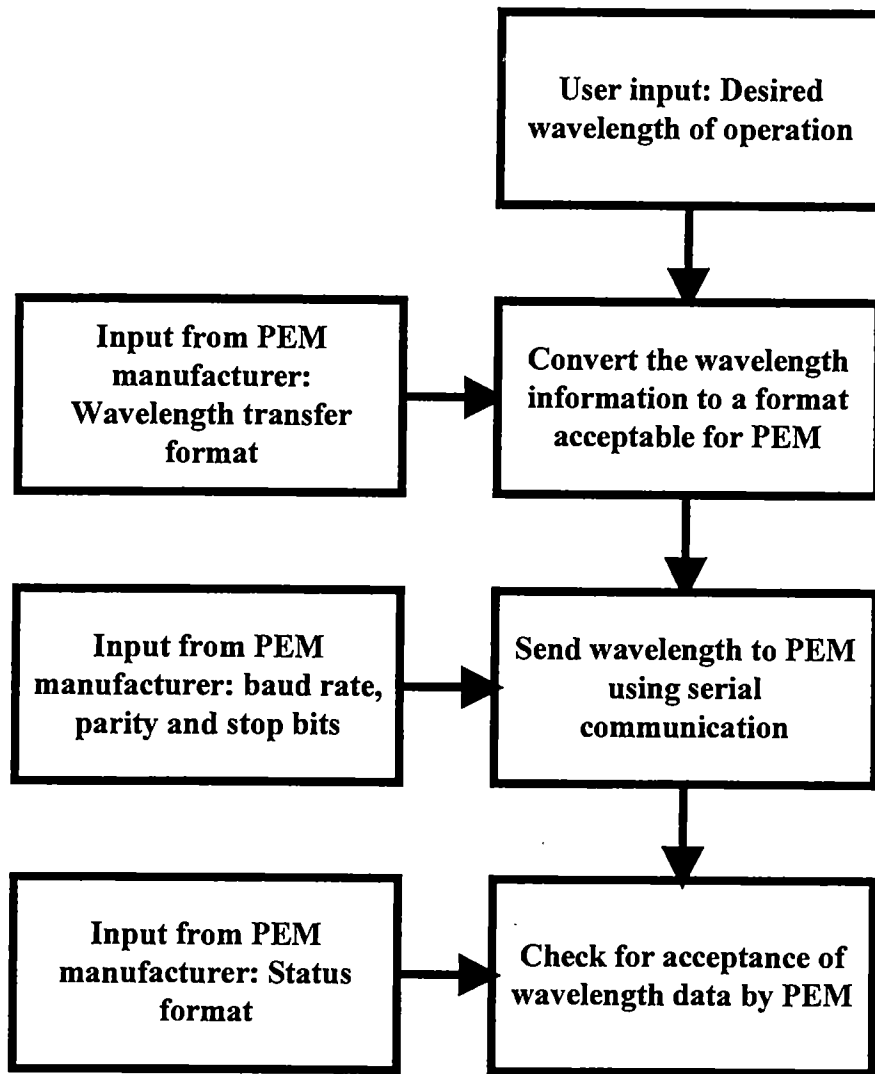


Figure 4.5 PEM Control

To maintain a constant maximum retardance produced in the PEM over different wavelengths, maximum linear birefringence of the crystal had to be varied such that the ratio $\Delta n'/\lambda$ in equation 4.1 was a constant. This was done internally by the PEM through wavelength information supplied through the computer. Maximum retardance of operation is fixed as explained in appendix B.

Figure 4.6 shows a block diagram for control of the spectropolarimeter. Here, the user defined the desired operating wavelength range and step size. This information was used to obtain a wavelength of operation. This wavelength was transferred to the AOTF as described in figure 4.4 and to the PEM as described in figure 4.5. Spectropolarimetry data was then collected. The instrument then moved to the next wavelength till data were collected at all wavelengths of interest.

Data were collected from the reference detector and two sample detectors. The reference detector produces a voltage signal that changes because of two factors: intensity changes with wavelength and lamp instability with time at the same wavelength. Since data analysis (explained in appendix B) was performed separately at each wavelength, we were more concerned with lamp instability over time at the same wavelength. These changes were at very low frequencies and could be measured as a direct current (DC) signal.

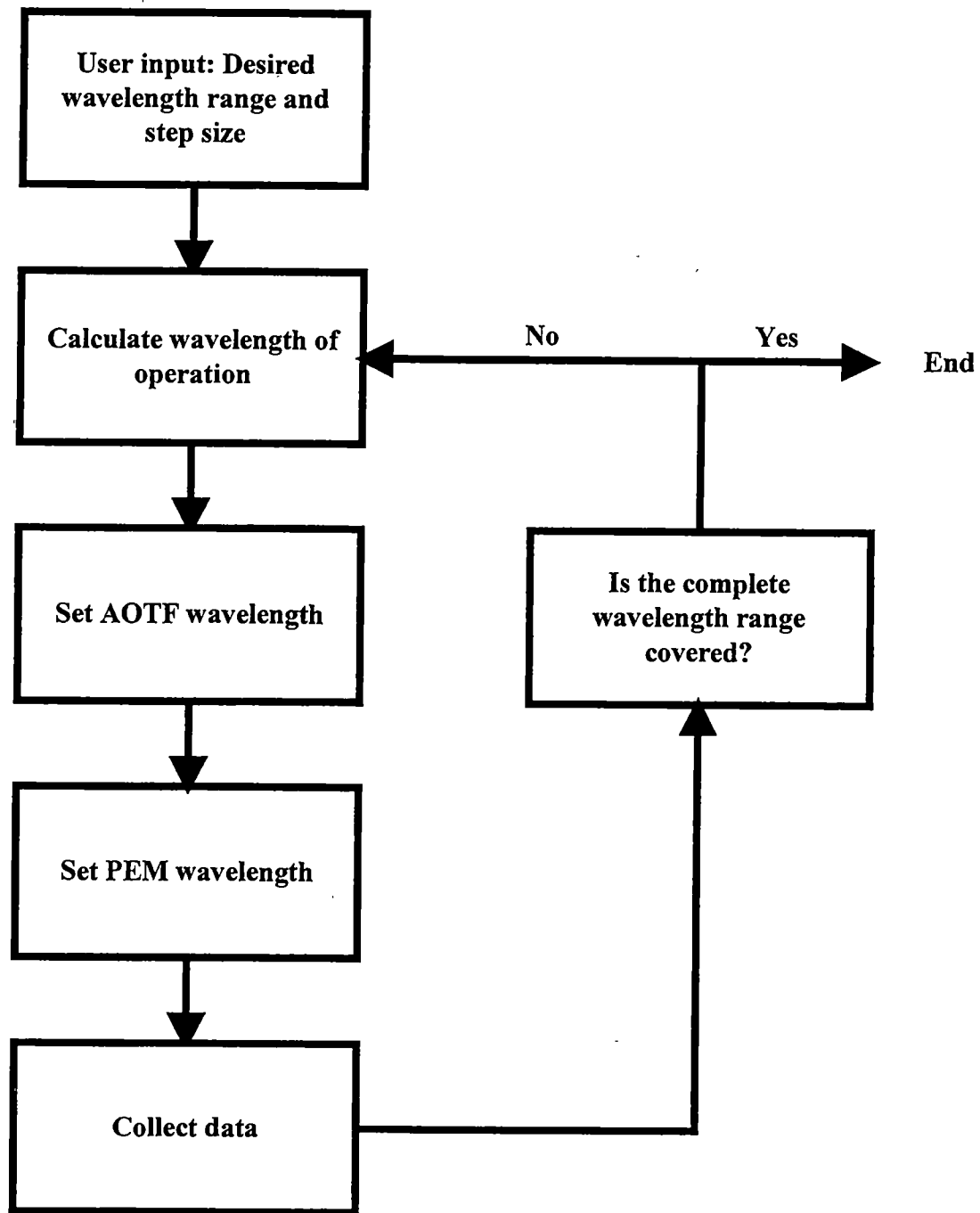


Figure 4.6 Spectropolarimeter Control

As explained in appendix B, signals at the sample detectors could be written in the form of a Fourier series shown in equation 4.2.

$$V_i(\lambda) = V_i^{DC}(\lambda) + V_i^{\omega}(\lambda)\sin \omega t + V_i^{2\omega}(\lambda)\sin 2\omega t + \dots \quad 4.2$$

In equation 4.1, i represents the sample detector with values 1 and 2, ω is the modulation frequency of the PEM (42 kHz) and λ is the wavelength of operation (1100-2200 nm). As explained in appendix B, we are interested in recording the first three coefficients of the Fourier series ($V_i^{DC}(\lambda)$, $V_i^{\omega}(\lambda)$, and $V_i^{2\omega}(\lambda)$) for both sample detectors.

A dynamic signal acquisition card, model PCI-4552 was obtained from National Instruments [48]. The card had four input channels and could accept sampling rates from 5 to 204.8×10^3 samples/s. The card was used for simultaneously obtaining the DC components from the reference detector and two sample detectors ($V_i^{DC}(\lambda)$). It was also used, though infrequently due to difficulties in computer programming, for obtaining the next two Fourier coefficients ($V_i^{\omega}(\lambda)$ and $V_i^{2\omega}(\lambda)$) in the sample detector signal. The ω and 2ω Fourier coefficients were usually obtained using analog lock-in amplifiers. Lock-in amplifiers use a technique known as phase-sensitive detection to single out the component of the signal at a specific frequency and phase. Noise signals at frequencies other than the reference frequency are rejected and do not affect the measurement. The PEM supplied the reference frequency. Reference frequencies supplied by the PEM were: ω and 2ω where ω is the

modulation frequency (~ 42 kHz). Thus both the ω and 2ω Fourier components in the sample detector signal were measured using the lock-in amplifier. Two model SR510 lock-in amplifiers from Stanford Research Systems, Inc. [49] were used in this work. The lock-in amplifiers were controlled through general-purpose interface bus (GPIB) commands from the personal computer. A GPIB card was obtained from National Instruments [48] for this purpose. Figure 4.7 shows a block diagram explaining the use of lock-in amplifiers for obtaining the ω and 2ω Fourier coefficients. As seen in figure 4.7, the same lock-in amplifier was used to obtain sequentially the ω and 2ω Fourier coefficients. Before the lock-in amplifiers could be used to obtain the Fourier coefficients phase angle information for each Fourier coefficient had to be obtained.

Figure 4.8 shows a block diagram illustrating the recording of required data when the lock-in amplifiers are used. The voltage signal from each of the sample detectors was split in two parts. The first part was fed to the dynamic signal analyzer card and the DC Fourier coefficient was measured. The second part was fed to the lock-in amplifiers to measure the ω and 2ω Fourier coefficients as explained in figure 4.7. Simultaneously, voltage signal from the reference detector was measured at the dynamic signal analyzer card, if needed.

4.4 Mechanical details

All the components in the spectropolarimeter had to be mechanically incorporated in a single working unit. Light emerging from the AOTF had to pass

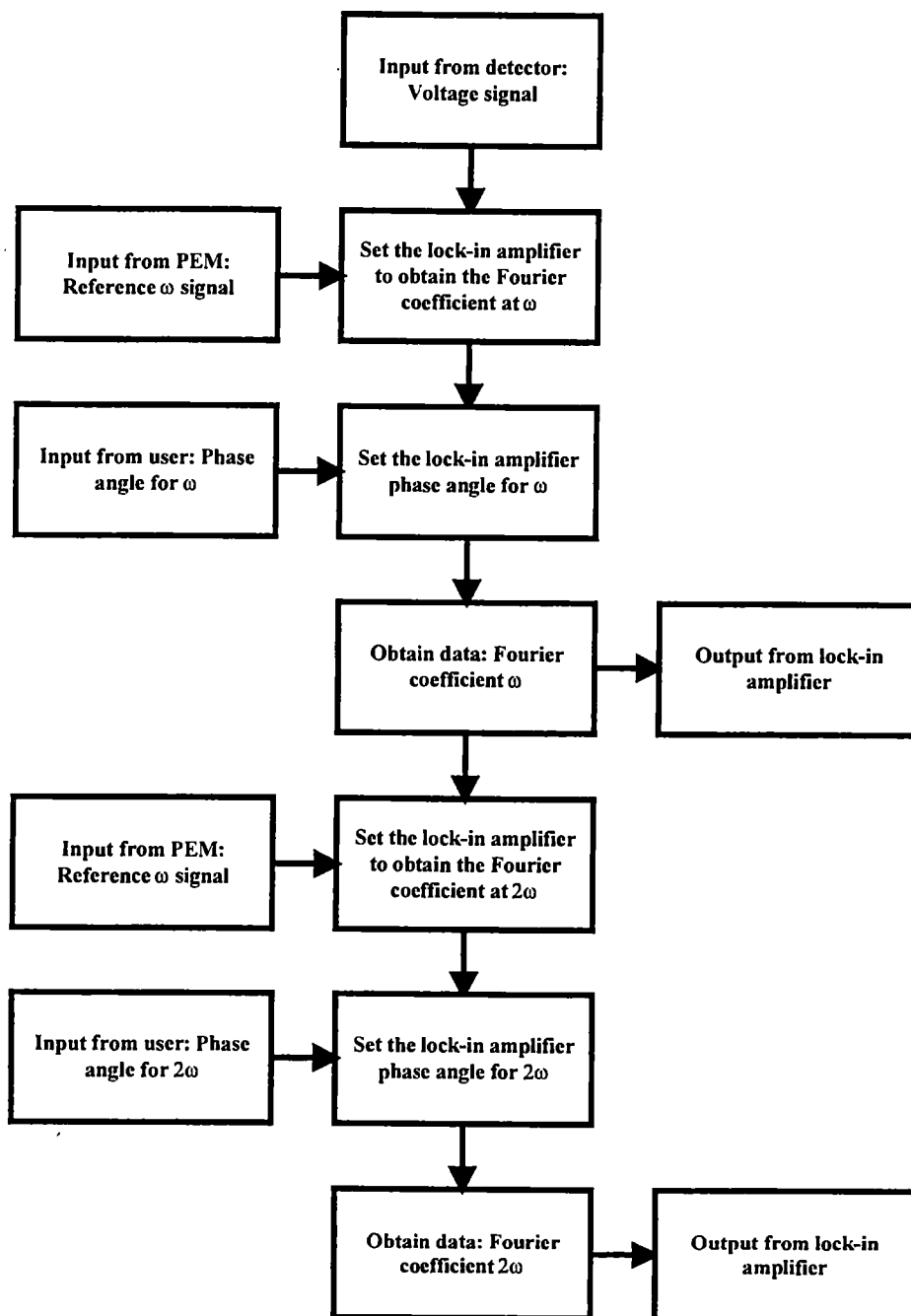


Figure 4.7 Data collection in a lock-in amplifier

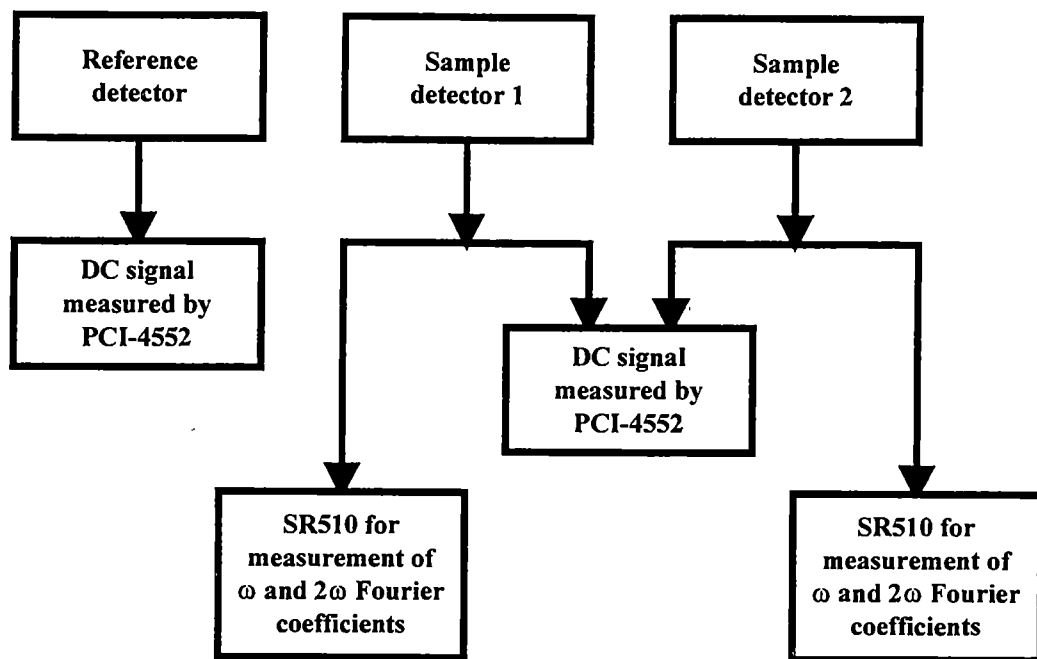


Figure 4.8 Block diagram illustrating the recording of data

through all the components shown in figure 4.1 with minimum losses. The details of the angles at which the various optical components had to be used are derived in appendix B. All the components were mounted on an optical bench obtained from Newport Corporation [50]. The optical bench had a 25-mm×25-mm square pattern for bolts. The AOTF monochromator is mounted directly on the optical bench. Light emerging from the AOTF was parallel to the optical bench at a height defined by the AOTF mounting. All other components had to be mounted at this height. The light emerging from the AOTF is linearly polarized in an orientation perpendicular to the optical bench.

The polarizing beam-splitter had to be used in two orientations: with faces at 0° and 90° and at 45° and 135° with respect to the linear polarizer respectively. The two orientations were used during calibration and actual use of the instrument. This is explained in greater detail in appendix B. Use of the polarizing beam-splitter in two orientations meant that the polarizing beam-splitter had to be rotated at some point. There were two beams emerging from the polarizing beam-splitter at an angle of 45° with respect to each other. Rotation of the polarizing beam-splitter will not change the direction of the emerging straight through beam. However, the direction of the totally reflected ordinary beam would change. This means that the sample detector corresponding to the ordinary beam had to be rotated with the polarizing beam-splitter. The polarizing beam-splitter was mounted with the two detectors on a plate as shown in figure 4.9. It was difficult to mechanically rotate the entire plate. Hence, bolt-holes

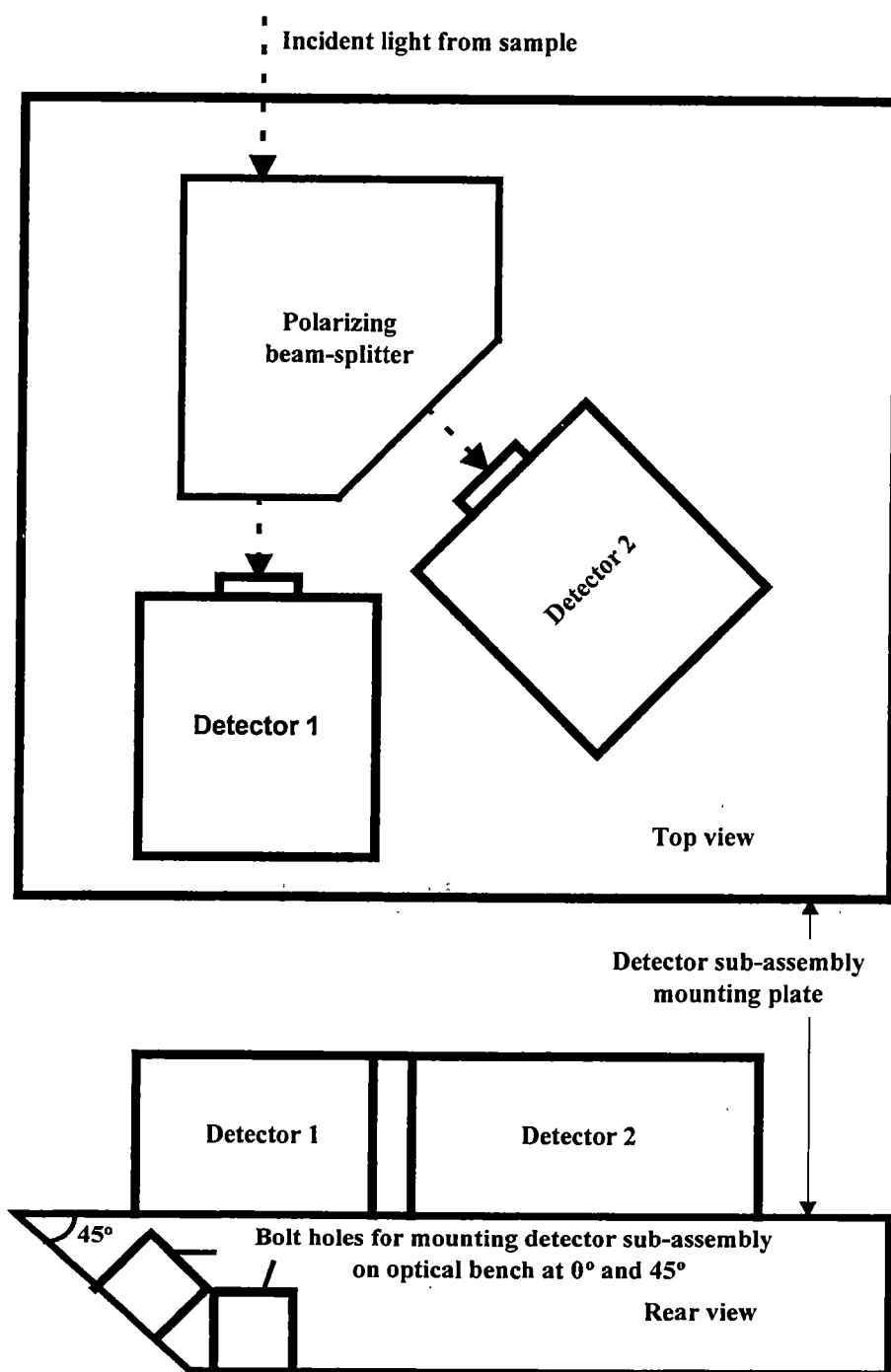


Figure 4.9 Mounting plate for polarizing beam-splitter and sample detectors

in two orientations at an angle of 45° to each other were built in the plate. The polarizing beam-splitter could thus be mounted in two orientations on the optical bench. It was first mounted so that the plate was parallel to the optical bench. The linear polarizer was mounted on a rotary mount. The linear polarizer was rotated such that the two faces of the polarizing beam-splitter are at 0° and 90° respectively with respect to the linear polarizer. If the other set of bolt-holes are used to mount the plate the polarizing beam-splitter oriented such that the two faces were at 45° and 135° to the linear polarizer. A mount was built for the PEM such that it would be at 45° to the horizontal.

4.5 Film stretcher

A uniaxial film stretcher was used in this work. Wong [51] has explained details of the film stretcher. The film stretcher consisted of two step motor driven linear actuators drawing in opposite directions. The horizontal actuators were mounted on columns that move the actuators motors vertically. This allowed the user to position the film sample in the beam of light for measurements. Flat film self-adjusting clamps were attached to the linear actuators to hold the film sample. Wong [51] has explained the design of the clamps. The clamps were adjusted to that the film would be perpendicular to the direction of propagating light. The actuators were capable of applying a maximum of 89 N of trust while achieving maximum speeds of 12.7 cm/s. Each actuator was positioned by steps of 6.35×10^{-6} m. A load cell was attached to one of the actuators to measure the load on the film sample. The load cell

was calibrated using known weights to directly convert the voltage signal to force. Figure 4.10 shows the calibration of the load cell. The solid line on figure 4.10 is the least squares fit used to obtain force from the voltage signal.

The film stretcher was controlled using programs written on the platform LabVIEW. The actuators were controlled via serial port communications from the personal computer. Wang [51] has explained the methodology for serial port communication and film stretcher control. The load cell produced a voltage signal that was measured by the PCI-4552 board.

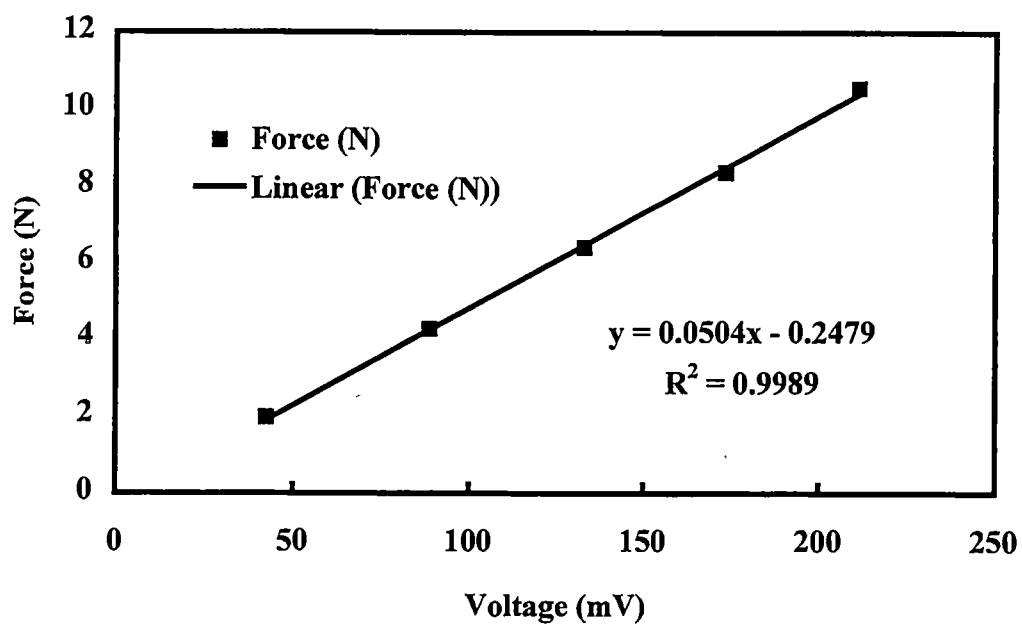


Figure 4.10 Calibration of the load cell

CHAPTER 5

EXPERIMENTS ON OPTICAL COMPENSATOR

5.1 Introduction

A Soleil-Babinet optical compensator generates a known retardance and orientation angle. Azzam [40] has explained the operating principle of a Soleil-Babinet compensator. As seen in figure 5.1, the compensator consists of two sections of quartz: a variable-thickness section and a fixed-thickness section. The variable-thickness section uses two wedges with parallel optic axes. The wedges move with respect to one another to vary the thickness of this section. The fixed-thickness section is made of a single plate of quartz. The two sections are cemented together with their optic axes orthogonal to one another. When the thickness of both sections are equal, the net retardation is zero. When the thickness difference is d , the retardation as explained in equation 3.23 is $(2\pi d / \lambda)\Delta n'$, where $\Delta n'$ is the linear birefringence of quartz and λ is the wavelength of operation.

A model 34-5918 Soleil-Babinet optical compensator from Ealing electro-optics, Inc [52] was used in this work. The optical wavelength operating range of this device was between 200nm and 2700 nm. The useful aperture was 10 mm and the thickness difference d remains constant through the entire aperture. The thickness was changed using a micrometer screw. A scale attached to the micrometer screw is

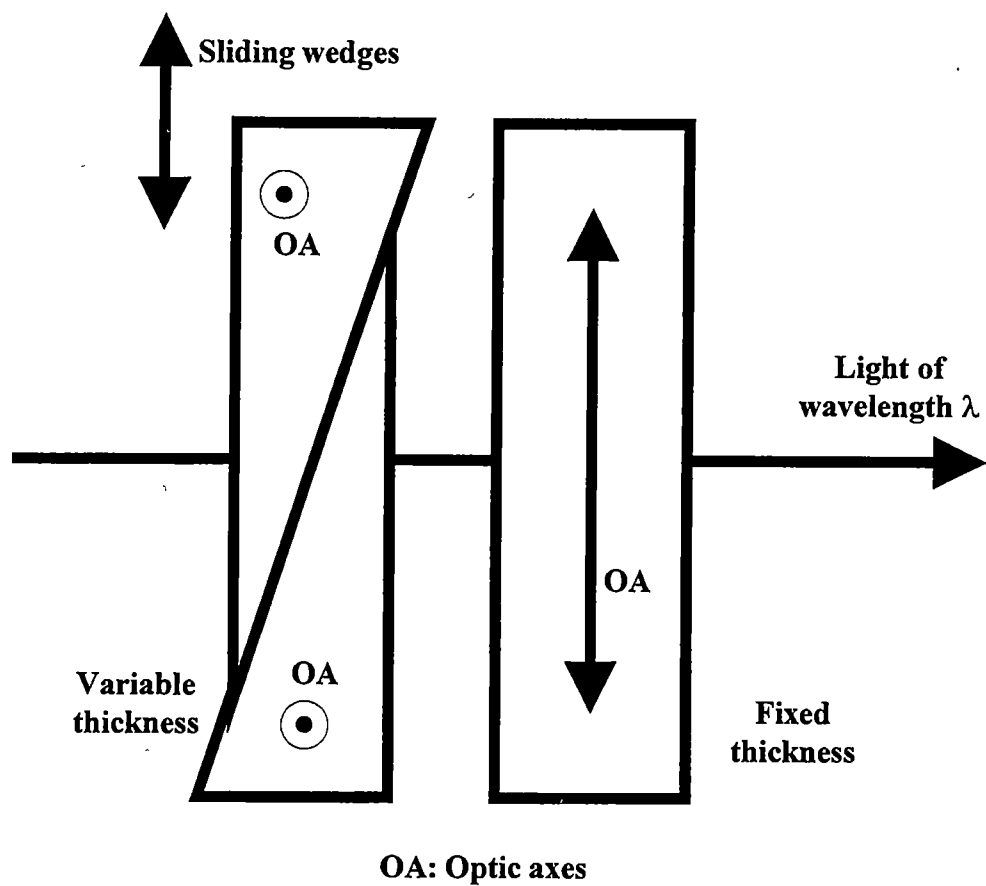


Figure 5.1 Schematic of a Soleil-Babinet compensator
Source: Azzam [40]

directly proportional to the thickness difference. The compensator was mounted on a precision ball-bearing indexing head with an accuracy of 1° of angular rotation.

The Soleil-Babinet compensator was used to test the spectropolarimeter. It acts as a purely linear birefringent optical sample. The theoretical response from the spectropolarimeter for a purely linear birefringent sample derived in appendix B (equation B.17) and reproduced here as equation 5.1.

$$\begin{aligned} V_1^{DC} &= \frac{c_1 I_0(\lambda)}{2} \\ V_1^\omega &= c_1 I_0(\lambda) J_1(\delta_0) \sin \mu \cos 2\chi \\ V_1^{2\omega} &= c_1 I_0(\lambda) J_2(\delta_0) (1 - \cos \mu) \sin 2\chi \cos 2\chi \end{aligned} \quad 5.1$$

Equation 5.1 is written for the spectropolarimeter condition in which maximum retardance of the photo-elastic modulator (PEM) was adjusted such that $J_0(\delta_0) = 0$. This was achieved by setting $\delta_0 = 2.405$ radians in the PEM. For such a spectropolarimeter setting measured values of the Fourier coefficients will vary with variation in retardance or orientation angle of the sample. Comparison of experimental response with the theoretical response in equation 5.1 was used to test the spectropolarimeter.

5.2 Experiments at a single wavelength

The compensator was introduced in the spectropolarimeter as the optical sample. It was oriented such that its orientation angle, χ , was 0° . At this orientation angle equation 5.1 reduces to equation 5.2.

$$\begin{aligned} V_1^{DC} &= \frac{c_1 I_0(\lambda)}{2} \\ V_1^\omega &= c_1 I_0(\lambda) J_1(\delta_0) \sin \mu \\ V_1^{2\omega} &= 0 \end{aligned} \tag{5.2}$$

From equation 5.2 it is clear that the direct current (DC) Fourier coefficient of the signal should be a constant, related to the lamp intensity at the wavelength of operation. The ω component should be a sine function, and the 2ω component should be zero. The compensator micrometer screw was rotated from 0 mm to 24 mm (the operating range of the compensator) and data were collected. Figure 5.2 shows the raw data collected from detector 1 at 1100 nm. We observe that the Fourier coefficients behave as expected, following trends given in equation 5.2. The variation in V_1^{DC} is due to changes in lamp intensity with time and alignment errors. The nominally non-zero values in $V_1^{2\omega}$ were due to alignment errors.

From equation 5.2 it is clear that the value of V_1^ω is zero at integer multiples (0, 1, 2, and so on) of π retardance. The compensator retardance attains a value 0° at the compensator screw setting of 3.5 mm and a value 180° at 21 mm. Retardance of the compensator is linearly related to the micrometer screw setting. Thus, knowing the

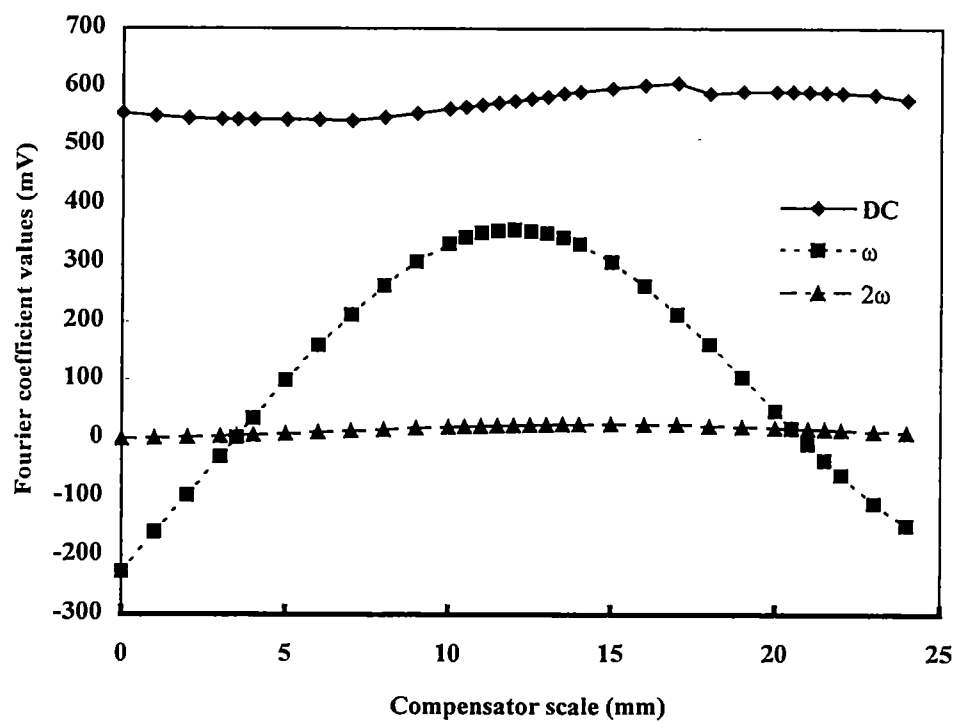


Figure 5.2 Raw data for compensator with $\chi = 0^\circ$

two retardance values and their respective screw settings we can obtain retardance at any screw setting. For example a retardance of 90° corresponds to a screw setting of 12.25 mm. Further results show linear retardance values obtained in this manner and not the micrometer screw setting.

Using equation 5.2 we can define the two ratios given in equation 5.3.

$$\begin{aligned} r_1 &= \frac{V_1^\omega}{2V_1^{DC}} = J_1(\delta_0) \sin \mu \\ r_2 &= \frac{V_1^{2\omega}}{2V_1^{DC}} = 0 \end{aligned} \tag{5.3}$$

Figure 5.3 shows the experimental values for the two ratios defined in equation 5.3. The two ratios are seen to behave as predicted by equation 5.3. The quantity $\sin(\mu)$ varies between +1 and -1. The maximum value of r_1 is thus $J_1(\delta_0)$. From figure 5.3 it is clear that $J_1(\delta_0) = 0.311$. As derived in appendix B, the theoretical value of $J_1(\delta_0)$ is 0.519 at $\delta_0 = 2.405$ radians. The difference in the experimental and actual values was attributed to alignment and beam collimating problems in the system. It was due to these difficulties that the spectropolarimeter was not calibrated as suggested in appendix B. Instead the experimentally obtained value $J_1(\delta_0) = 0.311$ was used.

The compensator retardance was set at 90° . At this value of retardance equation 5.1 reduces to equation 5.4.

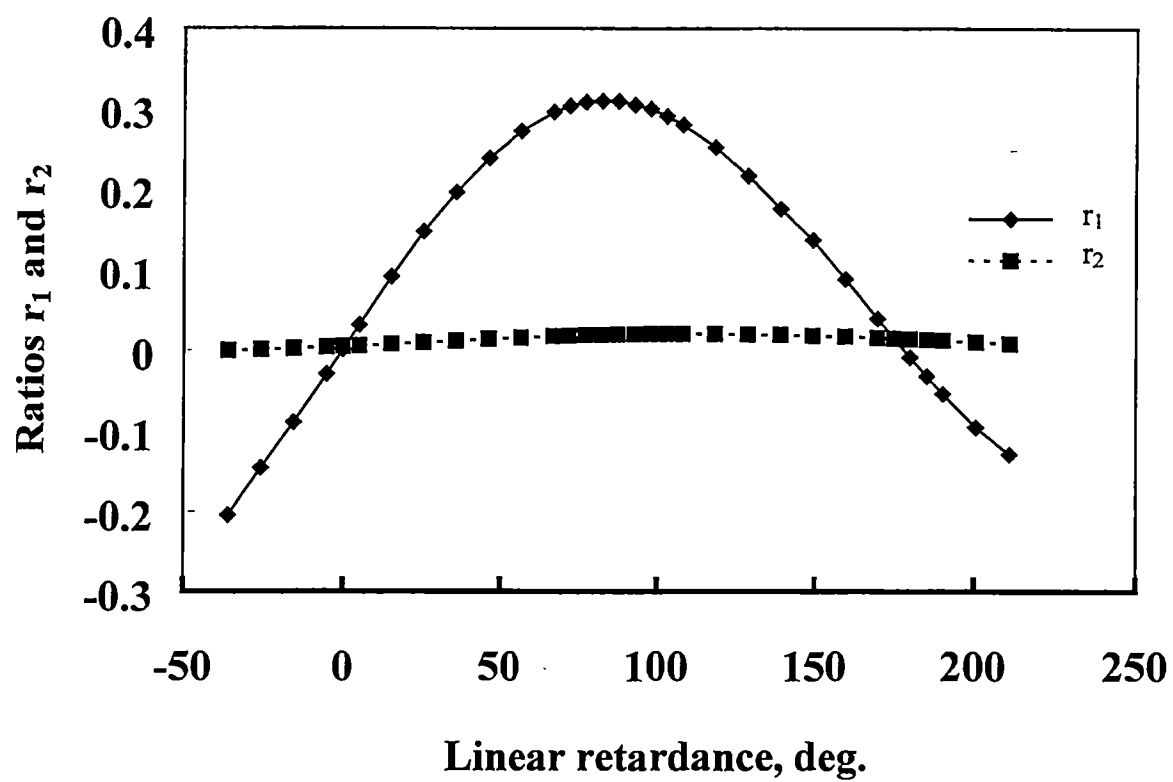


Figure 5.3 Ratios r_1 and r_2 for compensator with $\chi = 0^\circ$

$$\begin{aligned}
V_1^{DC} &= \frac{c_1 I_0(\lambda)}{2} \\
V_1^\omega &= c_1 I_0(\lambda) J_1(\delta_0) \cos 2\chi \\
V_1^{2\omega} &= c_1 I_0(\lambda) J_2(\delta_0) \sin 2\chi \cos 2\chi
\end{aligned} \tag{5.4}$$

The compensator was rotated at this value of retardance. Figure 5.4 shows the raw data collected from detector 1 at 1100 nm with rotation of the compensator. The Fourier coefficients in figure 5.4 are observed to follow the theoretical predictions in equation 5.4. The variation in the DC component can be attributed to lamp intensity changes with time and alignment changes as the compensator is rotated. Similar to equation 5.3 we can define two ratios from equation 5.4.

$$\begin{aligned}
r_1 &= \frac{V_1^\omega}{2V_1^{DC}} = J_1(\delta_0) \cos 2\chi \\
r_2 &= \frac{V_1^{2\omega}}{2V_1^{DC}} = J_2(\delta_0) \sin 2\chi \cos 2\chi
\end{aligned} \tag{5.5}$$

The theoretical value of r_2 at $\chi = 22.5^\circ$ is $0.5J_2(\delta_0)$. Ideally, this value should be $0.5 \times 0.4318 = 0.2159$. In the present setup we get an experimental value of 0.104. This gives us an experimental value $J_2(\delta_0) = 0.208$. This value is used in further work. Using equation 5.4 we can also define the two ratios given in equation 5.6.

$$\begin{aligned}
R_1 &= \frac{V_1^\omega}{2V_1^{DC} J_1(\delta_0)} = \cos 2\chi \\
R_2 &= \frac{V_1^{2\omega}}{2V_1^{DC} J_2(\delta_0)} = \sin 2\chi \cos 2\chi
\end{aligned} \tag{5.6}$$

Figure 5.5 shows the theoretical and experimental values of the two ratios defined in equation 5.6. The experimentally obtained values $J_1(\delta_0) = 0.311$ and $J_2(\delta_0) = 0.208$

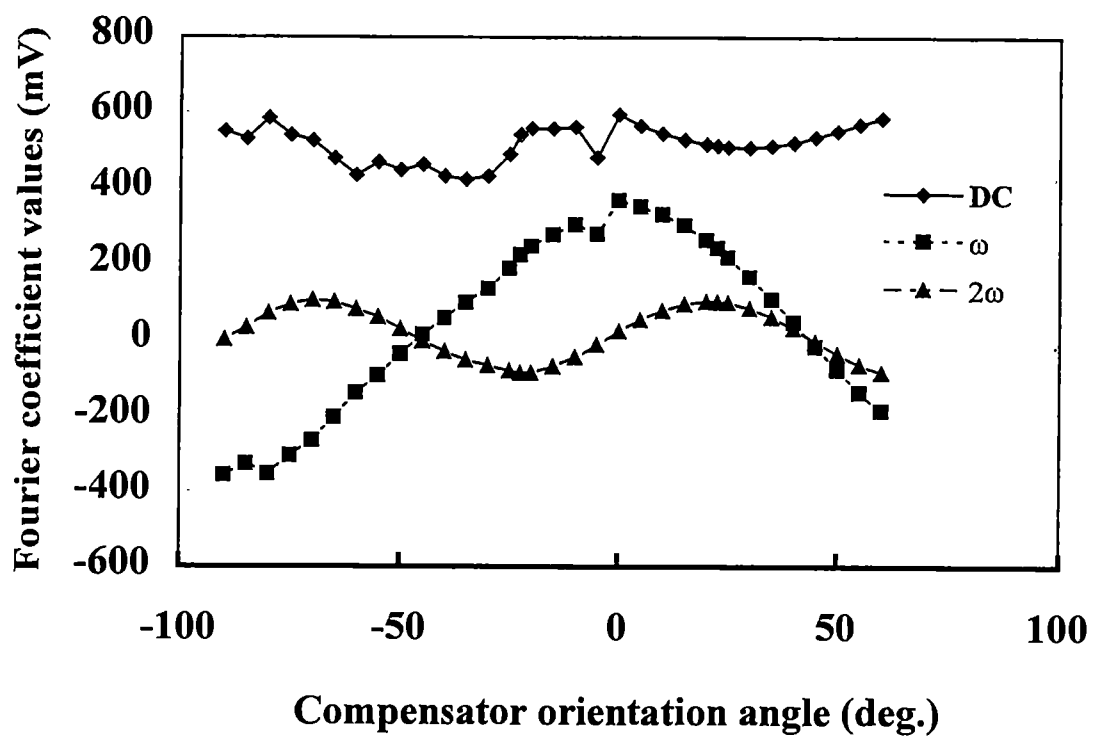


Figure 5.4 Raw data for compensator with $\mu = 90^\circ$

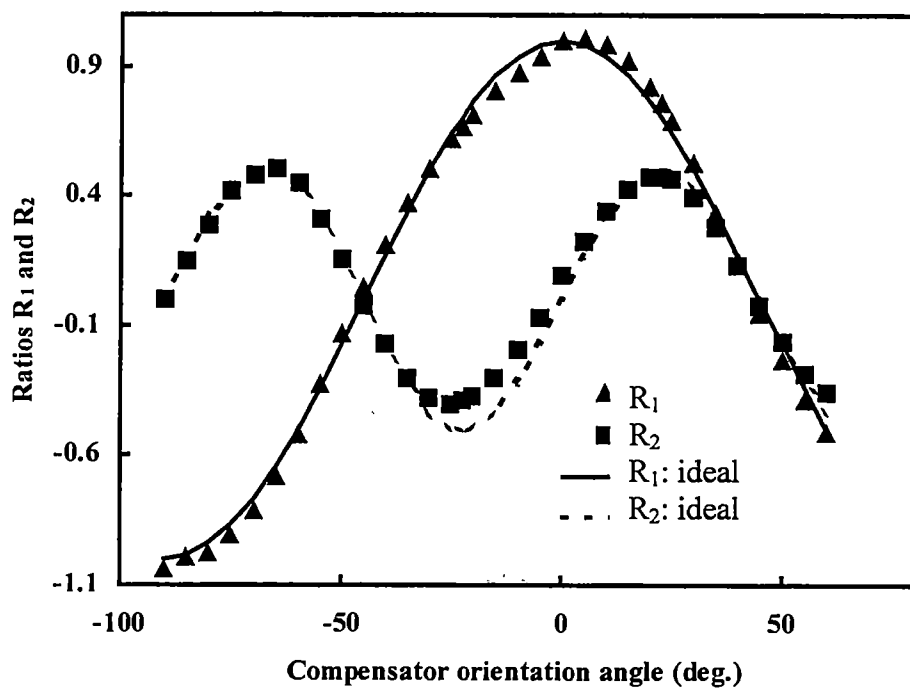


Figure 5.5 The ratios R_1 and R_2 for compensator with $\mu = 90^\circ$

were used to obtain figure 5.5. A close agreement is observed between the theoretical and experimental values.

We can draw several conclusions from work on the compensator at a single wavelength (1100 nm). The experimental response agrees with theoretical predictions. This is true for both changes in retardance at the same orientation angle and changes in orientation at the same value of retardance. The spectropolarimeter is sensitive to alignment errors. This is reflected in calibration constant values. There is a large difference in the experimental values of $J_1(\delta_0)$ and $J_2(\delta_0)$ and their theoretical values. The experimental values of $J_1(\delta_0)$ and $J_2(\delta_0)$ are 0.311 and 0.208 respectively. Their theoretical values (as derived in appendix B) are 0.519 and 0.4318. Due to these large differences the experimentally obtained values were used in further work.

5.2 Experiments at multiple wavelengths

The spectropolarimeter was used to obtain unknown retardance and orientation angle values over multiple wavelengths. This was achieved by using the compensator as an unknown sample. Retardance and orientation angle values were set in the compensator. Then these values were obtained experimentally. The experimentally obtained values were compared with the set values as a check for the spectropolarimeter. Equation 5.7 is used to obtain linear retardance and orientation angle for unknown linearly birefringent samples.

$$\cos \mu = \frac{-R_2^2 \pm R_1^2 \sqrt{1 - R_1^2 - R_2^2}}{R_1^2 + R_2^2} \quad 5.7$$

$$\cos 2\chi = \frac{R_1}{\sin \mu}$$

The ratios R_1 and R_2 in equation 5.7 are given in equation 5.8.

$$R_1 = \frac{V_1^\omega}{2V_1^{DC} J_1(\delta_0)} \quad 5.8$$

$$R_2 = \frac{V_1^{2\omega}}{2V_1^{DC} J_2(\delta_0)}$$

Equations 5.7 and 5.8 are derived in appendix B (equations B.18, B.19 and B.20 respectively).

To obtain values of the two ratios we need experimentally obtained Fourier coefficients and the calibration constants. The calibration constants were obtained earlier at 1100 nm. As calibration constants were observed to change with wavelength they were obtained from 1100 nm to 2200 nm using a step size of 100 nm following a procedure similar to that used at 1100 nm. Figure 5.6 shows the variation of calibration constants with wavelength. The triangular symbols represent experimental values for $J_1(\delta_0)$ and the squares represent $J_2(\delta_0)$. The solid curves are least squares fit third order polynomials using the experimental data. They were used to obtain the values of calibration constants at any wavelength in the range 1100-2200 nm. The third order polynomials are given in equation 5.9.

$$J_1(\delta_0) = 3.33 \times 10^{-12} \lambda^3 - 2.87 \times 10^{-7} \lambda^2 + 7.97 \times 10^{-4} \lambda - 0.212 \quad 5.9$$

$$J_2(\delta_0) = 2.56 \times 10^{-10} \lambda^3 - 1.34 \times 10^{-6} \lambda^2 + 3.00 \times 10^{-3} \lambda - 1.059$$

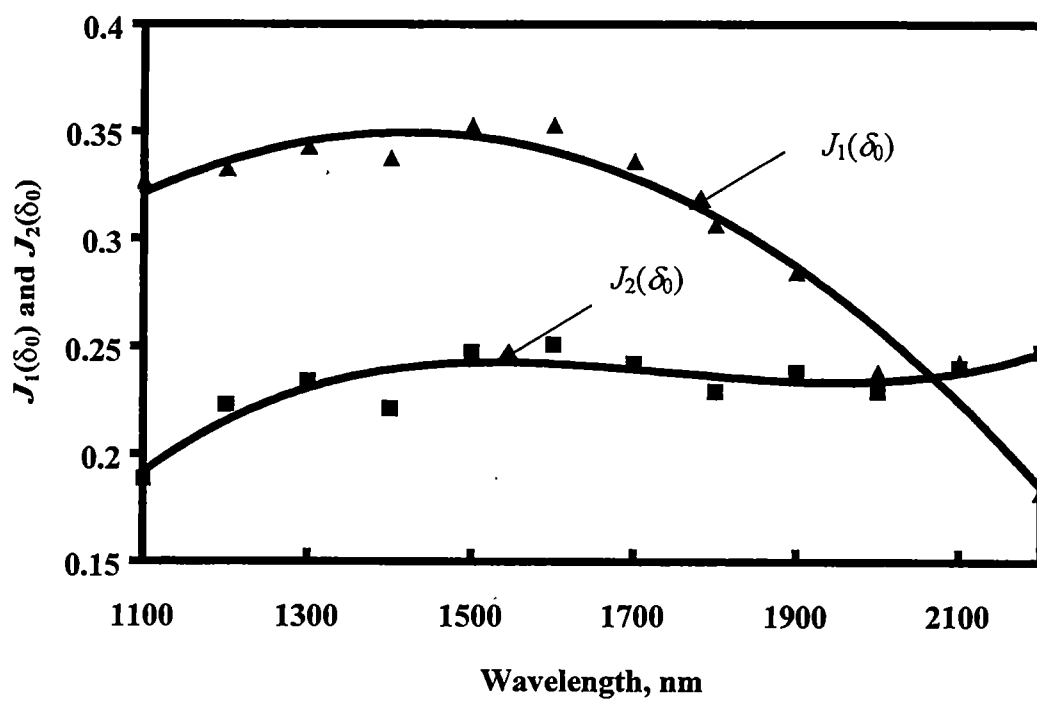
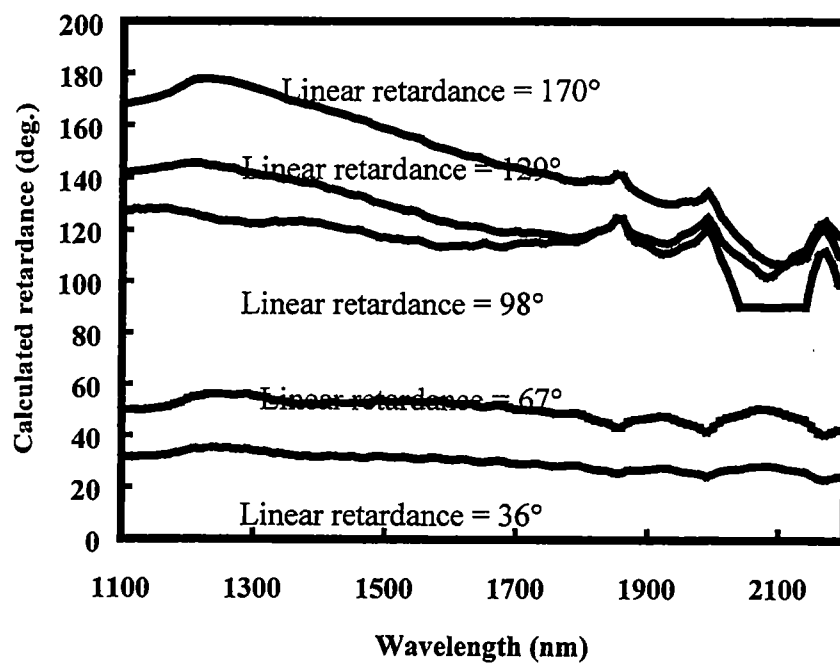


Figure 5.6 Calibration constants as a function of wavelength

In equation 5.9, λ is the wavelength of light in nanometers.

The spectropolarimeter was then used to obtain unknown values of retardance and orientation angle over multiple wavelengths. The compensator was first set such that its orientation angle $\chi = 0^\circ$. Various linear retardance values (using the micrometer screw settings) were selected. At each value, data were collected in the wavelength range 1100-2200 nm with a step size of 10 nm. Calibration constants were obtained at each wavelength using equation 5.9. Retardance and orientation angles were calculated using equations 5.7 and 5.8. Figure 5.7 shows the experimental results for retardance and orientation angles. The numbers written on figure 5.7 are the linear retardance values at which the compensator was set. These values were obtained using the procedure outlined earlier and figure 5.3. A close agreement exists between the set values and the experimentally obtained values. The retardance is observed to increase with an increase in the micrometer screw setting. Retardance values at different micrometer screw settings are nominally parallel. This is expected, as the only change that is expected by changing the micrometer screw is the thickness of the quartz optical element in the compensator. The retardance values are seen to change with wavelength. This can be explained with the use of equation 3.23. Linear retardance is linearly related to linear birefringence and inversely related to wavelength. Also, linear birefringence is a function of wavelength. Together, we observe the experimental changes in linear retardance seen in figure 5.7. A small part of the retardance curve for linear retardance 98° (compensator screw setting 13.2 mm) near 2100 nm shows some

a)



b)

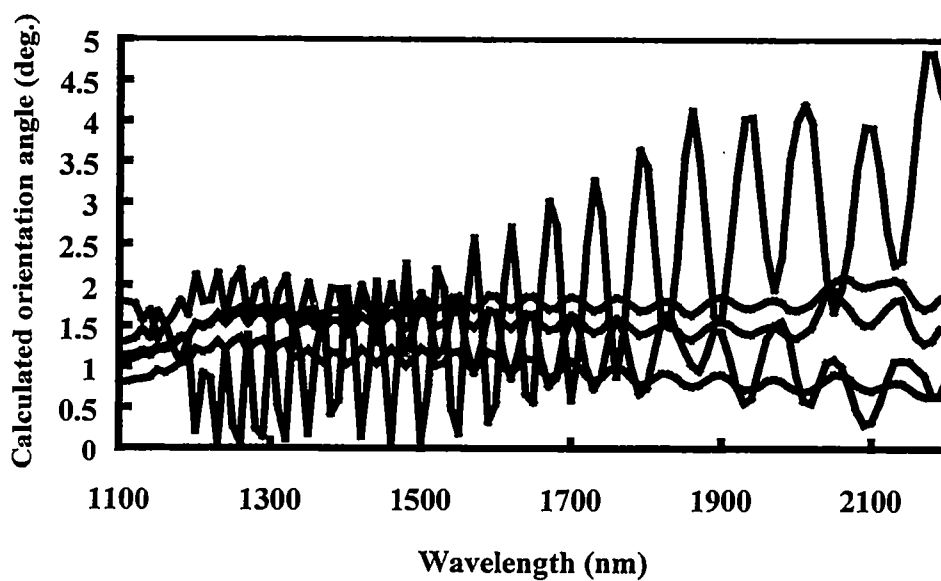


Figure 5.7 Retardance (a) and orientation angle (b) values for various compensator screw settings at $\chi = 0^\circ$.

discontinuity. This is because ratios R_1 and R_2 in equation 5.8 are greater than one for this region. The retardance values obtained in this region are complex numbers and figure 5.7 shows the real part of the curve.

The experimentally obtained orientation angles are also seen in figure 5.7. The orientation angles are all around zero degrees, however we observe oscillations in the experimental values. The period of oscillations increases with increasing wavelength. Chenault [53] attributes such oscillations to misalignment in the plates that make up the compensator (or other optical samples). Ideally, the orientation axes are exactly 90° apart, but some misalignment can exist in actual devices.

A problem occurs if both the retardance and orientation angles are equal to zero. Both ratios R_1 and R_2 in equation 5.8 are equal to zero and we cannot solve equation 5.9. Experimentally, the compensator was set to linear retardance value 0° (micrometer screw at 3.5 mm) and the orientation angle to 0° . Figure 5.8 shows the retardance and orientation angles obtained experimentally. We see that both the retardance and orientation angles are incorrect. The incorrectness of results increases as the actual retardance and orientation angle values approach zero.

The compensator was also used to obtain results for the same linear retardance and different orientation angles. A compensator setting of 10-mm nominally corresponding to a retardance of 60° at 1100 nm was selected. The compensator was

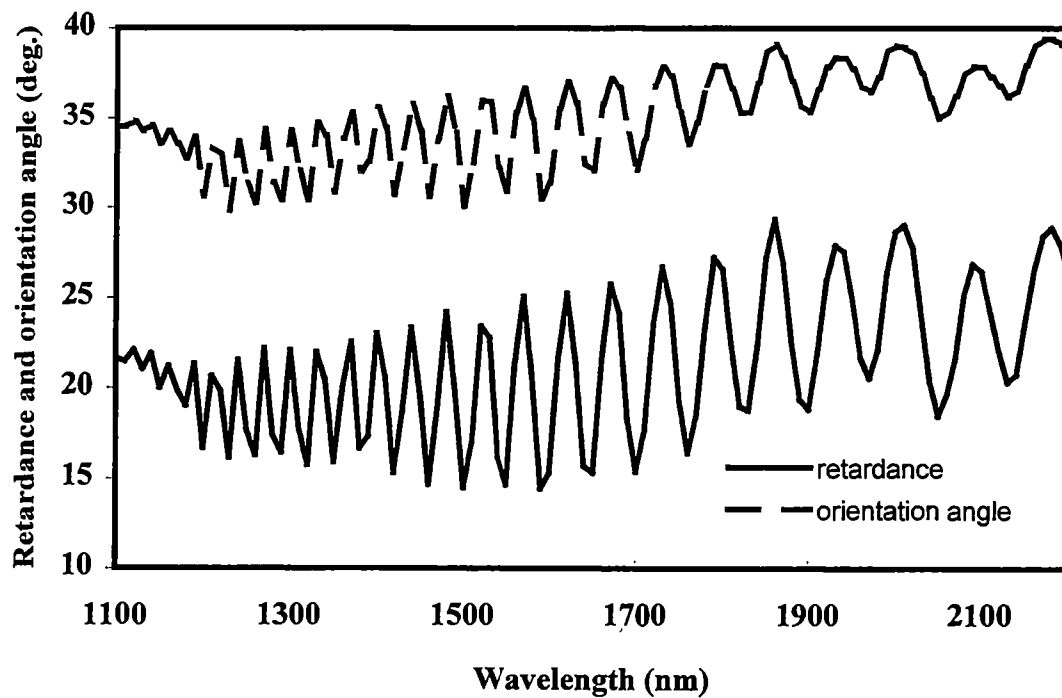
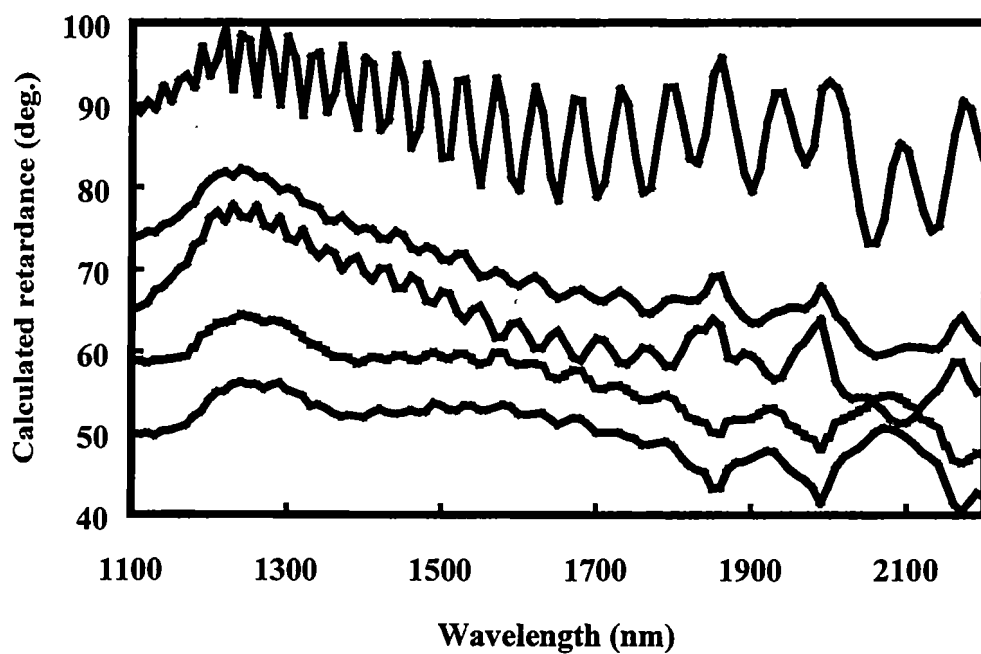


Figure 5.8 Retardance and orientation angle observed as a function of wavelength when the compensator is set at $\mu = \chi = 0^\circ$

set at five different orientation angles: 0° , 10° , 25° , 45° , and 60° . At each orientation angle, data were collected between 1100 nm and 2200 nm with a step size of 10 nm. Again, appropriate calibration constant values were obtained using equation 5.9. Figure 5.9 shows the results for this data set. Small random changes are observed in retardance values. The orientation angles obtained experimentally match the orientation angles set in the compensator (the orientation angles set in the compensator are written numerically in figure 5.9).

The spectropolarimeter can thus be used to obtain simultaneously linear retardance and its orientation angle values over multiple wavelengths. Calibration constants have to be determined at multiple wavelengths. The instrument was used in the wavelength range 1100 nm to 2200 nm.

a)



b)

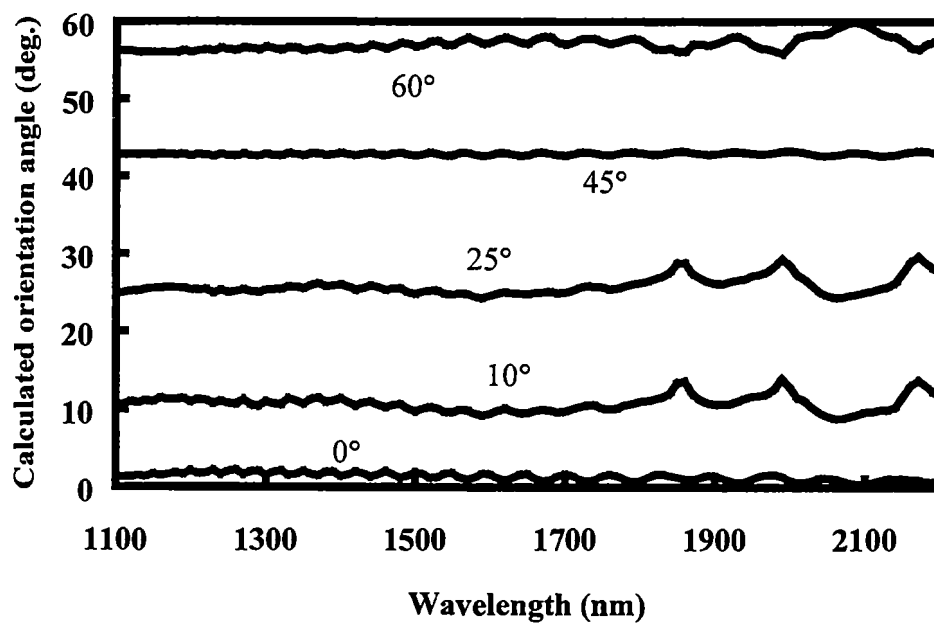


Figure 5.9 Retardance (a) and orientation angle (b) values for various orientation angles at compensator screw setting 10 mm.

CHAPTER 6

EXPERIMENTS ON POLYMER FILMS

6.1 Introduction

The spectropolarimeter was used as for in-line measurements on polymer films. Polymer films are usually uniaxially or biaxially oriented from cast films. Cast films have little or no orientation. The spectropolarimeter can be used to obtain absorbance spectra for isotropic optical samples. It was used to obtain isotropic absorbance spectra of cast polyethylene terephthalate films. As a film is oriented, linear birefringence and linear dichroism values increase. Two sets of experiments were conducted on oriented low-density polyethylene film samples. In the first set a series of film samples were studied to correlate spectropolarimetry data with the motor torque set value in the take-up roller used during film production. In the second set in-line spectropolarimetry and stress data were obtained during uniaxial film stretching operation.

6.2 Isotropic absorbance spectra of polyethylene terephthalate films

The spectropolarimeter was used to obtain isotropic absorbance in polyethylene terephthalate (PET) films. Two PET films with low orientation levels were obtained. The first film was cast out of a die onto a cold surface. The second was produced by length orienting the first film. It was stretched in the ratio 3.3 to 1.

Any film sample can have simultaneously one or more of the following optical anisotropies: isotropic absorbance (A_e), isotropic retardance, linear birefringence and linear dichroism. The theoretical Fourier coefficients obtained from the sample detectors in the spectropolarimeter for such a sample are given in equations 6.1 and 6.2.

$$\begin{aligned} V_1^{DC} &= \frac{c_1 I_0(\lambda)}{2} e^{-A_e} (\cosh \nu - \sinh \nu \sin 2\theta) \\ V_1^\omega &= c_1 I_0(\lambda) J_1(\delta_0) e^{-A_e} (\sin \mu \cos 2\theta) \\ V_1^{2\omega} &= c_1 I_0(\lambda) J_2(\delta_0) e^{-A_e} (-\sinh \nu \cos 2\theta + \sin 2\theta \cos 2\theta (\cosh \nu - \cos \mu)) \end{aligned} \quad 6.1$$

and

$$\begin{aligned} V_2^{DC} &= \frac{c_2 I_0(\lambda)}{2} e^{-A_e} (\cosh \nu + \sinh \nu \sin 2\theta) \\ V_2^\omega &= -c_2 I_0(\lambda) J_1(\delta_0) e^{-A_e} (\sin \mu \cos 2\theta) \\ V_2^{2\omega} &= -c_2 I_0(\lambda) J_2(\delta_0) e^{-A_e} (\sinh \nu \cos 2\theta + \sin 2\theta \cos 2\theta (\cosh \nu - \cos \mu)) \end{aligned} \quad 6.2$$

These equations were derived in appendix B (equations B.35 and B.36). For samples with low values of linear birefringence and linear dichroism the linear retardance and relative absorption coefficient values are zero. Substituting $\mu = 0$ and $\nu = 0$ in equations 6.1 and 6.2 we obtain the Fourier coefficients for isotropic samples. The Fourier coefficients obtained at sample detector 1 are given in equation 6.3 and that obtained at sample detector 2 are given in equation 6.4.

$$\begin{aligned} V_1^{DC} &= \frac{c_1 I_0(\lambda)}{2} e^{-A_e} \\ V_1^\omega &= 0 \\ V_1^{2\omega} &= 0 \end{aligned} \quad 6.3$$

$$\begin{aligned}
V_2^{DC} &= \frac{c_2 I_0(\lambda)}{2} e^{-A_e} \\
V_2^\omega &= 0 \\
V_2^{2\omega} &= 0
\end{aligned}
\tag{6.4}$$

To obtain isotropic absorbance from equations 6.3 and 6.4 we need to obtain a measure of lamp intensity $I_0(\lambda)$ and the electronic constants c_1 and c_2 . Voltage signals were obtained from both detectors in the absence of PEM and PET film samples. These signals derived in appendix B (equation B.29) are given in equation 6.5.

$$\begin{aligned}
V_1 &= \frac{c_1 I_0(\lambda)}{2} \\
V_2 &= \frac{c_2 I_0(\lambda)}{2}
\end{aligned}
\tag{6.5}$$

The experimental signals, shown in figure 6.1, were obtained between 1100 nm and 2200 nm with a step size of 10 nm.

We can use equations 6.3, 6.4 and 6.5 to obtain isotropic absorbance of optical samples as given in equation 6.6.

$$A_e = -\ln \left[\frac{1}{2} \left(\frac{V_1^{DC}}{V_1} + \frac{V_2^{DC}}{V_2} \right) \right]
\tag{6.6}$$

The PEM was then introduced in the optical setup at 45° and $\delta_0 = 2.405$ radians. At this value, data were obtained on PET films. Again data were collected between 1100 nm and 2200 nm with a step size of 10 nm. The first three Fourier coefficients from both detectors were collected and are presented in figure 6.2 for the cast PET film. It is clear from figure 6.2, that experimental values of Fourier coefficients of the PET cast

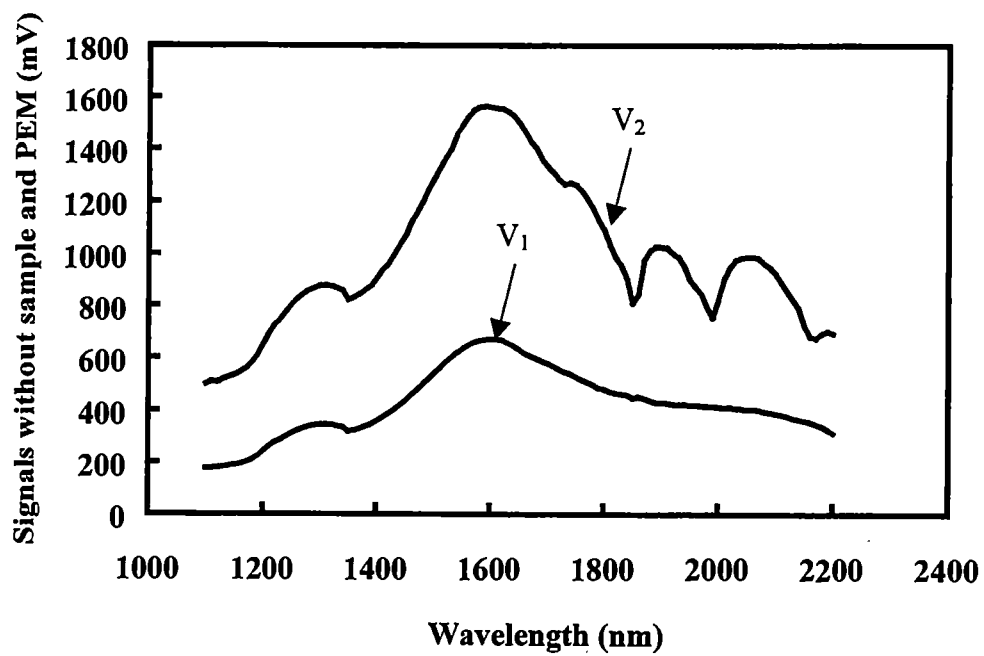
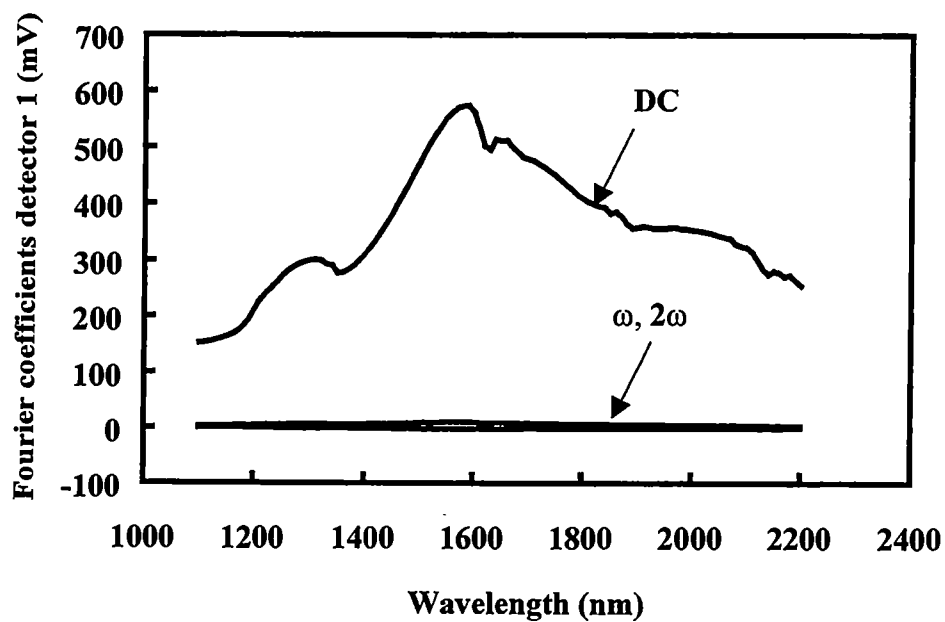


Figure 6.1 Voltage signals V_1 and V_2 from the spectropolarimeter in the absence of PEM and optical sample

a)



b)

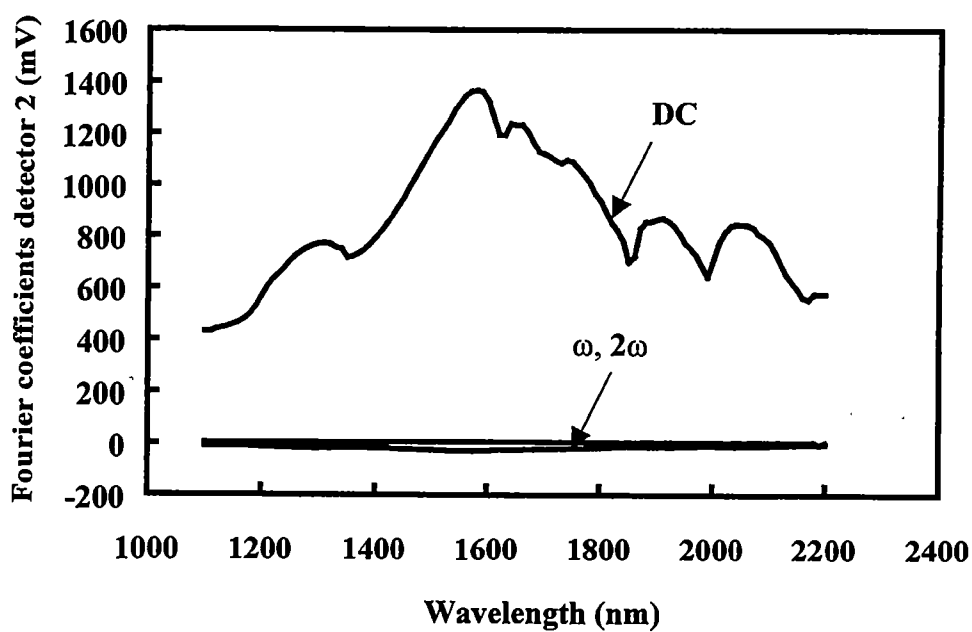


Figure 6.2 Fourier coefficients obtained from detector 1 (a) and detector 2 (b) for the cast PET film

film sample follow the mathematical forms of equations 6.3 and 6.4. Fourier coefficients for the second PET film sample are also similar.

Isotropic absorbance of the two PET film samples was obtained using equation 6.6. Figure 6.3 shows isotropic absorbance for the two samples as a function of wavelength.

6.3 Motor torque set values in low-density polyethylene films

A series of ten tube-blown low-density polyethylene (LDPE) film samples were used in this work. The films were of 1 mil thickness (2.54×10^{-5} m) and were produced at 165°C. Motor torque set value at the take-up roller was used as the primary variable in the samples. Figure 6.4 shows a schematic of the film blowing operation. Motor torque set value at the take-up roller defines the force with which the film is stretched. Changes in the motor torque set value lead to changes in the amount of orientation of polymer chains in the film.

Table 6.1 gives the conditions at which the tube-blown LDPE films were produced. The motor speed was unchanged through the production of the entire LDPE film sample set. The motor torque set value could be varied between 0 and 10 units. Various settings covering the entire range were used as the primary variable in the manufacture of these films. It was attempted to maintain a constant speed of the top

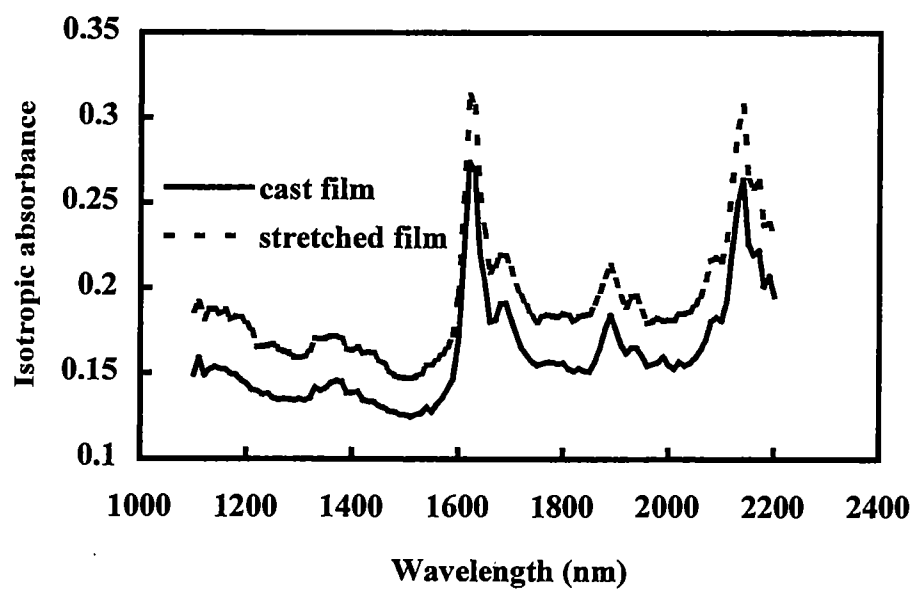
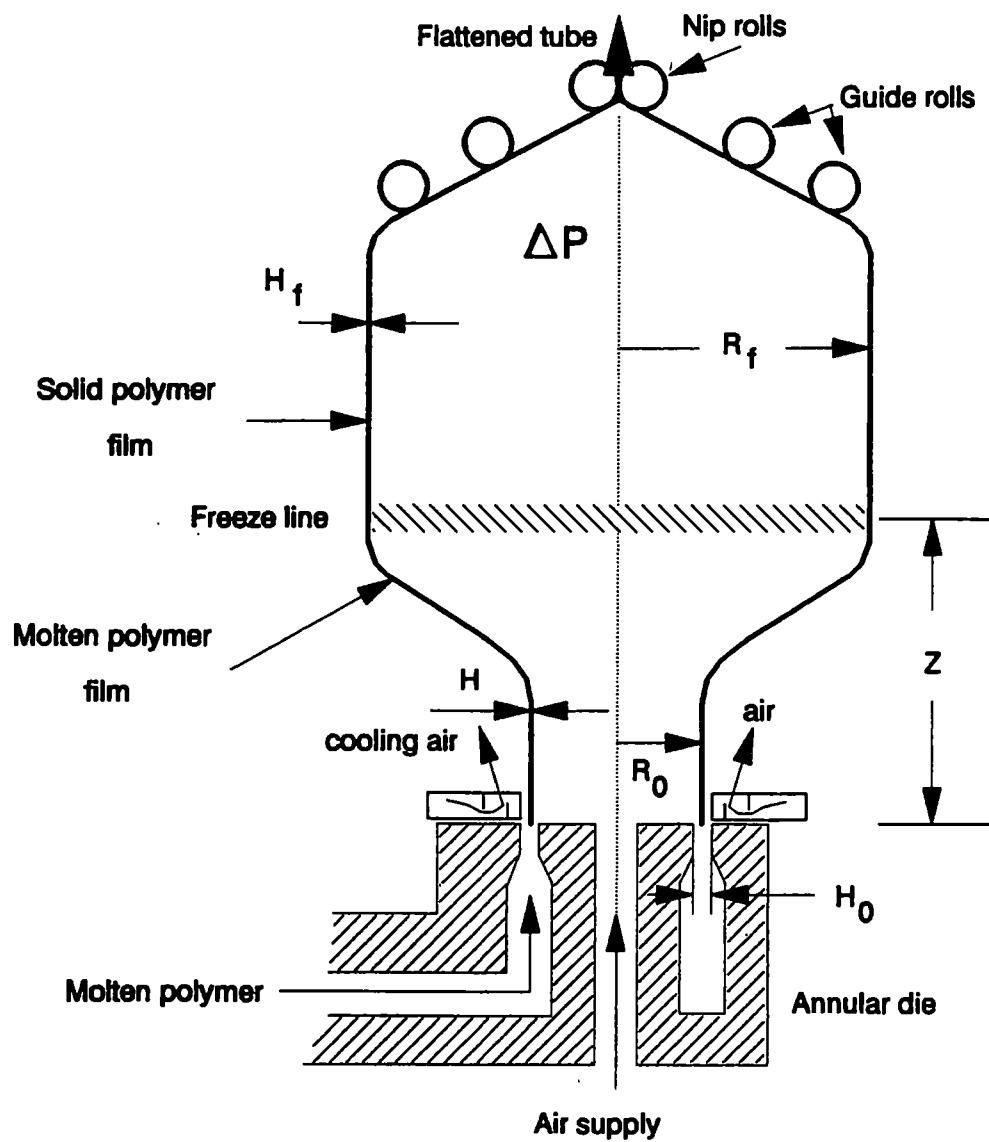


Figure 6.3 Isotropic absorbance spectra of PET film samples



H_0 : initial film thickness

H_f : final film thickness

Figure 6.4 Film-blowing operation. Source: Baird and Collias [54]

Table 6.1 Conditions for manufacture of tube-blown LDPE film samples.

Sample number	Motor speed	Top roller	Torque set
1	5.1	47	0.5
2	5.1	47	1
3	5.1	47	1.5
4	5.1	47	2
5	5.1	47	3
6	5.1	47	4
7	5.1	47	5
8	5.1	45	7
9	5.1	45	9
10	5.1	45	10 (max)

roller. However, the top roller speed was changed at the eighth film sample to maintain a constant film thickness (1 mil) between all samples.

Spectropolarimetry data were collected on all LDPE film samples. Data were collected between 1100 nm and 2200 nm with a step size of 10 nm. The first three Fourier coefficients (DC, ω , and 2ω) from both samples detectors were collected at each wavelength. Data were collected for all films in the same film orientation. The film samples had a primary direction of orientation - the uniaxial stretching direction. The films were oriented such that the film stretching direction was perpendicular to the orientation of the linear polarizer.

The Fourier coefficients obtained at each detector were correlated directly with the motor torque set values using partial least squares (PLS) regression analysis [55]. PLS regression using motor torque set values as the primary variable was carried out with version 2.6 of Pirouette[®] software [56]. Six PLS models, one for each Fourier coefficient were built. Results are presented for the model with the best results. Best results were obtained for the ω Fourier coefficient from detector 2.

Figure 6.5 shows the raw data collected for the ω Fourier coefficient from detector 2 for all LDPE film samples. A clear trend is seen to exist between the motor torque set values and the Fourier coefficient. Only sample eight did not follow the trend observed in the other samples and this is attributed to the change required in the

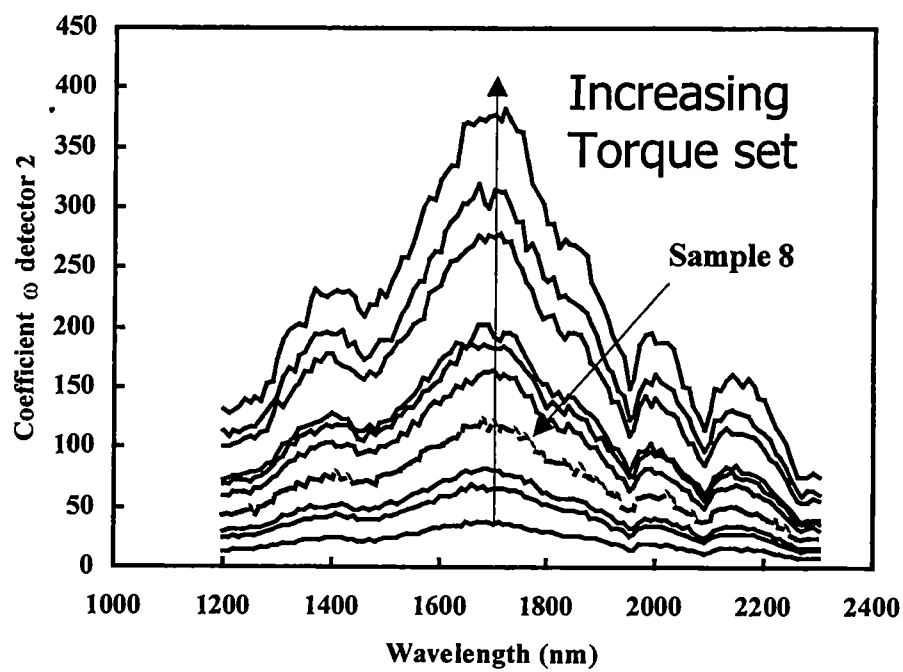


Figure 6.5 Raw data for the Fourier coefficient ω from detector 2

top roller at sample eight to maintain a constant film thickness. PLS regression was carried out after removing sample 8 from the data set. Figure 6.6 shows the scores plot obtained during PLS correlation. A clear linear trend is observed in the first score's values. The first principal component also explains 99.8 % of the variance in the data. Figure 6.7 shows the PLS leave-a-sample results for the predicted versus actual values of torque set. The two sets of results in figure 6.7 are for the raw data (ω Fourier component of detector 2) and referenced data. The referencing is done with the DC Fourier component for detector 2 in air. The minimum SEP obtained is 0.98 torque set for the raw data and 0.87 torque set for the referenced set. For both cases, minimum SEP is obtained with 2 principal components.

Raw data from the spectropolarimeter can thus be correlated with the motor torque set value during tube-blown film production. The torque set value defines the film properties and is an important parameter in film production. We could similarly correlate other process parameters (motor speed, temperature, etc.) to raw data from the spectropolarimeter.

6.4 In-line analysis during uniaxial film stretching

Polymer films are uniaxially or biaxially stretched to impart appropriate orientation and strength properties. Uniaxial stretching involves stretching a cast film along one axis. The film can be stretched at different strain rates and to different strains. In biaxial stretching the film is usually uniaxially stretched along one axis and

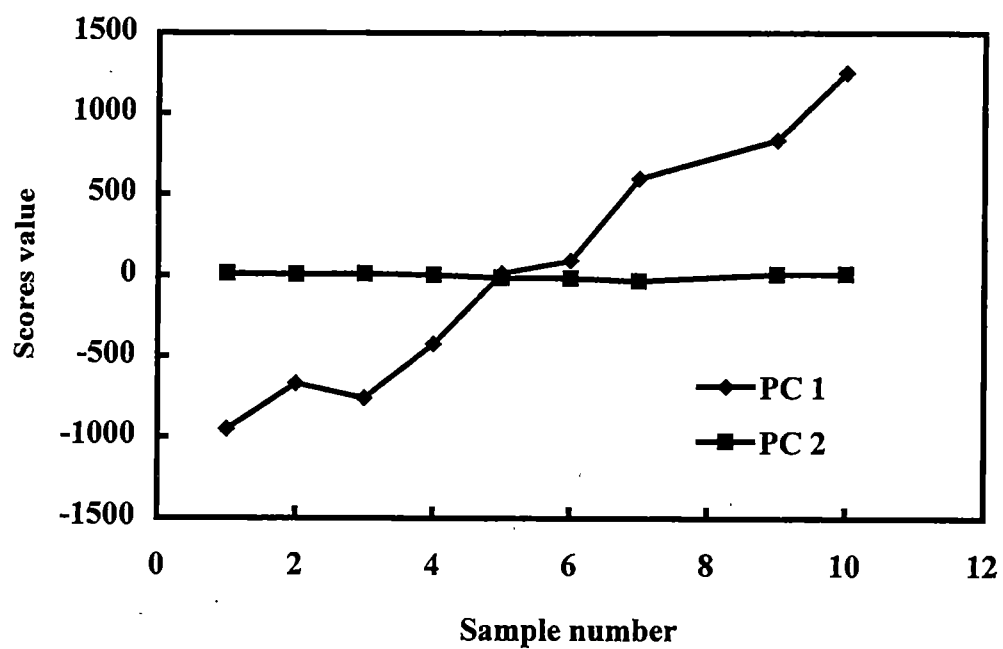


Figure 6.6 Scores plot obtained during PLS regression

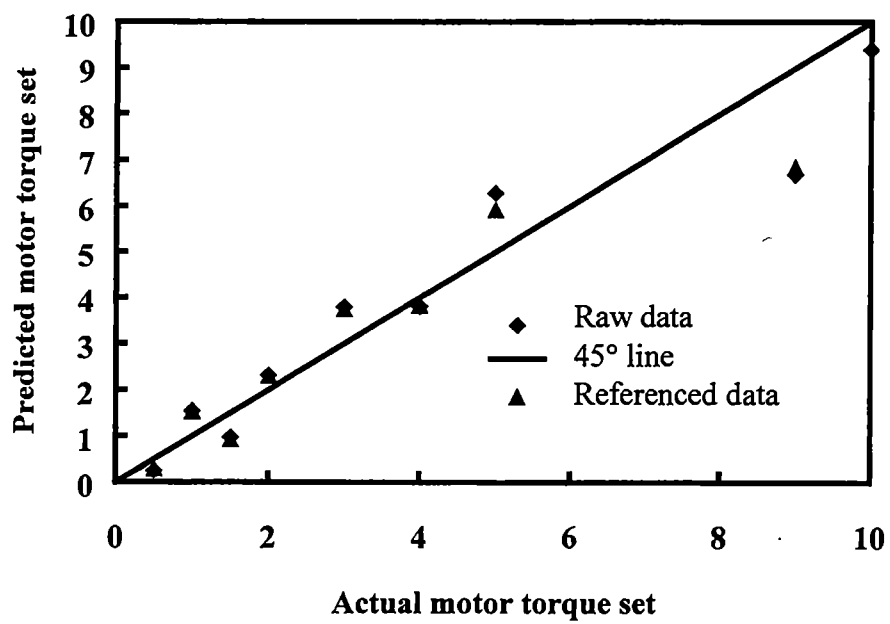


Figure 6.7 PLS regression results

then uniaxially stretched along an axis perpendicular to the first. When a polymer film is deformed, crystalline and non-crystalline components orient to relieve the stress. This orientation leads to a change in film properties, particularly its modulus, yield point, and fracture strength. Since films are marketed on the basis of these properties an understanding of the processes that impart these properties is important. Uniaxial film stretching was studied in this work. In-line spectropolarimetry data were obtained during uniaxial stretching. Simultaneously, the stress behavior of the film was studied.

The film stretcher used in this work was described by Wong [51]. It was introduced in the spectropolarimeter so that data could be obtained in-line during uniaxial stretching. Sample number 1 from the LDPE film sample set was used for this work. This film sample had the least initial orientation. Simultaneously, data were obtained from the load cell in the film stretcher. This data were converted to stress values. Stress (engineering) is defined as force obtained from the load cell divided by the initial cross-sectional area (thickness $\times$ width) of the film.

Spectropolarimetry data were obtained at 1100 nm. At this wavelength linear birefringence is the only optical anisotropy contained in the film sample. The film stretcher was arranged such that uniaxial stretching was perpendicular to the orientation of the linear polarizer. The orientation angle for linear birefringence is thus 90°. Data were collected from detector 2 in the system. The Fourier coefficients

obtained from detector 2 for a purely linear birefringent optical sample is given in equation 6.7.

$$\begin{aligned} V_2^{DC} &= \frac{c_2 I_0(\lambda)}{2} \\ V_2^\omega &= -c_2 I_0(\lambda) J_1(\delta_0) \sin \mu \cos 2\chi \\ V_2^{2\omega} &= -c_2 I_0(\lambda) J_2(\delta_0) (1 - \cos \mu) \sin 2\chi \cos 2\chi \end{aligned} \quad 6.7$$

Since the orientation angle $\chi = 90^\circ$ equation 6.7 reduces to equation 6.8.

$$\begin{aligned} V_2^{DC} &= \frac{c_2 I_0(\lambda)}{2} \\ V_2^\omega &= c_2 I_0(\lambda) J_1(\delta_0) \sin \mu \\ V_2^{2\omega} &= 0 \end{aligned} \quad 6.8$$

Equation 6.9 gives linear retardance of the film obtained from equation 6.8.

$$\mu = \sin^{-1} \left(\frac{V_2^\omega}{2V_2^{DC} J_1(\delta_0)} \right) \quad 6.9$$

Figure 6.8 shows the raw data obtained from detector 2 of the spectropolarimeter. The figure shows the DC and ω Fourier coefficients. The 2ω Fourier coefficient is essentially zero and is not shown on this figure. Once it was verified that the 2ω coefficient was zero it was not measured so as to improve the data collection speed. Data shown in figure 6.8 is for LDPE film that was stretched at a rate 0.3 cm/s. Strain defined, as extension divided by original length of the film, was 0.8.

Data were obtained at the same strain rate (0.3 cm/s) for a series of strains. Strains applied were 0.4, 0.6, and 0.8. Simultaneously, stress curves were also

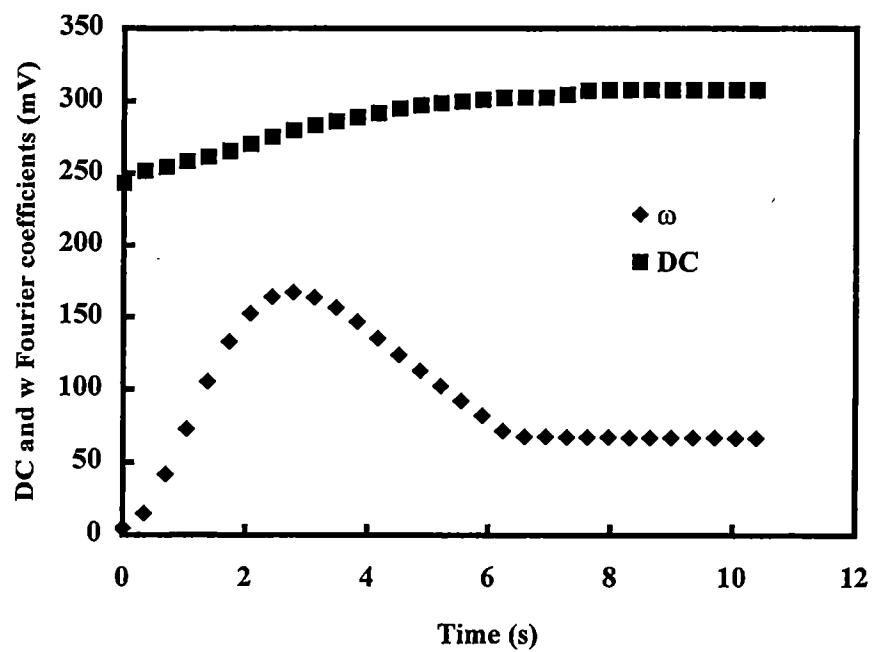
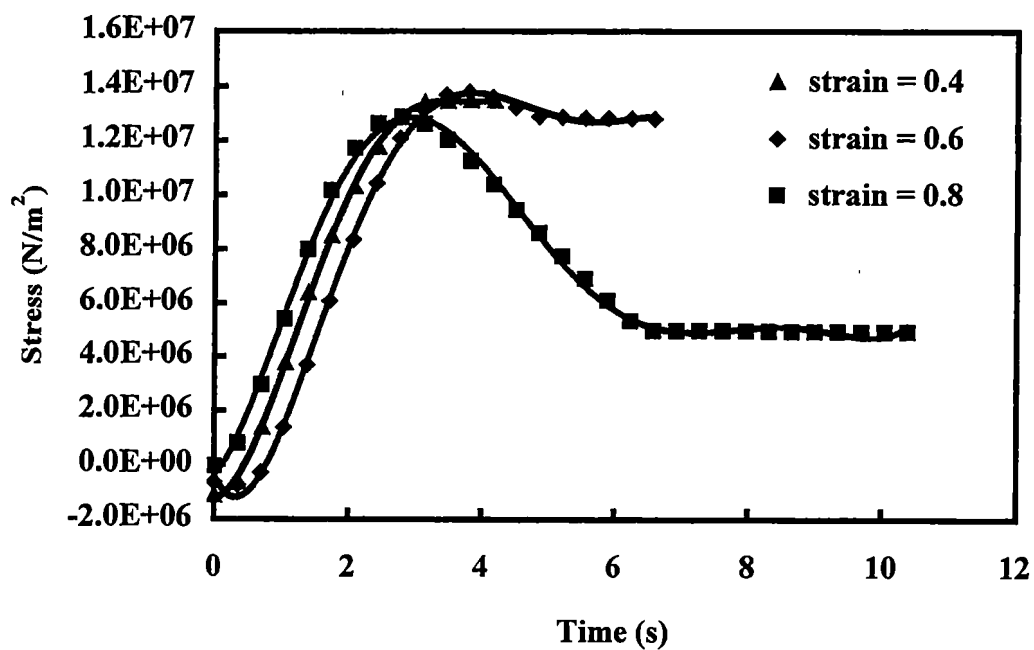


Figure 6.8 DC and ω Fourier coefficients obtained during film stretching

obtained. Figure 6.9 shows the development of stress and linear retardance with time. In figure 6.9 the solid lines are smooth least-squares fit (5th order polynomials) drawn for clarity. The symbols are actual experimental points. The calibration constant $J_1(\delta_0)$ used was obtained using the compensator following the procedure given in chapter 5. The value of $J_1(\delta_0)$ obtained was 0.31. We observe that the stress behaviors at times below 3 s. are the same for all films. This is expected as the strain rate is the same and the strain to this point is the same in all films. The stress curve for film with a 0.8 strain shows a large difference at times above 3 s. This is because of necking phenomena in which stress is relieved by the formation of highly oriented material. In polymer films the neck region can propagate further relieving stress. Necking phenomena was observed to take place for 0.8 strain dramatically changing stress behavior. Figure 6.9 also shows linear retardance curves for the three films. Again, linear retardance values are observed to be similar up to 3 seconds. Beyond 3 s. necking caused the formation of highly oriented film. This causes linear retardance to increase for 0.8 strain.

Data were also obtained for films stretched at different strain rates to the same strain. The rates applied were 0.3, 0.35, 0.4, and 0.45 cm/s. A 0.6 strain was applied to all films. Figure 6.10 shows the real-time stress and retardance curves for the same strain at different strain rates. We can clearly see in figure 6.10 that modulus of film samples increases with increasing strain rate. The films stretched at 0.35, 0.4, and 0.45 cm/s show some necking phenomena. The development of linear retardance at small

a)



b)

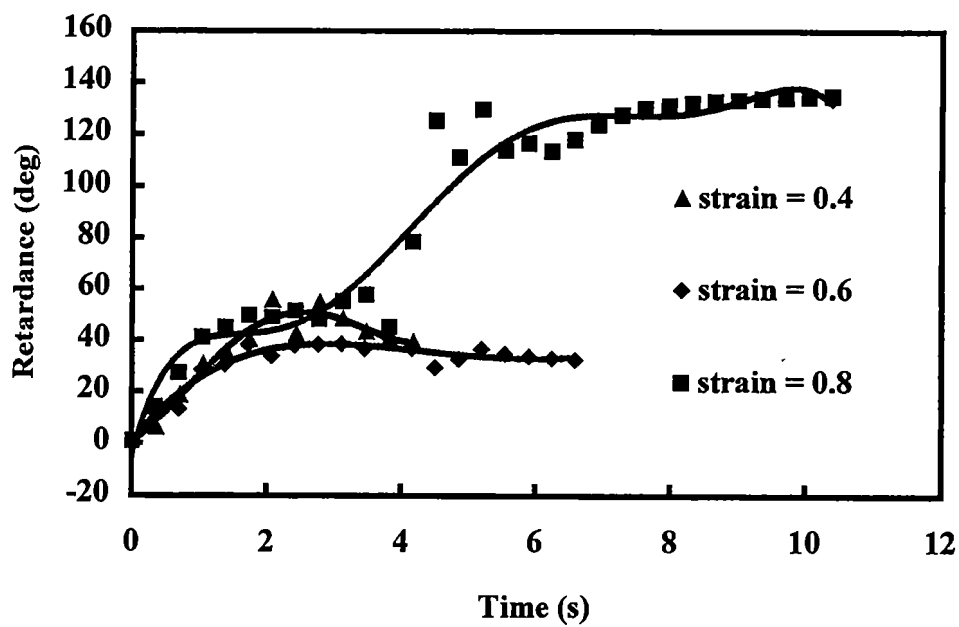


Figure 6.9 Real-time stress (a) and linear retardance (b) curves for the same strain rate.

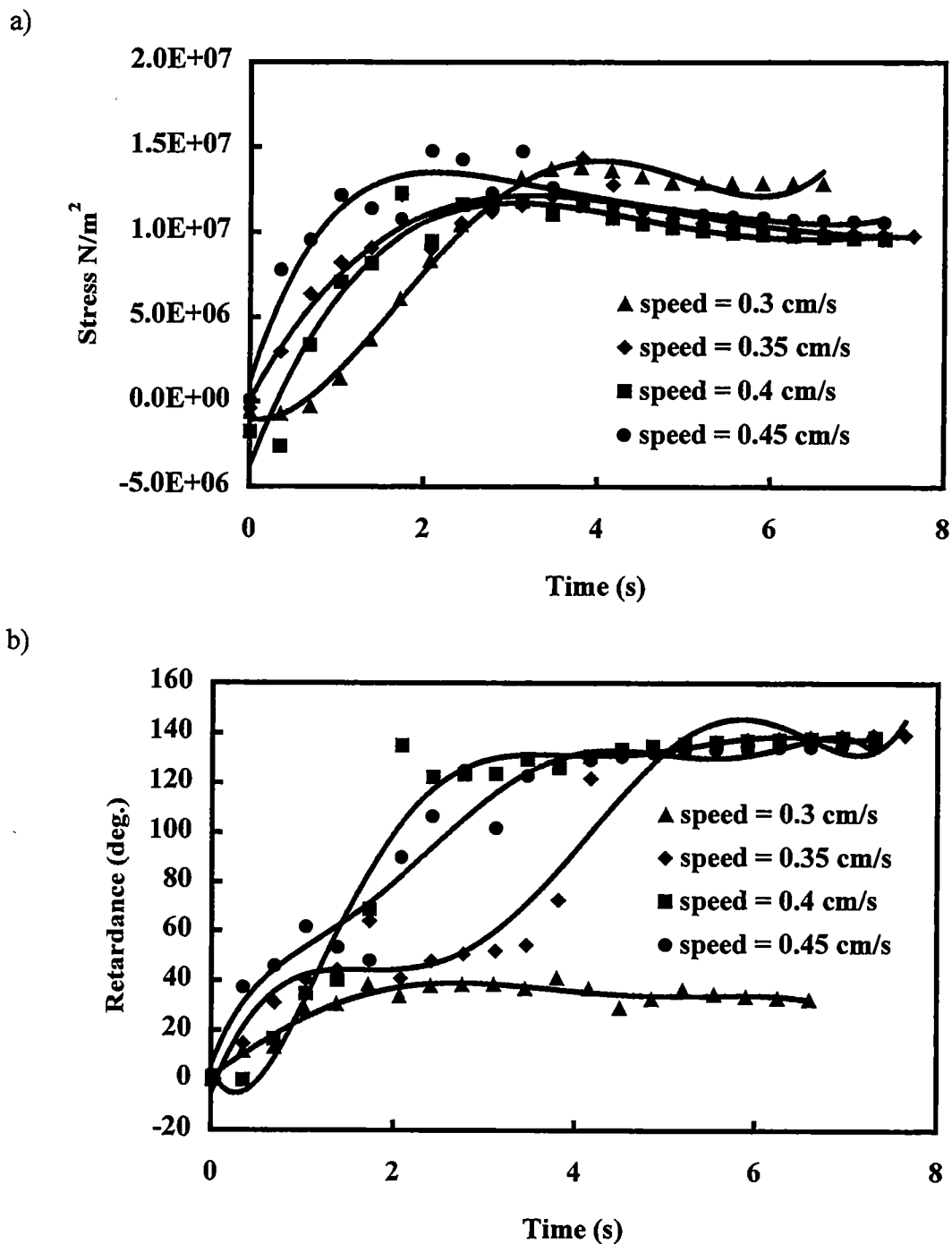


Figure 6.10 Real-time stress (a) and linear retardance (b) curves for the same strain at different strain rates.

times follows a similar pattern as stress development. Linear retardance is seen to increase with necking.

We can thus follow in-line orientation in polymer films. The spectropolarimeter was used to obtain linear retardance during film stretching operations. Linear retardance is observed to increase dramatically with the formation of "necking" in polymer films. A loose linear trend is observed in the initial slope of the stress curve and linear retardance curve.

CHAPTER 7

CONCLUSIONS

In this work, a new instrument - *near-infrared spectropolarimeter* (NIRSP) was designed and built. The NIRSP was built to analyze oriented samples. It was designed theoretically to obtain information from samples containing simultaneously coaxial linear birefringence and linear dichroism.

The NIRSP operated in the wavelength range 1100-2200 nm. Similar devices have operated at restricted wavelengths (usually 632.8 nm using a He-Ne laser). A large and useful region of the electromagnetic spectrum was studied in this work. The operation was a wavelength at a time. An acousto-optic tunable filter (AOTF) monochromator was used to obtain the desired wavelength. A photo-elastic modulator (PEM) was used to modulate the polarization state of light. A novel technique of using a polarizing beam-splitter was introduced in this work. This allowed for analysis of complex optical samples.

Theoretical expressions were derived for samples containing different anisotropies. The instrument was tested using an optical compensator - a standard sample for linear birefringence. Data was obtained at a single wavelength and compared with theoretical expressions. A close match was observed between the two. It was observed that the calibration constants were different from theoretical

predictions. However, that could be attributed to alignment and collimation difficulties. The spectropolarimeter was then used to obtain unknown linear retardance and its orientation angle values over multiple wavelengths.

The spectropolarimeter was also used to obtain isotropic absorbance data. This is helpful in determining composition of a sample. Isotropic absorbance data was obtained for polyethylene terephthalate (PET) film samples. Spectropolarimetry data was correlated directly to motor torque set values in a set of low-density polyethylene (LDPE) films. PLS regression models were built using the primary motor torque set values and the values of the Fourier coefficients over multiple wavelengths. The best model gave a value 0.87 units for the minimum standard error of prediction using two principal components. The range of variation in the samples was between 0 and 10 units. The spectropolarimeter was used to analyze in-line uniaxial film stretching. Simultaneously, spectropolarimetry data at 1100 nm and stress data were obtained. The "necking" phenomenon in which highly oriented material is formed was observed with a drop in stress and an increase in linear retardance. The modulus and initial slope for the development of linear retardance are observed to be similar.

In this work, a new technique was presented to observe orientation and orientation effects.

CHAPTER 8

FUTURE WORK

A near-infrared spectropolarimeter (NIRSP) was designed and tested in this work. The instrument was used to obtain data over multiple wavelengths in static films and in-line data at a single wavelength during uniaxial film stretching. Lock-in amplifiers were used for data acquisition in the NIRSP. The same lock-in amplifier was used to collect two Fourier coefficients (ω and 2ω). This reduced data acquisition speed. It was thus not possible to collect in-line data over multiple wavelengths. Data acquisition speed would be improved if the dynamic analyzer card can be programmed and used. This would allow for simultaneous collection of all the required Fourier coefficients. Once in-line data is collected over multiple wavelengths simultaneous development of linear dichroism and linear birefringence during film stretching can be carried out. This data can then be correlated to the internal structure and morphology development in the film.

A standard sample has to be determined for linear dichroism and the instrument has to be tested in the same manner as that using the compensator for linear birefringence. Also, standard samples for simultaneous linear dichroism and linear birefringence have to be determined. The NIRSP can also be used to obtain circular birefringence and circular dichroism. These measurements have to be explored further.

The NIRSP can also be used with molten sample if proper optical probes or windows are developed for molten samples. The probes in use for molten polymers are usually made of quartz, which has a high linear birefringence value. This would interfere with spectropolarimetry measurements. New isotropic materials have to be developed for use as optical windows. Once the NIRSP can be used with molten polymer samples, it can be used as a probe for rheological measurements through the use of the stress-optical law.

The NIRSP would lead to improved results if optical components in the instrument are machined with lower tolerances and optimized.

The NIRSP is a novel instrument and its use is only limited by imagination.

REFERENCES

REFERENCES

- 1) Hansen, M. G. and Vedula, S., *J. Appl. Polym. Sci.*, **68**, 859-872 (1998).
- 2) Vedula, S. and Hansen, M. G., *J. Appl. Polym. Sci.*, **68**, 873-889 (1998).
- 3) Janeschitz-Kriegl, H., *Polymer melt rheology and flow birefringence*, Springer-Verlag, Berlin (1983).
- 4) Samuels, R. J., *Structured polymer properties: The identification, interpretation, and application of crystalline polymer structure*, John Wiley and Sons, New York (1974).
- 5) Troxell, T.C. and Scheraga, H. A., *Macromolecules*, **4**, 519-527 (1971).
- 6) Troxell, T.C. and Scheraga, H. A., *Macromolecules*, **4**, 528-539 (1971).
- 7) Collett, E., *Polarized light: Fundamentals and applications*, Marcel Dekker, Inc. (1993).
- 8) Hauge, P. S., *Proceedings of the SPIE*, **88**, 3-10 (1976).
- 9) Fymat, A. L., *Proceedings of the SPIE*, **112**, 14-27 (1977).
- 10) Birich, G. N., Bogdanov, Yu. V., Kanorskii, S. I., Sobelman, I. I., Struk, and Yukov, E. A., *Journal of Russian laser research*, **15**, 455-476 (1994).
- 11) Thompson, R., Fry, E., and Bottiger, J., *Proceedings of the SPIE*, **112**, 152-157 (1977).
- 12) Thompson, R., Bottiger, J., and Fry, E., *Proceedings of the SPIE*, **160**, 43-48 (1978).
- 13) Thompson, R., Bottiger, J., and Fry, E., *Appl. Opt.*, **19**, 1323-1332 (1980).

- 14) Azzam, R. M. A., *Opt. Lett.*, **2**, 148-150 (1978).
- 15) Delplancke, F., *Appl. Opt.*, **36**, 5388-5395 (1997).
- 16) Delplancke, F., *Appl. Opt.*, **36**, 7621-7628 (1997).
- 17) Delplancke, F., *Proceedings of the SPIE*, **3121**, 454-464 (1997).
- 18) Delplancke, F., Badoz, J., and Boccara, A. C., *Proceedings of the SPIE*, **3121**, 465-475 (1997).
- 19) Chenault, D. B. and Chipman, R. A., *Proceedings of the SPIE*, **1166**, 254-266 (1989).
- 20) Chenault, D. B. and Chipman, R. A., *Appl. Opt.*, **32**, 3513-3519 (1993).
- 21) Chenault, D. B. and Chipman, R. A., *Appl. Opt.*, **32**, 4223-4227 (1993).
- 22) Kemp, J. C., *J. Opt. Soc. Am.*, **59**, 950-954 (1969).
- 23) Jensen, H. P., Schellman, J. A., and Troxell, T., *Appl. Spec.*, **32**, 192-200 (1978).
- 24) Hipps, K. W. and Crosby, G. A., *J. Phys. Chem.*, **83**, 555-562 (1979).
- 25) Shindo, Y., *Opt. Eng.*, **34**, 3369-3384 (1995).
- 26) Schellman, J. and Jensen, H. P., *Chem. Rev.*, **87**, 1359-1399 (1987).
- 27) Frattini, P. L. and Fuller, G. G., *J. Rheol.*, **28**, 61-70 (1984).
- 28) Frattini, P. L. and Fuller, G. G., *J. Colloid Interface Sci.*, **100**, 506-518 (1984).
- 29) Johnson, S. J., Frattini, P. L., and Fuller, G. G., *J. Colloid Interface Sci.*, **104**, 440-455 (1985).
- 30) Abetz, V. and Fuller, G. G., *Rheol. Acta*, **29**, 11-15 (1990).
- 31) Fuller, G. G., *Annu. Rev. Fluid Mech.*, **22**, 387-417 (1990).
- 32) Kalogrianitis, S. G. and vanEgmond, J. W., *J. Rheol.*, **41**, 343-364 (1997).

- 33) Ghaneh-Fard, A., Carreau, P. J., and Lafleur, P. G., *Journal of Plastic film and sheeting*, **12**, 68-86 (1996).
- 34) Ghaneh-Fard, A., Carreau, P. J., and Lafleur, P. G., *Intern. Polymer Processing*, **12**, 136-146 (1997).
- 35) Ajji, A., Guevremont, J., Matthews, R. G., and Dumoulin, M. M., *ANTEC*, 1588-1592 (1998).
- 36) Ajji, A. and Guevremont, J., U.S. Patent 5,864,403 (1999).
- 37) Stokes, G.G., *Trans. of the Camb. Phil. Soc.*, **IX**, 399 (1852).
- 38) Jones, R.C., *J. Opt. Soc. Am.*, **31**, 488-493 (1941).
- 39) Jones, R.C., *J. Opt. Soc. Am.*, **31**, 493-499 (1941).
- 40) Azzam, R. M. A. and Bashara, M. M., '*Ellipsometry and polarized light*', Elsevier Science B. V., The Netherlands (1996).
- 41) Brimrose Corporation of America, 5020 Campbell Blvd., Baltimore, MD 21236.
- 42) Wang, X., Soos, J., Li, Q., and Crystal J., *Process Control and Quality*, **5**, 9-16 (1993).
- 43) CASIX, P. O. Box 1103, Fuzhou, Fujian 350014 The People's Republic of China.
- 44) Hinds Instruments, Inc., 3175 NW Alcock Drive, Hillsboro, OR 97124.
- 45) Karl Lambrecht Corporation, 4204 N. Lincoln Ave., Chicago, IL 60618.
- 46) Epitaxx, Inc., 7 Graphics drive, West Trenton, NJ 08628.
- 47) EG&G Judson, 221 Commerce drive, Montgomeryville, PA 18936.
- 48) National Instruments, 6504 Bridge Point Parkway, Austin, TX 78730.
- 49) Stanford Research Systems, Inc., 1290D Reamwood Ave., Sunnyvale, CA 94089.

- 50) Newport Corporation, 18235 Mt. Baldy Circle, Fountain Valley, CA 92708.
- 51) Wong R. P., Ph.D. dissertation, University of Tennessee (1991).
- 52) Ealing electro-optics, Inc. 22 Pleasant Street, South Natick, MA 01760.
- 53) Chenault, D. B., Ph. D. dissertation, University of Alabama (1992).
- 54) Baird, D. G. and Collias, D. I., *Polymer processing: Principles and design*, Butterworth-Heinemann, Newton (1995).
- 55) Piovoso, M. J. and Kosanovich, K. A., *The use of multivariate statistics in process control*, CRC Press (1996).
- 56) Infometrix, Inc., P. O. Box 1528, Woodinville, WA 98072.
- 57) Jones, R. C., *J. Opt. Soc. Am.*, **38**, 671-685 (1948).
- 58) Fuller, G. G., *Optical rheometry of complex fluids*, Oxford University Press, New York (1995).
- 59) Johnson, S. J., Frattini, P. L., and Fuller, G. G., *J. Colloid Interface Sci.*, **104**, 330-316 (1985).
- 60) Johnson, S. J., Ph.D. dissertation, Stanford University (1987).

APPENDICES

APPENDIX A

JONES AND MUELLER MATRICES OF OPTICAL SAMPLES

A.1 Introduction

An optical sample under consideration can contain simultaneously different optical anisotropies. The optical anisotropies can vary for the same optical sample based on the wavelength of operation. Some of the optical anisotropies important in this work have been discussed in chapter 3. The optical anisotropies considered in this work are as follows:

- 1) Isotropic retardation of the phase of incident light
- 2) Isotropic attenuation (absorbance) of the amplitude of incident light
- 3) Linear birefringence and
- 4) Linear dichroism

In this appendix are derived the Mueller matrices for samples containing various combinations of the optical anisotropies. A procedure outlined by Jones [57], to obtain the Jones matrix of samples with mixed anisotropies is followed here. Once the Jones matrices have been derived, they are converted to the corresponding Mueller matrices using equations 3.19, 3.20, and 3.21.

A.2 Differential propagation Jones matrix

An optical sample modifies the electric field vector of the incident light beam continuously, as it propagates through the sample. The resultant over-all change in the state of polarization is the cumulative effect of incremental changes that take place as light travels through successive incremental distances in the optical sample. Jones [57] introduced the differential propagation Jones matrix, $N(z)$, to characterize the change in the state of polarization of light as it propagates through an element of infinitesimal thickness in the sample. He also related the Jones matrix of the sample, $J(z)$, to the differential propagation Jones matrix through the differential equation A.1.

$$\frac{dJ(z)}{dz} = N(z)J(z) \quad \text{A.1}$$

Jones [57] has shown that we can obtain the differential propagation Jones matrix for simple anisotropies using an alternative definition, given in equation A.2, of the same.

$$N(z) = \lim_{\Delta z \rightarrow 0} \frac{J(\Delta z) - I}{\Delta z} \quad \text{A.2}$$

The 2×2 matrix $J(\Delta z)$ is the Jones matrix for an infinitesimal layer of thickness Δz . The 2×2 matrix I is the identity matrix. Table A.1 lists the differential propagation Jones matrices for simple anisotropies. Fuller [58] gives a more detailed listing. Jones [57] solved equation A.1 to obtain the Jones matrix of an optical sample from its differential propagation Jones matrix. The solution is subject to the boundary condition in equation A.3.

$$J(z \rightarrow 0) = I \quad \text{A.3}$$

Table A.1 Differential propagation Jones matrices for various optical effects (Source: Fuller [57]).

Optical Effect	Definition	N matrix
Isotropic retarder	n' is the scalar, real part of the refractive index	$\frac{i2\pi n'}{\lambda} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$
Isotropic attenuator	n'' is the scalar, imaginary part of the refractive index	$-\frac{2\pi n''}{\lambda} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$
Linear birefringent material	$\Delta n'$ is the birefringence and χ is the orientation of the principal axes of the real part of the refractive index tensor	$\frac{i\pi\Delta n'}{\lambda} \begin{bmatrix} \cos 2\chi & \sin 2\chi \\ \sin 2\chi & -\cos 2\chi \end{bmatrix}$
Linear dichroic material	$\Delta n''$ is the dichroism and ϕ_d is the orientation of the principal axes of the imaginary part of the refractive index tensor	$-\frac{\pi\Delta n''}{\lambda} \begin{bmatrix} \cos 2\phi_d & \sin 2\phi_d \\ \sin 2\phi_d & -\cos 2\phi_d \end{bmatrix}$

The boundary condition reflects that the Jones vector starts undergoing a change at the incident surface of the optical sample. The Jones matrix, J , of the optical sample of thickness d given the differential propagation Jones matrix, N , is given in equation A.4

$$J = e^{T_N d} \begin{bmatrix} \cosh Q_N d + \frac{1}{2}(N_{11} - N_{22}) \frac{\sinh Q_N d}{Q_N} & N_{12} \frac{\sinh Q_N d}{Q_N} \\ N_{21} \frac{\sinh Q_N d}{Q_N} & \cosh Q_N d - \frac{1}{2}(N_{11} - N_{22}) \frac{\sinh Q_N d}{Q_N} \end{bmatrix} \quad \text{A.4}$$

The parameters N_{ij} in equation A.4 are the elements of N and

$$\begin{aligned} T_N &= \frac{1}{2}(N_{11} + N_{22}) \\ Q_N &= \sqrt{T_N^2 - D_N} \\ D_N &= N_{11}N_{22} - N_{12}N_{21} \end{aligned} \quad \text{A.5}$$

Equations A.4 and A.5 can be used to obtain the Jones matrix of a sample if its differential propagation Jones matrix is known.

Jones [57] showed that when used with equations A.4 and A.5, the differential propagation Jones matrix for a sample with mixed anisotropies is the sum of the differential propagation Jones matrices for simple anisotropies present in the sample. That is, the differential propagation Jones matrix for an optical sample with n anisotropies is given by

$$N = \sum_{i=1}^n N_i \quad \text{A.6}$$

In equation A.6, N_i is the differential propagation Jones matrix of the i^{th} anisotropy in the sample and is obtained from table A.1. For an optical sample containing

simultaneously isotropic retardance, isotropic absorbance, noncoaxial linear birefringence, and linear dichroism $n = 4$. Using equation A.6 and table A.1 the differential propagation Jones matrix of the optical sample under consideration is given by equation A.7.

$$N = \frac{i2\pi n'}{\lambda} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} - \frac{2\pi n''}{\lambda} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} + \frac{i\pi\Delta n'}{\lambda} \begin{bmatrix} \cos 2\chi & \sin 2\chi \\ \sin 2\chi & -\cos 2\chi \end{bmatrix} - \frac{\pi\Delta n''}{\lambda} \begin{bmatrix} \cos 2\phi_d & \sin 2\phi_d \\ \sin 2\phi_d & -\cos 2\phi_d \end{bmatrix} \quad \text{A.7}$$

A.3 Jones matrix of the optical sample

We shall now obtain the Jones matrix of the optical sample represented by the differential propagation Jones matrix in equation A.7 using equations A.4 and A.5.

From equations A.5 and A.7 we get

$$T_N = \frac{1}{2} \left[\frac{i4\pi n'}{\lambda} - \frac{4\pi n''}{\lambda} + \frac{i\pi\Delta n'}{\lambda} (\cos 2\chi - \cos 2\chi) - \frac{\pi\Delta n''}{\lambda} (\cos 2\phi_d - \cos 2\phi_d) \right]$$

$$T_N = \frac{i2\pi n'}{\lambda} - \frac{2\pi n''}{\lambda} \quad \text{A.8}$$

Using equations A.5, A.7, and A.8 we get

$$Q_N^2 = T_N^2 - D_N = T_N^2 - N_{11}N_{22} + N_{12}N_{21}$$

$$Q_N^2 = \left(i\frac{2\pi n'}{\lambda} - \frac{2\pi n''}{\lambda} \right)^2 - \left(\frac{i2\pi n'}{\lambda} - \frac{2\pi n''}{\lambda} + \frac{i\pi\Delta n'}{\lambda} \cos 2\chi - \frac{\pi\Delta n''}{\lambda} \cos 2\phi_d \right) \cdot$$

$$\left(\frac{i2\pi n'}{\lambda} - \frac{2\pi n''}{\lambda} - \frac{i\pi\Delta n'}{\lambda} \cos 2\chi + \frac{\pi\Delta n''}{\lambda} \cos 2\phi_d \right) + \left(\frac{i\pi\Delta n'}{\lambda} \sin 2\chi - \frac{\pi\Delta n''}{\lambda} \sin 2\phi_d \right)^2$$

$$\begin{aligned}
Q_N^2 &= \frac{\pi^2}{\lambda^2} (i2n' - 2n'')^2 - \frac{\pi^2}{\lambda^2} (i2n' - 2n'' + i\Delta n' \cos 2\chi - \Delta n'' \cos 2\phi_d) \cdot \\
&\quad (i2n' - 2n'' - i\Delta n' \cos 2\chi + \Delta n'' \cos 2\phi_d) + \frac{\pi^2}{\lambda^2} (i\Delta n' \sin 2\chi - \Delta n'' \sin 2\phi_d)^2 \\
Q_N^2 &= \frac{\pi^2}{\lambda^2} \left\{ \begin{aligned} &(-4n'^2 - i8n'n'' + 4n''^2) - \left(-4n'^2 - i8n'n'' + 4n''^2 + \Delta n'^2 \cos^2 2\chi \right. \\ &\quad \left. + i2\Delta n' \Delta n'' \cos 2\chi \cos 2\phi_d - \Delta n''^2 \cos^2 2\phi_d \right) \\ &\quad \left. + (-\Delta n'^2 \sin^2 2\chi - i2\Delta n' \Delta n'' \sin 2\chi \sin 2\phi_d + \Delta n''^2 \sin^2 2\phi_d) \right\} \\
Q_N^2 &= \frac{\pi^2}{\lambda^2} \left\{ \begin{aligned} &-\Delta n'^2 (\sin^2 2\chi + \cos^2 2\chi) + \Delta n''^2 (\sin^2 2\phi_d + \cos^2 2\phi_d) \\ &-i2\Delta n' \Delta n'' (\cos 2\chi \cos 2\phi_d + \sin 2\chi \sin 2\phi_d) \end{aligned} \right\} \\
Q_N^2 &= \frac{\pi^2}{\lambda^2} [-\Delta n'^2 + \Delta n''^2 - i2\Delta n' \Delta n'' \cos(2\chi - 2\phi_d)]
\end{aligned}$$

Multiplying by $4d^2$ where d is the thickness of the optical sample we get

$$4Q_N^2 d^2 = -\frac{4\pi^2 \Delta n'^2 d^2}{\lambda^2} + \frac{4\pi^2 \Delta n''^2 d^2}{\lambda^2} - i2 \frac{2\pi \Delta n' d}{\lambda} \frac{2\pi \Delta n'' d}{\lambda} \cos(2\chi - 2\phi_d)$$

Using equations 3.23 and 3.24 we get

$$4Q_N^2 d^2 = -\mu^2 + \nu^2 + i2\mu\nu \cos(2\chi - 2\phi_d)$$

To use with equation A.4 we need to convert the equation given above to the mathematically useful form $Q_N d$. For mathematical simplicity we write

$$\begin{aligned}
(Q_N d)^2 &= \frac{1}{4}(a + ib) \text{ where} \\
a &= -\mu^2 + \nu^2 \text{ and} \\
b &= 2\mu\nu \cos(2\chi - 2\phi_d)
\end{aligned} \tag{A.9}$$

Figure A.1 shows the variation of the parameters a and b with retardance and relative absorption coefficient. As is clear from equation A.9, a is not related to the difference

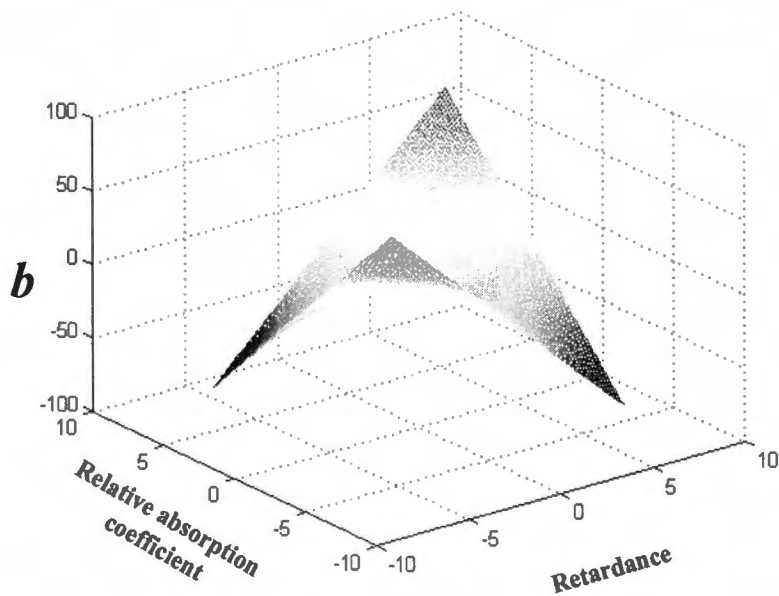
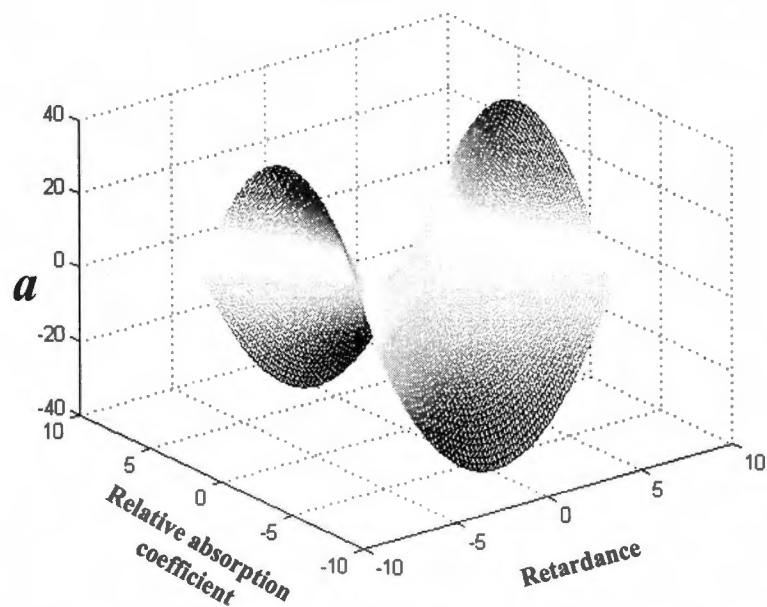


Figure A.1 The parameters a and b . The parameter b is shown for the case of coaxial linear birefringence and linear dichroism.

in orientation angles for linear birefringence and linear dichroism. The parameter b is however, dependent on the difference in the orientation angles. Figure A.1 shows the parameter b for the case of coaxial linear birefringence and linear dichroism. For this case the absolute value of b is the greatest. As the anisotropies become noncoaxial, the absolute value of b keeps decreasing till $b = 0$ for $(\chi - \phi_d) = 45^\circ$. We obtain $Q_N d$ by conversion of $(a + ib)$ to polar coordinates using

$$\begin{aligned} a &= r \cos \theta \quad \text{and} \\ b &= r \sin \theta \end{aligned}$$

Using polar coordinates we can show

$$\begin{aligned} H &\equiv Q_N d = h + i\bar{h} \quad \text{where} \\ h &= \frac{1}{2} r^{1/2} \cos \frac{\theta}{2} \quad \text{and} \\ \bar{h} &= \frac{1}{2} r^{1/2} \sin \frac{\theta}{2} \end{aligned} \tag{A.10}$$

The absolute value $|H|$ is easily obtained as follows

$$\begin{aligned} |H| &= \sqrt{h^2 + \bar{h}^2} \\ |H| &= \frac{1}{2} r^{1/2} \end{aligned}$$

From the definition of r during polar conversion we get

$$|H| = \frac{1}{2} (a^2 + b^2)^{1/4} \tag{A.11}$$

We know that

$$\begin{aligned}
|H| &= \frac{1}{2} r^{1/2} \\
4|H|^2 + a &= r + a = r + r \cos \theta \\
4|H|^2 + a &= 2r \cos^2 \frac{\theta}{2}
\end{aligned}$$

Substituting for $r \cos \theta/2$ using equation A.10 in the above we get

$$h = \frac{1}{2\sqrt{2}} \left(4|H|^2 + a \right)^{1/2} \quad \text{A.12}$$

We can similarly show that

$$\bar{h} = \frac{1}{2\sqrt{2}} \left(4|H|^2 - a \right)^{1/2} \quad \text{A.13}$$

We now use equations A.4 and A.5 to obtain the Jones matrix of the optical sample under consideration. For the optical sample of thickness d , containing isotropic retardance, isotropic absorbance, linear birefringence, and linear dichroism T_N is given by equation A.8. From the definition of H given in equation A.10 we have $Q_N d = H$. The N_{ij} 's in equation A.4 are elements of the differential propagation Jones matrix of the optical sample given in equation A.7. At this time let us write the Jones matrix of the sample as

$$\mathbf{J} = e^{T_N d} \begin{bmatrix} T_1 & T_2 \\ T_2 & T_3 \end{bmatrix} \quad \text{A.14}$$

Using equations A.4, A.5, A.7, and A.10 we get

$$T_1 = \cosh H + \frac{1}{2} \left(\frac{i2\pi n'}{\lambda} - \frac{2\pi n''}{\lambda} - \frac{i2\pi n'}{\lambda} + \frac{2\pi n''}{\lambda} + \frac{i\pi\Delta n'}{\lambda} \cos 2\chi - \frac{\pi\Delta n''}{\lambda} \cos 2\phi_d + \frac{i\pi\Delta n'}{\lambda} \cos 2\chi - \frac{\pi\Delta n''}{\lambda} \cos 2\phi_d \right) \frac{\sinh H}{Q_N}$$

Using equations 3.23, 3.24 and A.10 we get

$$T_1 = \cosh H - \frac{1}{2} (i\mu \cos 2\chi + \nu \cos 2\phi_d) \frac{\sinh H}{H} \quad \text{A.15}$$

We can similarly show that

$$T_3 = \cosh H + \frac{1}{2} (i\mu \cos 2\chi + \nu \cos 2\phi_d) \frac{\sinh H}{H} \quad \text{A.16}$$

Also,

$$T_2 = \left(\frac{i\pi\Delta n'}{\lambda} \sin 2\chi - \frac{\pi\Delta n''}{\lambda} \sin 2\phi_d \right) \frac{\sinh H}{Q_N}$$

$$T_2 = -\frac{1}{2} (i\mu \sin 2\chi + \nu \sin 2\phi_d) \frac{\sinh H}{H} \quad \text{A.17}$$

We can write $T_N d$ as equation A.18 using equation A.8 and equations in a form similar to equations 3.23 and 3.24

$$T_N d = -in_i - \frac{A_e}{2} \quad \text{A.18}$$

In equation A.18, n_i is the isotropic retardance of the optical sample and A_e is the isotropic absorbance. The Jones matrix of the optical sample is given in equation A.19.

$$\mathbf{J} = e^{T_N d} \begin{bmatrix} \cosh H - \frac{1}{2} (i\mu \cos 2\chi + \nu \cos 2\phi_d) \frac{\sinh H}{H} & -\frac{1}{2} (i\mu \sin 2\chi + \nu \sin 2\phi_d) \frac{\sinh H}{H} \\ -\frac{1}{2} (i\mu \sin 2\chi + \nu \sin 2\phi_d) \frac{\sinh H}{H} & \cosh H + \frac{1}{2} (i\mu \cos 2\chi + \nu \cos 2\phi_d) \frac{\sinh H}{H} \end{bmatrix} \quad \text{A.19}$$

The parameter $T_N d$ in equation A.19 is defined in equation A.18.

A.4 Special forms of the Jones matrix

The Jones matrix given in equation A.19 can be simplified for various special cases. This will serve as a check for the validity of equation A.19, as the Jones matrices for various special cases are published by Fuller [58]. Let us first examine the Jones matrix for non-coaxial linear birefringence and linear dichroism without isotropic retardance or isotropic absorbance. For such a sample, equation A.7 is modified to equation A.20

$$N = \frac{i\pi\Delta n'}{\lambda} \begin{bmatrix} \cos 2\chi & \sin 2\chi \\ \sin 2\chi & -\cos 2\chi \end{bmatrix} - \frac{\pi\Delta n''}{\lambda} \begin{bmatrix} \cos 2\phi_d & \sin 2\phi_d \\ \sin 2\phi_d & -\cos 2\phi_d \end{bmatrix} \quad \text{A.20}$$

For an optical sample with the differential propagation Jones matrix given in equation A.20 we have

$$T_N = 0 \quad \text{A.21}$$

We can also show that $Q_N d$ is the same as given in equation A.9. Since $Q_N d$ is the same, further mathematics in determining the elements of the Jones matrix is the same. The only change is in T_N , which changes the exponent in the multiplier, to all the matrix elements in equation A.19. The Jones matrix of an optical sample containing simultaneously non-coaxial linear birefringence and linear dichroism is given in equation A.22.

$$J = \begin{bmatrix} \cosh H - \frac{1}{2}(i\mu \cos 2\chi + \nu \cos 2\phi_d) \frac{\sinh H}{H} & -\frac{1}{2}(i\mu \sin 2\chi + \nu \sin 2\phi_d) \frac{\sinh H}{H} \\ -\frac{1}{2}(i\mu \sin 2\chi + \nu \sin 2\phi_d) \frac{\sinh H}{H} & \cosh H + \frac{1}{2}(i\mu \cos 2\chi + \nu \cos 2\phi_d) \frac{\sinh H}{H} \end{bmatrix} \quad A.22$$

Let us now examine the Jones matrix for coaxial linear birefringence and linear dichroism. We shall observe this situation in optical samples that are deformed by shear flows such that constituents generating linear birefringence and linear dichroism are the same. The mathematical condition describing coaxial linear birefringence and linear dichroism given in equation A.23

$$\chi = \phi_d = \theta \quad A.23$$

For this condition the parameters a and b defined in equation A.9 are given by equation A.24.

$$\begin{aligned} a &= -\mu^2 + \nu^2 \\ b &= 2\mu\nu \end{aligned} \quad A.24$$

From the definition of $|H|$ in equation A.11 we have

$$\begin{aligned} |H| &= \frac{1}{2}(a^2 + b^2)^{1/4} \\ |H| &= \frac{1}{2}[(-\mu^2 + \nu^2)^2 + (2\mu\nu)^2]^{1/4} \\ |H| &= \frac{1}{2}(\mu^2 + \nu^2)^{1/2} \end{aligned} \quad A.25$$

The expressions for a in equation A.24 and $|H|$ in equation A.25 allow us to calculate h and $\bar{h}$ defined in equations A.12 and A.13 as follows

$$h = \frac{1}{2\sqrt{2}} \left(4|H|^2 + a \right)^{1/2}$$

$$h = \frac{1}{2\sqrt{2}} \left[4 \times \frac{1}{4} (\mu^2 + \nu^2) - \mu^2 + \nu^2 \right]^{1/2}$$

$$h = \frac{\nu}{2}$$

Similarly

$$\bar{h} = \frac{\mu}{2}$$

From the definition of H in equation A.10 we get

$$H = \frac{\nu}{2} + i \frac{\mu}{2} \quad \text{A.26}$$

Using equations A.23 and A.26 in equation A.22 the Jones matrix for coaxial linear birefringence and linear dichroism is given in equation A.27.

$$\mathbf{J} = \begin{bmatrix} \cosh H - \cos 2\theta \sinh H & -\sin 2\theta \sinh H \\ -\sin 2\theta \sinh H & \cosh H + \cos 2\theta \sinh H \end{bmatrix} \quad \text{A.27}$$

The parameter H in equation A.27 is defined in equation A.26. Figure A.2 shows the real part of the Jones matrix for coaxial linear birefringence and linear dichroism with $\theta = 0^\circ$. Similarly, figure A.3 shows the imaginary part of the Jones matrix. The pattern seen in figures A.2 and A.3 keeps repeating for higher values of retardance and relative absorption coefficient.

The Jones matrix in equation A.27 can be further simplified if needed, using the expressions in equation A.28 (for H given in equation A.26)

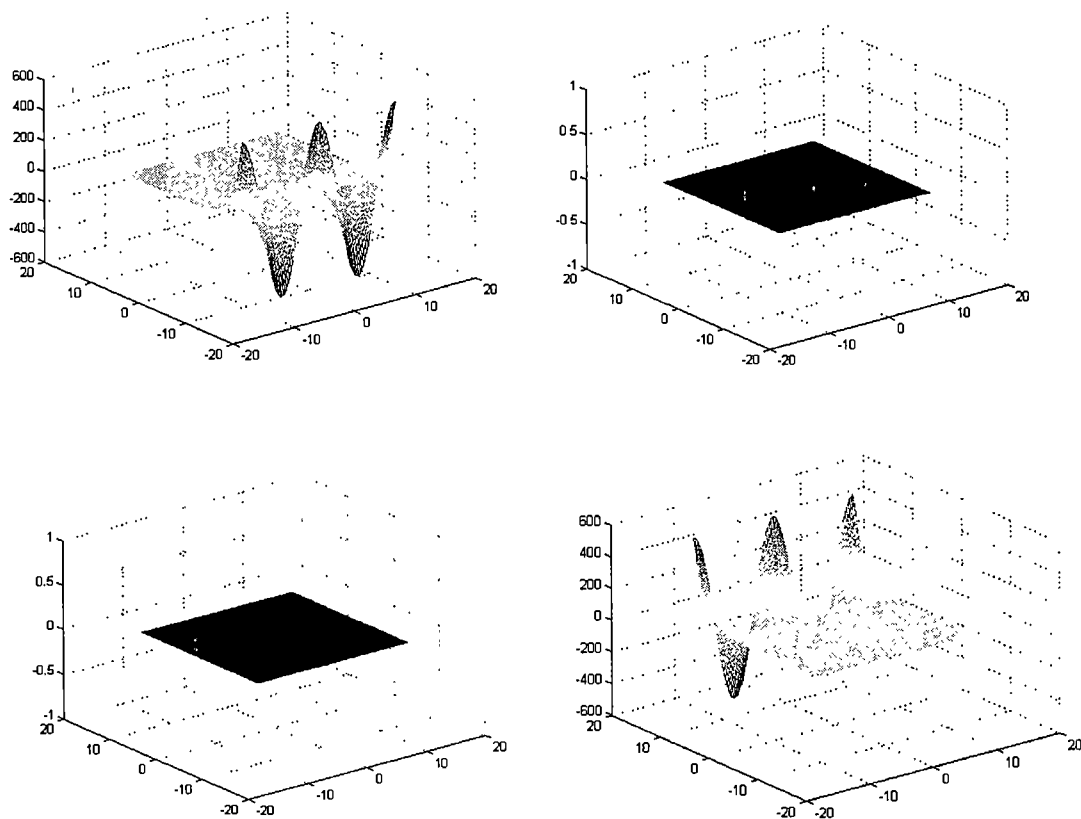


Figure A.2 The real part of the elements of the Jones matrix for the case of coaxial linear birefringence and linear dichroism. The drawings are arranged in the same order of the elements of the Jones matrix. The two horizontal axes for each figure are for retardance and relative absorption coefficient with the axis for retardance going into the right. The figures are for $\theta = 0^\circ$

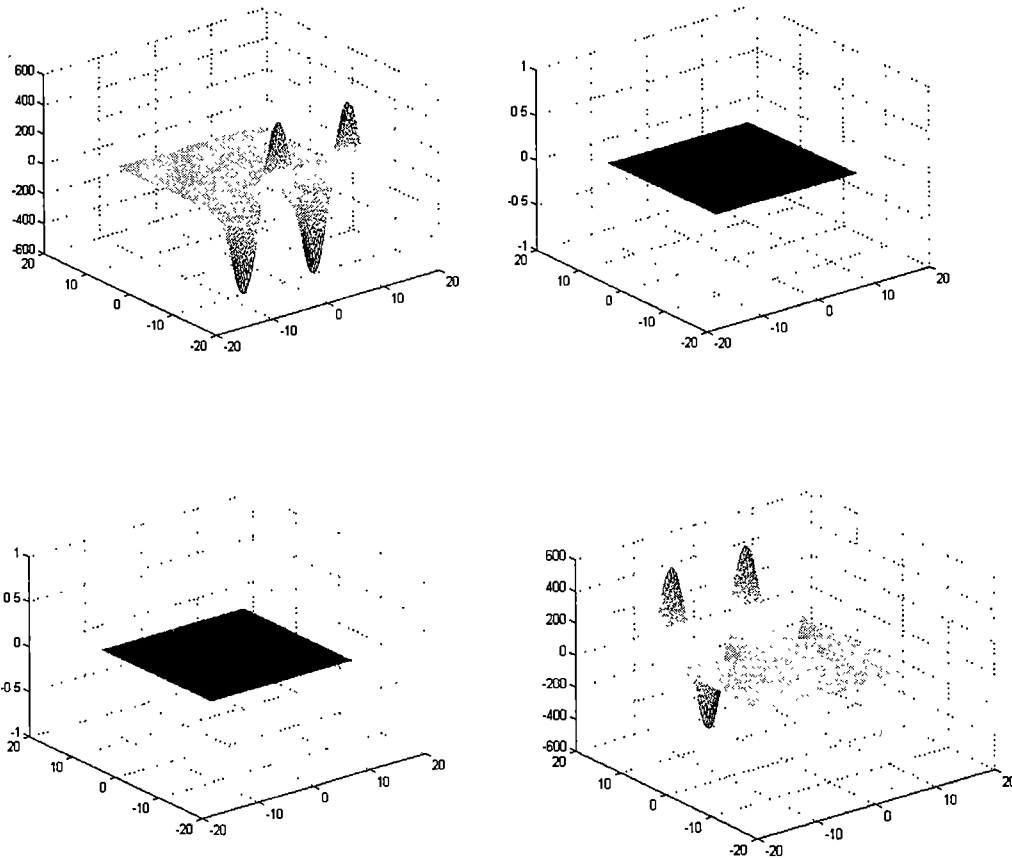


Figure A.3 The imaginary part of the elements of the Jones matrix for the case of coaxial linear birefringence and linear dichroism. The drawings are arranged in the same order of the elements of the Jones matrix. The two horizontal axes for each figure are for retardance and relative absorption coefficient with the axis for retardance going into the right. The figures are for $\theta = 0^\circ$

$$\begin{aligned}\cosh H &= \cosh \frac{\nu}{2} \cos \frac{\mu}{2} + i \sinh \frac{\nu}{2} \sin \frac{\mu}{2} \\ \sinh H &= \sinh \frac{\nu}{2} \cos \frac{\mu}{2} + i \cosh \frac{\nu}{2} \sin \frac{\mu}{2}\end{aligned}\tag{A.28}$$

We can also use the Jones matrix in equation A.27 to obtain the Jones matrices for purely linear birefringent or linear dichroic optical samples. For a purely linear birefringent optical sample we have

$$\nu = 0 \text{ and } \theta = \chi \tag{A.29}$$

Substituting equation A.29 in equation A.28 and then in equation A.27 the Jones matrix for a purely linear birefringent optical sample is given in equation A.30

$$\mathbf{J} = \begin{bmatrix} \cos \frac{\mu}{2} - i \cos 2\chi \sin \frac{\mu}{2} & -i \sin 2\chi \sin \frac{\mu}{2} \\ -i \sin 2\chi \sin \frac{\mu}{2} & \cos \frac{\mu}{2} + i \cos 2\chi \sin \frac{\mu}{2} \end{bmatrix} \tag{A.30}$$

Similarly for a purely linear dichroic sample the condition in A.31 applies.

$$\mu = 0 \text{ and } \theta = \phi_d \tag{A.31}$$

The Jones matrix for a purely linear dichroic sample is given in equation A.32

$$\mathbf{J} = \begin{bmatrix} \cosh \frac{\nu}{2} - \cos 2\phi_d \sinh \frac{\nu}{2} & -\sin 2\phi_d \sinh \frac{\nu}{2} \\ -\sin 2\phi_d \sinh \frac{\nu}{2} & \cosh \frac{\nu}{2} + \cos 2\phi_d \sinh \frac{\nu}{2} \end{bmatrix} \tag{A.32}$$

The Jones matrix for simultaneous noncoaxial linear birefringence and linear dichroism can also be simplified in the limit of small anisotropies. Mathematically the meaning of small anisotropies is explained in equation A.33

$$|\nu| \ll 1 \quad \text{and} \quad |\mu| \ll 1 \quad \text{A.33}$$

Under the condition given in equation A.33, the parameter H has to be small. For small H we have

$$\begin{aligned} \cosh H &= 1 + \frac{H^2}{2!} + \frac{H^4}{4!} + \dots \approx 1 \\ \sinh H &= H + \frac{H^3}{3!} + \frac{H^5}{5!} + \dots \approx H \\ \frac{\sinh H}{H} &\approx 1 \end{aligned} \quad \text{A.34}$$

Under the conditions given in equation A.34 we can simplify the Jones matrix in equation A.22 to obtain the Jones matrix in the limit of small anisotropies given in equation A.35

$$\mathbf{J} = \begin{bmatrix} 1 - \frac{1}{2}(i\mu \cos 2\chi + \nu \cos 2\phi_d) & -\frac{1}{2}(i\mu \sin 2\chi + \nu \sin 2\phi_d) \\ -\frac{1}{2}(i\mu \sin 2\chi + \nu \sin 2\phi_d) & 1 + \frac{1}{2}(i\mu \cos 2\chi + \nu \cos 2\phi_d) \end{bmatrix} \quad \text{A.35}$$

A.5 Mueller matrix

The Mueller matrix for an optical sample containing simultaneously isotropic retardance, isotropic absorbance, and noncoaxial linear birefringence and linear dichroism is obtained from the corresponding Jones matrix given in equation A.19. Equations 3.19, 3.20, and 3.21 are used to obtain the Mueller matrix. For mathematical ease let us define

$$\begin{aligned}
X &\equiv \cosh H \\
Y &\equiv -\frac{1}{2}(\nu \cos 2\phi_d + i\mu \cos 2\chi) \frac{\sinh H}{H} \\
Z &\equiv -\frac{1}{2}(\nu \sin 2\phi_d + i\mu \sin 2\chi) \frac{\sinh H}{H}
\end{aligned} \tag{A.36}$$

With the definitions in equation A.36 the Jones matrix of equation A.19 is

$$\mathbf{J} = \exp\left(-in_i - \frac{A_e}{2}\right) \begin{bmatrix} X+Y & Z \\ Z & X-Y \end{bmatrix}$$

Let us now obtain the parameters E_i , F_{ij} , and G_{ij} defined in equation 3.21. Note that for the Jones matrix under consideration we have $J_3 = J_4$ in equation 3.21.

$$\begin{aligned}
E_1 &= |J_1|^2 \\
E_1 &= \exp\left(-in_i - \frac{A_e}{2}\right) \exp\left(in_i - \frac{A_e}{2}\right) (X+Y)(X+Y)^* \\
E_1 &= \exp(-A_e) (|X|^2 + XY^* + YX^* + |Y|^2)
\end{aligned}$$

$$\begin{aligned}
E_2 &= |J_2|^2 \\
E_2 &= \exp(-A_e) (X-Y)(X-Y)^* \\
E_2 &= \exp(-A_e) (|X|^2 - XY^* - YX^* + |Y|^2)
\end{aligned}$$

$$E_3 = E_4 = |J_3|^2 = \exp(-A_e) |Z|^2$$

$$\begin{aligned}
F_{12} &= \text{Re}(J_1 J_2^*) \\
F_{12} &= \text{Re} \left[\exp\left(-in_i - \frac{A_e}{2}\right) (X+Y) \exp\left(in_i - \frac{A_e}{2}\right) (X-Y)^* \right] \\
F_{12} &= \exp(-A_e) \text{Re}[(X+Y)(X-Y)^*] \\
F_{12} &= \exp(-A_e) (|X|^2 - |Y|^2)
\end{aligned}$$

$$F_{13} = F_{14} = \text{Re}(J_1 J_3^*) = \exp(-A_e) \text{Re}(XZ^* + YZ^*)$$

$$F_{32} = F_{23} = F_{42} = \text{Re}(J_2 J_3^*) = \exp(-A_e) \text{Re}(XZ^* - YZ^*)$$

$$F_{34} = \text{Re}(J_3 J_4^*) = \exp(-A_e) |Z|^2$$

$$G_{12} = \text{Im}(J_1^* J_2)$$

$$G_{12} = \text{Im} \left[\exp \left(in_i - \frac{A_e}{2} \right) (X + Y)^* \exp \left(-in_i - \frac{A_e}{2} \right) (X - Y) \right]$$

$$G_{12} = \exp(-A_e) \text{Im}[(X + Y)^*(X - Y)]$$

$$G_{12} = \exp(-A_e) \text{Im}(-X^*Y + Y^*X)$$

$$G_{13} = G_{14} = \text{Im}(J_1^* J_3)$$

$$G_{13} = G_{14} = \exp(-A_e) \text{Im}[(X + Y)^*(Z)]$$

$$G_{13} = G_{14} = \exp(-A_e) \text{Im}(X^*Z + Y^*Z)$$

$$G_{32} = G_{42} = -G_{23} = -\text{Im}(J_2^* J_3)$$

$$G_{32} = G_{42} = -G_{23} = -\exp(-A_e) \text{Im}[(X - Y)^*(Z)]$$

$$G_{32} = G_{42} = -G_{23} = \exp(-A_e) \text{Im}(-X^*Z + Y^*Z)$$

$$G_{34} = \text{Im}(J_3^* J_4)$$

$$G_{34} = \exp(-A_e) \text{Im}(|Z|^2) = 0$$

Based on the values of the parameters E_i , F_{ij} , and G_{ij} obtained above let us now obtain the elements of the Mueller matrix for an optical sample containing simultaneously isotropic retardance, isotropic absorbance, and noncoaxial linear birefringence and linear dichroism using equation 3.20.

$$M_{11} = \frac{1}{2}(E_1 + E_2 + E_3 + E_4) = \exp(-A_e) (|X|^2 + |Y|^2 + |Z|^2)$$

$$M_{12} = \frac{1}{2}(E_1 - E_2 - E_3 + E_4)$$

$$M_{12} = \exp(-A_e)(XY^* + YX^*) = 2 \exp(-A_e) \operatorname{Re}(X^*Y)$$

$$M_{13} = F_{13} + F_{42} = 2 \exp(-A_e) \operatorname{Re}(XZ^*)$$

$$M_{14} = -G_{13} - G_{42} = -2 \exp(-A_e) \operatorname{Im}(Y^*Z)$$

$$M_{14} = 2 \exp(-A_e) \operatorname{Im}(YZ^*)$$

$$M_{21} = \frac{1}{2}(E_1 - E_2 + E_3 - E_4)$$

$$M_{21} = \exp(-A_e)(+XY^* + YX^*) = 2 \exp(-A_e) \operatorname{Re}(X^*Y)$$

$$M_{22} = \frac{1}{2}(E_1 + E_2 - E_3 - E_4) = \exp(-A_e)(|X|^2 + |Y|^2 - |Z|^2)$$

$$M_{23} = F_{13} - F_{42} = 2 \exp(-A_e) \operatorname{Re}(YZ^*)$$

$$M_{24} = -G_{13} + G_{42} = -2 \exp(-A_e) \operatorname{Im}(X^*Z) = 2 \operatorname{Im} \exp(-A_e)(Z^*X)$$

$$M_{31} = F_{14} + F_{32} = 2 \exp(-A_e) \operatorname{Re}(XZ^*) = 2 \exp(-A_e) \operatorname{Re}(X^*Z)$$

$$M_{32} = F_{14} - F_{32} = 2 \exp(-A_e) \operatorname{Re}(YZ^*)$$

$$M_{33} = F_{12} + F_{34} = \exp(-A_e)(|X|^2 - |Y|^2 + |Z|^2)$$

$$M_{34} = -G_{12} + G_{34} = 2 \exp(-A_e) \operatorname{Im}(X^*Y)$$

$$M_{41} = G_{14} + G_{32} = 2 \exp(-A_e) \operatorname{Im}(Y^*Z)$$

$$M_{42} = G_{14} - G_{32} = 2 \exp(-A_e) \operatorname{Im}(X^*Z)$$

$$M_{43} = G_{12} + G_{34} = 2 \exp(-A_e) \operatorname{Im}(Y^*X)$$

$$M_{44} = F_{12} - F_{34} = \exp(-A_e)(|X|^2 - |Y|^2 - |Z|^2)$$

Based on the elements of the Mueller matrix obtained above the Mueller matrix for an optical sample containing simultaneously isotropic retardance, isotropic absorbance, and noncoaxial linear birefringence and linear dichroism is given in equation A.37

$$M = e^{-A_e} \begin{bmatrix} |X|^2 + |Y|^2 + |Z|^2 & 2 \operatorname{Re}(X^*Y) & 2 \operatorname{Re}(X^*Z) & 2 \operatorname{Im}(YZ^*) \\ 2 \operatorname{Re}(X^*Y) & |X|^2 + |Y|^2 - |Z|^2 & 2 \operatorname{Re}(YZ^*) & 2 \operatorname{Im}(Z^*X) \\ 2 \operatorname{Re}(X^*Z) & 2 \operatorname{Re}(YZ^*) & |X|^2 - |Y|^2 + |Z|^2 & 2 \operatorname{Im}(X^*Y) \\ 2 \operatorname{Im}(Y^*Z) & 2 \operatorname{Im}(X^*Z) & 2 \operatorname{Im}(Y^*X) & |X|^2 - |Y|^2 - |Z|^2 \end{bmatrix} \quad \text{A.37}$$

The quantities X , Y , and Z in equation A.37 are defined in equation A.36.

A.6 Special forms of the Mueller matrix

Similar to the Jones matrix, the Mueller matrix given in equation A.37 can be simplified for various special cases. Let us first examine the Mueller matrix for an optical sample containing simultaneously non-coaxial linear birefringence and linear dichroism without isotropic retardance or isotropic absorbance. For such a case $A_e = 0$ and equation A.38 gives the appropriate Mueller matrix.

$$M = \begin{bmatrix} |X|^2 + |Y|^2 + |Z|^2 & 2 \operatorname{Re}(X^*Y) & 2 \operatorname{Re}(X^*Z) & 2 \operatorname{Im}(YZ^*) \\ 2 \operatorname{Re}(X^*Y) & |X|^2 + |Y|^2 - |Z|^2 & 2 \operatorname{Re}(YZ^*) & 2 \operatorname{Im}(Z^*X) \\ 2 \operatorname{Re}(X^*Z) & 2 \operatorname{Re}(YZ^*) & |X|^2 - |Y|^2 + |Z|^2 & 2 \operatorname{Im}(X^*Y) \\ 2 \operatorname{Im}(Y^*Z) & 2 \operatorname{Im}(X^*Z) & 2 \operatorname{Im}(Y^*X) & |X|^2 - |Y|^2 - |Z|^2 \end{bmatrix} \quad \text{A.38}$$

Let us now examine the Mueller matrix for coaxial linear birefringence and linear dichroism. The mathematical condition for coaxial linear birefringence and linear dichroism is explained in equation A.23. The parameter H is given in equation A.26. Using equations A.26, A.28, and A.36 we get equation A.39

$$X = \cosh \frac{\nu}{2} \cos \frac{\mu}{2} + i \sinh \frac{\nu}{2} \sin \frac{\mu}{2} \quad \text{A.39}$$

Using equations A.36, A.26, and A.23 we get

$$Y = -\cos 2\theta \sinh H$$

Substituting for $\sinh H$ using equation A.28 we get

$$Y = -\sinh \frac{\nu}{2} \cos \frac{\mu}{2} \cos 2\theta - i \cosh \frac{\nu}{2} \sin \frac{\mu}{2} \cos 2\theta \quad \text{A.40}$$

And similarly

$$Z = -\sinh \frac{\nu}{2} \cos \frac{\mu}{2} \sin 2\theta - i \cosh \frac{\nu}{2} \sin \frac{\mu}{2} \sin 2\theta \quad \text{A.41}$$

We obtain the Mueller matrix for an optical sample containing simultaneously coaxial linear birefringence and linear dichroism by substituting equations A.39, A.40, and A.41 in equation A.38. The elements of the Mueller matrix are obtained as follows

$$\begin{aligned} M_{11} &= |X|^2 + |Y|^2 + |Z|^2 \\ M_{11} &= \cosh^2 \frac{\nu}{2} \cos^2 \frac{\mu}{2} + \sinh^2 \frac{\nu}{2} \sin^2 \frac{\mu}{2} + \sinh^2 \frac{\nu}{2} \cos^2 \frac{\mu}{2} (\cos^2 2\theta + \sin^2 2\theta) \\ &\quad + \cosh^2 \frac{\nu}{2} \sin^2 \frac{\mu}{2} (\cos^2 2\theta + \sin^2 2\theta) \\ M_{11} &= \cosh^2 \frac{\nu}{2} \left(\cos^2 \frac{\mu}{2} + \sin^2 \frac{\mu}{2} \right) + \sinh^2 \frac{\nu}{2} \left(\cos^2 \frac{\mu}{2} + \sin^2 \frac{\mu}{2} \right) = \cosh \nu \end{aligned}$$

$$M_{12} = M_{21} = 2 \operatorname{Re}(X^* Y)$$

$$M_{12} = M_{21} = -2 \cosh \frac{\nu}{2} \sinh \frac{\nu}{2} \cos^2 \frac{\mu}{2} \cos 2\theta - 2 \cosh \frac{\nu}{2} \sinh \frac{\nu}{2} \sin^2 \frac{\mu}{2} \cos 2\theta$$

$$M_{12} = M_{21} = -\sinh \nu \cos 2\theta$$

$$M_{13} = M_{31} = 2 \operatorname{Re}(X^* Z) = -\sinh \nu \sin 2\theta$$

$$M_{14} = M_{41} = 2 \operatorname{Im}(YZ^*) = 0$$

$$M_{22} = |X|^2 + |Y|^2 - |Z|^2$$

$$M_{22} = \cosh^2 \frac{\nu}{2} \cos^2 \frac{\mu}{2} + \sinh^2 \frac{\nu}{2} \sin^2 \frac{\mu}{2} + \sinh^2 \frac{\nu}{2} \cos^2 \frac{\mu}{2} \cos^2 2\theta$$

$$+ \cosh^2 \frac{\nu}{2} \sin^2 \frac{\mu}{2} \cos^2 2\theta - \sinh^2 \frac{\nu}{2} \cos^2 \frac{\mu}{2} \sin^2 2\theta - \cosh^2 \frac{\nu}{2} \sin^2 \frac{\mu}{2} \sin^2 2\theta$$

$$M_{22} = \left(\frac{\cosh \nu + 1}{2} \right) \left(\frac{\cos \mu + 1}{2} \right) + \left(\frac{\cosh \nu - 1}{2} \right) \left(\frac{1 - \cos \mu}{2} \right)$$

$$+ \left(\frac{\cosh \nu - 1}{2} \right) \left(\frac{\cos \mu + 1}{2} \right) \cos^2 2\theta + \left(\frac{\cosh \nu + 1}{2} \right) \left(\frac{1 - \cos \mu}{2} \right) \cos^2 2\theta$$

$$- \left(\frac{\cosh \nu - 1}{2} \right) \left(\frac{\cos \mu + 1}{2} \right) \sin^2 2\theta - \left(\frac{\cosh \nu + 1}{2} \right) \left(\frac{1 - \cos \mu}{2} \right) \sin^2 2\theta$$

$$M_{22} = \cosh \nu \cos^2 2\theta + \cos \mu \sin^2 2\theta$$

$$M_{23} = M_{32} = 2 \operatorname{Re}(YZ^*)$$

$$M_{23} = M_{32} = 2 \sin 2\theta \cos 2\theta \left(\sinh^2 \frac{\nu}{2} \cos^2 \frac{\mu}{2} + \cosh^2 \frac{\nu}{2} \sin^2 \frac{\mu}{2} \right)$$

$$M_{23} = M_{32} = 2 \sin 2\theta \cos 2\theta \left[\left(\sinh^2 \frac{\nu}{2} - \cosh^2 \frac{\nu}{2} \right) \cos^2 \frac{\mu}{2} + \cosh^2 \frac{\nu}{2} \right]$$

$$M_{23} = M_{32} = \sin 2\theta \cos 2\theta (\cosh \nu - \cos \mu)$$

$$M_{24} = -M_{42} = 2 \operatorname{Im}(Z^* X)$$

$$M_{24} = -M_{42} = 2 \cosh^2 \frac{\nu}{2} \sin \frac{\mu}{2} \cos \frac{\mu}{2} \sin 2\theta - 2 \sinh^2 \frac{\nu}{2} \sin \frac{\mu}{2} \cos \frac{\mu}{2} \sin 2\theta$$

$$M_{24} = -M_{42} = \sin \mu \sin 2\theta$$

$$M_{33} = |X|^2 - |Y|^2 + |Z|^2$$

$$M_{33} = \cosh^2 \frac{\nu}{2} \cos^2 \frac{\mu}{2} + \sinh^2 \frac{\nu}{2} \sin^2 \frac{\mu}{2} - \sinh^2 \frac{\nu}{2} \cos^2 \frac{\mu}{2} \cos^2 2\theta$$

$$- \cosh^2 \frac{\nu}{2} \sin^2 \frac{\mu}{2} \cos^2 2\theta + \sinh^2 \frac{\nu}{2} \cos^2 \frac{\mu}{2} \sin^2 2\theta + \cosh^2 \frac{\nu}{2} \sin^2 \frac{\mu}{2} \sin^2 2\theta$$

$$M_{33} = \frac{1}{4} \left\{ \begin{aligned} &2 \cosh \nu + 2 \cos \mu - 2 \cosh \nu \cos^2 2\theta \\ &+ 2 \cosh \nu \sin^2 2\theta + 2 \cos \mu \cos^2 2\theta - 2 \cos \mu \sin^2 2\theta \end{aligned} \right\}$$

$$M_{33} = \cosh \nu \sin^2 2\theta + \cos \mu \cos^2 2\theta$$

$$M_{34} = -M_{43} = 2 \operatorname{Im}(X^* Y)$$

$$M_{34} = -M_{43} = 2 \sinh^2 \frac{\nu}{2} \sin \frac{\mu}{2} \cos \frac{\mu}{2} \cos 2\theta - 2 \cosh^2 \frac{\nu}{2} \sin \frac{\mu}{2} \cos \frac{\mu}{2} \cos 2\theta$$

$$M_{34} = -M_{43} = -\sin \mu \cos 2\theta$$

$$M_{44} = |X|^2 - |Y|^2 - |Z|^2$$

$$M_{44} = \cosh^2 \frac{\nu}{2} \left(\cos^2 \frac{\mu}{2} - \sin^2 \frac{\mu}{2} \right) - \sinh^2 \frac{\nu}{2} \left(\cos^2 \frac{\mu}{2} - \sin^2 \frac{\mu}{2} \right)$$

$$M_{44} = \cos \mu$$

Using the elements derived above the Mueller matrix for an optical sample with coaxial linear birefringence and linear dichroism is given in equation A.42

$$M = \begin{bmatrix} \cosh \nu & -\sinh \nu \cos 2\theta & -\sinh \nu \sin 2\theta & 0 \\ -\sinh \nu \cos 2\theta & \cosh \nu \cos^2 2\theta + \cos \mu \sin^2 2\theta & \sin 2\theta \cos 2\theta (\cosh \nu - \cos \mu) & \sin \mu \sin 2\theta \\ -\sinh \nu \sin 2\theta & \sin 2\theta \cos 2\theta (\cosh \nu - \cos \mu) & \cosh \nu \sin^2 2\theta + \cos \mu \cos^2 2\theta & -\sin \mu \cos 2\theta \\ 0 & -\sin \mu \sin 2\theta & \sin \mu \cos 2\theta & \cos \mu \end{bmatrix}$$

A.42

The Mueller matrix for an optical sample containing simultaneously, isotropic absorbance, isotropic retardance, and coaxial linear birefringence and linear dichroism is given in equation A.43.

$$M = e^{-A_e} \begin{bmatrix} \cosh \nu & -\sinh \nu \cos 2\theta & -\sinh \nu \sin 2\theta & 0 \\ -\sinh \nu \cos 2\theta & \cosh \nu \cos^2 2\theta + \cos \mu \sin^2 2\theta & \sin 2\theta \cos 2\theta (\cosh \nu - \cos \mu) & \sin \mu \sin 2\theta \\ -\sinh \nu \sin 2\theta & \sin 2\theta \cos 2\theta (\cosh \nu - \cos \mu) & \cosh \nu \sin^2 2\theta + \cos \mu \cos^2 2\theta & -\sin \mu \cos 2\theta \\ 0 & -\sin \mu \sin 2\theta & \sin \mu \cos 2\theta & \cos \mu \end{bmatrix}$$

A.43

Similar to the Jones matrix we can simplify equation A.42 for the cases of purely linear birefringent and purely linear dichroic samples. For a purely linear birefringent sample the condition in equation A.29 applies and we have

$$M = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos^2 2\chi + \cos \mu \sin^2 2\chi & (1 - \cos \mu) \sin 2\chi \cos 2\chi & \sin \mu \sin 2\chi \\ 0 & (1 - \cos \mu) \sin 2\chi \cos 2\chi & \sin^2 2\chi + \cos \mu \cos^2 2\chi & -\sin \mu \cos 2\chi \\ 0 & -\sin \mu \sin 2\chi & \sin \mu \cos 2\chi & \cos \mu \end{bmatrix} \quad A.44$$

Similarly for a purely linear dichroic sample we apply the condition in equation A.31 to equation A.42 and we get

$$M = \begin{bmatrix} \cosh \nu & -\sinh \nu \cos 2\phi_d & -\sinh \nu \sin 2\phi_d & 0 \\ -\sinh \nu \cos 2\phi_d & \cosh \nu \cos^2 2\phi_d + \sin^2 2\phi_d & (\cosh \nu - 1) \sin 2\phi_d \cos 2\phi_d & 0 \\ -\sinh \nu \sin 2\phi_d & (\cosh \nu - 1) \sin 2\phi_d \cos 2\phi_d & \cosh \nu \sin^2 2\phi_d + \cos^2 2\phi_d & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \quad A.45$$

Similar to the Jones matrix we can simplify the Mueller matrix for simultaneous noncoaxial linear birefringence and linear dichroism in the limit of small anisotropies. To do this we apply the condition in equation A.33 and equation A.34 to the Mueller matrix in equation A.42. Doing so, equation A.46 gives the Mueller

matrix for simultaneous noncoaxial linear birefringence and linear dichroism in the limit of small anisotropies

$$M = \begin{bmatrix} 1 & -\nu \cos 2\phi_d & -\nu \sin 2\phi_d & 0 \\ -\nu \cos 2\phi_d & 1 & 0 & \mu \sin 2\chi \\ -\nu \sin 2\phi_d & 0 & 1 & -\mu \cos 2\chi \\ 0 & -\mu \sin 2\chi & \mu \cos 2\chi & 1 \end{bmatrix} \quad \text{A.46}$$

A.7 Comparison of the Jones and Mueller matrices with published literature

Jensen *et al.* [23] have derived the Jones and Mueller matrices for samples with simultaneous isotropic absorbance, isotropic refractive index, linear birefringence, linear dichroism, circular birefringence and circular dichroism. The methodology followed by Jensen *et al.* [23] to obtain these matrices is different from that followed here. They have used an approach called as the Parkes coherency representation. The results are in terms of two linear birefringence and linear dichroism quantities. In contrast, orientation angles are used in this work. The Jones matrix derived in this paper (equation A.22) and all the parameters involved agree with the Jones matrix derived by Jensen *et al.* [23]. However, the Mueller matrix is in a formulation that is difficult to compare. The simplified cases considered by Jensen *et al.* [23] limit us to the cases in which light is linearly polarized in the direction of the optic axis. We are not limited by angle in the present work. We have also considered other simplifications: coaxial linear birefringence and linear dichroism and the limit of small anisotropies in this work.

Schellman and Jensen [26] list the Mueller matrix for an optical sample similar to that considered by Jensen *et al.* [23]. However, the parameters, h and $\bar{h}$ differ by a factor of $1/\sqrt{2}$ in the present work and Jensen *et al.* [23] with that by Schellman and Jensen [26]. Schellman and Jensen [26] have not considered any simplifying cases of the general Mueller matrix. They also do not list the Jones matrix of the sample.

Johnson *et al.* [59] lists the Jones matrix of the optical sample containing simultaneously isotropic absorbance, isotropic refractive index, linear birefringence and linear dichroism. This result is in terms of the angles between the optic axes of linear birefringence and linear dichroism. The Jones matrix listed however, does not consider the angle made by the optic axes with components of the electric field vector. The Jones matrix also does not simplify to the corresponding Jones matrix for coaxial linear birefringence and linear dichroism (see equation A.27). In contrast Johnson [60] lists the Jones matrix in terms of orientation angles for linear birefringence and linear dichroism. The definition of retardance used by Johnson [60] does not include the negative sign shown in equation 3.23. The Jones matrix and the parameters listed by Johnson [60] are however the same as in this paper. It is thought that the absence of the negative sign is a typographic error.

Fuller [58] lists the Jones and Mueller matrices for the cases considered here. However, he does not consider the presence of isotropic retardance and isotropic absorbance. Fuller [58] defines retardance without the negative sign and obtains the

corresponding changes in the Jones matrix. It is however, difficult to see how Fuller [58] obtains the Mueller matrix from his listed Jones matrix of the sample. For example the Jones matrix listed for a sample with simultaneous linear birefringence and linear dichroism by Fuller [58] is in the form

$$\mathbf{J} = \begin{bmatrix} X - Y & -Z \\ -Z & X + Y \end{bmatrix} \quad \text{A.47}$$

Using equation A.46 with the definitions in equation 3.21 we get

$$\begin{aligned} E_1 &= |X|^2 - XY^* - YX^* + |Z|^2 \\ E_2 &= |X|^2 + XY^* + YX^* + |Z|^2 \\ E_3 &= E_4 = |Z|^2 \end{aligned}$$

We now obtain the Mueller matrix element for the first row and second column

$$\begin{aligned} M_{12} &= \frac{1}{2}(E_1 - E_2 - E_3 + E_4) \\ M_{12} &= \frac{1}{2}(-2XY^* - 2YX^*) \\ M_{12} &= -2 \operatorname{Re}(X^*Y) \end{aligned}$$

Fuller [58] however lists this element without the negative sign.

APPENDIX B

OPERATION OF THE SPECTROPOLARIMETER

B.1 Mathematics of the optical train

Mathematical equations on which the spectropolarimeter is designed are derived in this appendix. The optical setup is shown in figure 4.1. The near-infrared acousto-optic tunable filter (NIR-AOTF) produces monochromatic light of wavelength λ . A general Stokes vector given in equation B.1 represents the polarization state for this light beam

$$\mathbf{S} = \begin{bmatrix} S_0(\lambda) \\ S_1(\lambda) \\ S_2(\lambda) \\ S_3(\lambda) \end{bmatrix} \quad \text{B.1}$$

The light produced by the NIR-AOTF is incident on a linear polarizer. The linear polarizer is aligned such that the intensity of light emerging from the polarizer is maximized. This angle is defined as 0° and all angles in the system are referenced to this angle. The Mueller matrix for a linear polarizer aligned at 0° ($\mathbf{M}_{lp}$) can be obtained from the Mueller matrix for linear polarizer given in table 3.3 with $\theta_{LP} = 0^\circ$. The Stokes vector of light emerging from the linear polarizer ($\mathbf{S}_I$) is derived using equation 3.13 as shown below

$$\mathbf{S}_I = \mathbf{M}_{lp} \cdot \mathbf{S}$$

$$\mathbf{S}_I = \frac{1}{2} \begin{bmatrix} 1 & 1 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} S_0(\lambda) \\ S_1(\lambda) \\ S_2(\lambda) \\ S_3(\lambda) \end{bmatrix}$$

$$\mathbf{S}_I = \frac{S_0(\lambda) + S_1(\lambda)}{2} \begin{bmatrix} 1 \\ 1 \\ 0 \\ 0 \end{bmatrix} = I_0(\lambda) \begin{bmatrix} 1 \\ 1 \\ 0 \\ 0 \end{bmatrix} \quad \text{B.2}$$

In equation B.2 we have written

$$I_0(\lambda) = \frac{S_0(\lambda) + S_1(\lambda)}{2}$$

The intensity of light, $I_0(\lambda)$, emerging from the linear polarizer is different from the lamp intensity $S_0(\lambda)$. This should be taken in consideration if it desired to use the lamp intensity for referencing. Linearly polarized light obtained through the linear polarizer passes through the photoelastic modulator (PEM) aligned at 45° . Procedure for aligning the PEM to 45° is given in section B.5. The PEM is essentially a retarder with a variable retardance. Mueller matrix for a retarder is given in table 3.3. We obtain the Mueller matrix for the PEM ($\mathbf{M}_{PEM}$) from table 3.3 on substituting $\chi = 45^\circ$. The Stokes vector for light emerging from the PEM ($\mathbf{S}_2$) can be obtained using equation 3.13 and equation B.2 as follows

$$\mathbf{S}_2 = \mathbf{M}_{PEM} \cdot \mathbf{S}_I$$

$$S_2 = I_0(\lambda) \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos \mu_{PEM} & 0 & \sin \mu_{PEM} \\ 0 & 0 & 1 & 0 \\ 0 & -\sin \mu_{PEM} & 0 & \cos \mu_{PEM} \end{bmatrix} \cdot \begin{bmatrix} 1 \\ 1 \\ 0 \\ 0 \end{bmatrix}$$

$$S_2 = I_0(\lambda) \begin{bmatrix} 1 \\ \cos \mu_{PEM} \\ 0 \\ -\sin \mu_{PEM} \end{bmatrix} \quad \text{B.3}$$

Light modulated by the PEM passes through the sample. The sample can be in any form (solid or liquid). At this time, a general Mueller matrix given in equation B.4 represents the Mueller matrix of the sample.

$$M_{\text{sample}} = \begin{bmatrix} M_{11} & M_{12} & M_{13} & M_{14} \\ M_{21} & M_{22} & M_{23} & M_{24} \\ M_{31} & M_{32} & M_{33} & M_{34} \\ M_{41} & M_{42} & M_{43} & M_{44} \end{bmatrix} \quad \text{B.4}$$

The Stokes vector of light emerging from the sample (S_3) can be obtained using equations 3.13, B.3, and B.4 as follows

$$S_3 = M_{\text{sample}} \cdot S_2$$

$$S_3 = I_0(\lambda) \begin{bmatrix} M_{11} & M_{12} & M_{13} & M_{14} \\ M_{21} & M_{22} & M_{23} & M_{24} \\ M_{31} & M_{32} & M_{33} & M_{34} \\ M_{41} & M_{42} & M_{43} & M_{44} \end{bmatrix} \cdot \begin{bmatrix} 1 \\ \cos \mu_{PEM} \\ 0 \\ -\sin \mu_{PEM} \end{bmatrix}$$

$$S_3 = I_0(\lambda) \begin{bmatrix} M_{11} + M_{12} \cos \mu_{PEM} - M_{14} \sin \mu_{PEM} \\ M_{21} + M_{22} \cos \mu_{PEM} - M_{24} \sin \mu_{PEM} \\ M_{31} + M_{32} \cos \mu_{PEM} - M_{34} \sin \mu_{PEM} \\ M_{41} + M_{42} \cos \mu_{PEM} - M_{44} \sin \mu_{PEM} \end{bmatrix} \quad \text{B.5}$$

Light emerging from the sample is incident on the polarizing beam-splitter. This light is split into two beams in the polarizing beam-splitter. The beam-splitter is aligned such that the emerging beams are polarized at 45° and 135° with respect to the linear polarizer. The beam emerging from face 1 is aligned at 45° and from face 2 at 135° respectively. The alignment procedure is detailed in B.4. The polarizing beam-splitter is assumed to act as two linear polarizers one of which is aligned at 45° and the other at 135° . We can get Mueller matrices for the two faces from table 3.3 by substituting $\theta_{LP} = 45^\circ$ (M_{face1}) and $\theta_{LP} = 135^\circ$ (M_{face2}) in the Mueller matrix of a linear polarizer. The Stokes vector of light emerging from face 1 (S_{face1}) of the polarizing beam-splitter obtained using equations 3.13 and B.5 as follows

$$S_{face1} = M_{face1} \cdot S_3$$

$$S_{face1} = I_0(\lambda) \cdot \frac{1}{2} \begin{bmatrix} 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \\ 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \cdot \begin{bmatrix} M_{11} + M_{12} \cos \mu_{PEM} - M_{14} \sin \mu_{PEM} \\ M_{21} + M_{22} \cos \mu_{PEM} - M_{24} \sin \mu_{PEM} \\ M_{31} + M_{32} \cos \mu_{PEM} - M_{34} \sin \mu_{PEM} \\ M_{41} + M_{42} \cos \mu_{PEM} - M_{44} \sin \mu_{PEM} \end{bmatrix}$$

$$S_{face1} = \frac{I_0(\lambda)}{2} \begin{bmatrix} (M_{11} + M_{31}) + (M_{12} + M_{32}) \cos \mu_{PEM} - (M_{14} + M_{34}) \sin \mu_{PEM} \\ 0 \\ (M_{11} + M_{31}) + (M_{12} + M_{32}) \cos \mu_{PEM} - (M_{14} + M_{34}) \sin \mu_{PEM} \\ 0 \end{bmatrix} \quad B.6$$

Similarly, the Stokes vector of light emerging from face 2 (S_{face2}) of the polarizing beam-splitter can be obtained as follows

$$S_{face2} = M_{face2} \cdot S_3$$

$$\begin{aligned}
S_{face_2} &= I_0(\lambda) \cdot \frac{1}{2} \begin{bmatrix} 1 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 \\ -1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \cdot \begin{bmatrix} M_{11} + M_{12} \cos \mu_{PEM} - M_{14} \sin \mu_{PEM} \\ M_{21} + M_{22} \cos \mu_{PEM} - M_{24} \sin \mu_{PEM} \\ M_{31} + M_{32} \cos \mu_{PEM} - M_{34} \sin \mu_{PEM} \\ M_{41} + M_{42} \cos \mu_{PEM} - M_{44} \sin \mu_{PEM} \end{bmatrix} \\
S_{face_2} &= \frac{I_0(\lambda)}{2} \begin{bmatrix} (M_{11} - M_{31}) + (M_{12} - M_{32}) \cos \mu_{PEM} - (M_{14} - M_{34}) \sin \mu_{PEM} \\ 0 \\ (-M_{11} + M_{31}) + (-M_{12} + M_{32}) \cos \mu_{PEM} - (-M_{14} + M_{34}) \sin \mu_{PEM} \\ 0 \end{bmatrix} \quad B.7
\end{aligned}$$

Light emerging from the two faces of the polarizing beam-splitter is incident on the two sample detectors (detectors 1 and 2 in figure 4.1). The first element of the Stokes vectors in equations B.6 and B.7 give the intensities of light incident on the two detectors. At the detectors light intensity is linearly converted to a voltage signal. The voltage signals obtained from the detectors are given in equations B.8 and B.9

$$V_1 = \frac{c_1 I_0(\lambda)}{2} [(M_{11} + M_{31}) + (M_{12} + M_{32}) \cos \mu_{PEM} - (M_{14} + M_{34}) \sin \mu_{PEM}] \quad B.8$$

$$V_2 = \frac{c_2 I_0(\lambda)}{2} [(M_{11} - M_{31}) + (M_{12} - M_{32}) \cos \mu_{PEM} - (M_{14} - M_{34}) \sin \mu_{PEM}] \quad B.9$$

The effects of linear conversion from light intensity to voltage and of the detector electronics are compiled in the constants c_1 and c_2 in equations B.8 and B.9 respectively. These constants may be a function of wavelength based on the wavelength dependence of the detector electronics.

B.2 Mathematical effects of the PEM

The retardance of the PEM (μ_{PEM}) is a sinusoidal function of time as given in equation B.10.

$$\mu_{\text{PEM}} = \delta_0 \sin \omega t \quad \text{B.10}$$

In equation B.10 the maximum retardance is δ_0 (in radians) and ω is the frequency (in kHz) of the sinusoidal variation in retardance of the PEM. The time, t , is in seconds $\times 1000$. In the present work $\omega = 42$ kHz. Substituting equation B.10 in equation B.8 we get

$$V_1 = \frac{c_1 I_0(\lambda)}{2} \left[(M_{11} + M_{31}) + (M_{12} + M_{32}) \cos(\delta_0 \sin \omega t) - (M_{14} + M_{34}) \sin(\delta_0 \sin \omega t) \right] \quad \text{B.11}$$

We can write equation B.11 in a different mathematical form using equation B.12

$$\begin{aligned} \cos(\delta_0 \sin \omega t) &= J_0(\delta_0) + 2 \sum_{k=1}^{\infty} J_{2k}(\delta_0) \cos(2k\omega t) \\ \sin(\delta_0 \sin \omega t) &= 2 \sum_{k=1}^{\infty} J_{2k-1}(\delta_0) \sin[(2k-1)\omega t] \end{aligned} \quad \text{B.12}$$

In equation B.12, the term $J_i(\delta_0)$ is the value of the Bessel's function of order i at δ_0 .

Substituting equation B.12 in equation B.11 we get

$$V_1 = \frac{c_1 I_0(\lambda)}{2} \left\{ (M_{11} + M_{31}) + (M_{12} + M_{32}) [J_0(\delta_0) + 2J_2(\delta_0) \cos 2\omega t + \dots] \right. \\ \left. - (M_{14} + M_{34}) [2J_1(\delta_0) \sin \omega t + \dots] \right\}$$

The maximum amplitude of retardance, δ_0 , is in radians. It can be adjusted to different values. In this work, it is adjusted such that $J_0(\delta_0) = 0$. This occurs at $\delta_0 = 2.405$ radians. For this value we get

$$V_1 = \frac{c_1 I_0(\lambda)}{2} \left\{ (M_{11} + M_{31}) + (M_{12} + M_{32}) [2J_2(\delta_0) \cos 2\omega t + \dots] \right. \\ \left. - (M_{14} + M_{34}) [2J_1(\delta_0) \sin \omega t + \dots] \right\}$$

At the value of δ_0 being used (2.405 radians) the Bessel function values for orders greater than 2 can be neglected. For example, at $\delta_0 = 2.405$ radians we have $J_1(\delta_0) = 0.519$, $J_2(\delta_0) = 0.432$, $J_3(\delta_0) = 0.199$, and $J_4(\delta_0) = 0.0648$. Ignoring Bessel function terms with orders greater than two we get

$$V_1 = \frac{c_1 I_0(\lambda)}{2} \{ (M_{11} + M_{31}) + (M_{12} + M_{32}) [2J_2(\delta_0) \cos 2\omega t] - (M_{14} + M_{34}) [2J_1(\delta_0) \sin \omega t] \}$$

And rearranging we get

$$V_1 = \frac{c_1 I_0(\lambda)}{2} \{ (M_{11} + M_{31}) - 2J_1(\delta_0) (M_{14} + M_{34}) \sin \omega t + 2J_2(\delta_0) (M_{12} + M_{32}) \cos 2\omega t \}$$

B.13

We can similarly write for light incident on detector 2, by substituting equations B.10 and B.12 in equation B.9

$$V_2 = \frac{c_2 I_0(\lambda)}{2} \{ (M_{11} - M_{31}) - 2J_1(\delta_0) (M_{14} - M_{34}) \sin \omega t + 2J_2(\delta_0) (M_{12} - M_{32}) \cos 2\omega t \}$$

B.14

Equations B.13 and B.14 are the mathematical equations of the voltage signals produced by the detectors taking in account the sinusoidal variation in PEM retardance. We measure the three Fourier coefficients (direct current, component at ω , and component at 2ω) for both the sample detectors. The three coefficients measured for detector 1 are given in equation B.15.

$$\begin{aligned}
V_1^{DC} &= \frac{c_1 I_0(\lambda)}{2} (M_{11} + M_{31}) \\
V_1^\omega &= -c_1 I_0(\lambda) J_1(\delta_0) (M_{14} + M_{34}) \\
V_1^{2\omega} &= c_1 I_0(\lambda) J_2(\delta_0) (M_{12} + M_{32})
\end{aligned} \tag{B.15}$$

Similarly, the three coefficients measured for detector 2 are given in equation B.16.

$$\begin{aligned}
V_2^{DC} &= \frac{c_2 I_0(\lambda)}{2} (M_{11} - M_{31}) \\
V_2^\omega &= -c_2 I_0(\lambda) J_1(\delta_0) (M_{14} - M_{34}) \\
V_2^{2\omega} &= c_2 I_0(\lambda) J_2(\delta_0) (M_{12} - M_{32})
\end{aligned} \tag{B.16}$$

B.3.1 Mathematical analysis for various forms of optical sample

Equations B.15 and B.16 give the quantities recorded through the experimental setup. We have six recorded quantities. As seen in appendix A, we have at the most five physical unknowns - isotropic absorbance (A_e), linear retardance (μ) of the sample and its orientation angle (χ) and relative absorption coefficient of the sample (ν) and its orientation angle (ϕ_d). We have also the unknown intensity of light emerging from the linear polarizer $I_0(\lambda)$ and constants due to electronics in the system c_1 and c_2 . The expansion carried out using equation B.12 have left us with two calibration constants $J_1(\delta_0)$ and $J_2(\delta_0)$. The procedure for determining the calibration constants is detailed in appendix B.6. The mathematical analysis for optical samples with different optical anisotropies is presented in the following sub-sections.

B.3.2 Purely linear birefringent optical sample

The Mueller matrix for a purely linear birefringent optical sample was derived in appendix A. Substituting the appropriate elements of the Mueller matrix from equation A.43 in equation B.15 we get equation B.17.

$$\begin{aligned} V_1^{DC} &= \frac{c_1 I_0(\lambda)}{2} \\ V_1^\omega &= c_1 I_0(\lambda) J_1(\delta_0) \sin \mu \cos 2\chi \\ V_1^{2\omega} &= c_1 I_0(\lambda) J_2(\delta_0) (1 - \cos \mu) \sin 2\chi \cos 2\chi \end{aligned} \quad \text{B.17}$$

Equation B.17 can be solved to obtain simultaneously linear retardance and orientation angle as shown below. Let us define the parameters R_1 and R_2 by equation B.18.

$$\begin{aligned} R_1 &= \frac{V_1^\omega}{2V_1^{DC} J_1(\delta_0)} = \sin \mu \cos 2\chi \\ R_2 &= \frac{V_1^{2\omega}}{2V_1^{DC} J_2(\delta_0)} = (1 - \cos \mu) \sin 2\chi \cos 2\chi \end{aligned} \quad \text{B.18}$$

From equation B.18 we get

$$\cos 2\chi = \frac{R_1}{\sin \mu} \quad \text{B.19}$$

Equation B.19 gives

$$\sin 2\chi = \sqrt{1 - \cos^2 2\chi} = \sqrt{1 - \frac{R_1^2}{\sin^2 \mu}} = \frac{\sqrt{\sin^2 \mu - R_1^2}}{\sin \mu}$$

Substituting in equation B.18 we get

$$R_2 = (1 - \cos \mu) \frac{\sqrt{\sin^2 \mu - R_1^2}}{\sin \mu} \frac{R_1}{\sin \mu}$$

$$\begin{aligned}
R_2 &= (1 - \cos \mu) \frac{R_1 \sqrt{\sin^2 \mu - R_1^2}}{\sin^2 \mu} \\
R_2 &= \frac{R_1 \sqrt{1 - \cos^2 \mu - R_1^2}}{1 + \cos \mu} \\
R_2^2 (1 + \cos \mu)^2 &= R_1^2 (1 - \cos^2 \mu - R_1^2) \\
R_2^2 + 2R_2^2 \cos \mu + R_2^2 \cos^2 \mu &= R_1^2 - R_1^2 \cos^2 \mu - R_1^4 \\
(R_1^2 + R_2^2) \cos^2 \mu + 2R_2^2 \cos \mu + (-R_1^2 + R_2^2 + R_1^4) &= 0 \\
\cos \mu &= \frac{-2R_2^2 \pm \sqrt{4R_2^4 - 4(R_1^2 + R_2^2)(-R_1^2 + R_2^2 + R_1^4)}}{2(R_1^2 + R_2^2)} \\
\cos \mu &= \frac{-R_2^2 \pm R_1^2 \sqrt{1 - R_1^2 - R_2^2}}{R_1^2 + R_2^2} \tag{B.20}
\end{aligned}$$

We can use equation B.20 to obtain the linear retardance of the sample. It is clear from equation B.20 that two possible solutions exist for $\cos(\mu)$. If we know that $|\mu| \leq \pi/2$ we must use the positive root. We use the negative root for $\pi/2 \leq |\mu| \leq \pi$. We alternate the roots every $\pi/2$ radians. We must also add the appropriate multiples of $\pi/2$ radians to the value obtained through the use of equation B.20. Once the value of linear retardance is obtained using B.20, we use equation B.19 to obtain the corresponding orientation angle. In the case for purely linear birefringent material we require only a single sample detector (we use detector 1 in figure 4.1) to obtain linear retardance and its orientation angle. If necessary, linear retardance can be converted to linear birefringence using equation 3.23.

B.3.3 Purely linear dichroic optical sample

The Mueller matrix for a purely linear birefringent optical sample was derived in appendix A. Substituting the appropriate elements of the Mueller matrix from equation A.44 in equation B.15 we get equation B.21.

$$\begin{aligned} V_1^{DC} &= \frac{c_1 I_0(\lambda)}{2} (\cosh \nu - \sinh \nu \sin 2\phi_d) \\ V_1^\omega &= 0 \\ V_1^{2\omega} &= c_1 I_0(\lambda) J_2(\delta_0) (\sinh \nu \cos 2\phi_d + (\cosh \nu - 1) \sin 2\phi_d \cos 2\phi_d) \end{aligned} \quad \text{B.21}$$

Similarly, substituting the appropriate elements from equation A.44 in equation B.16 we get equation B.22

$$\begin{aligned} V_2^{DC} &= \frac{c_2 I_0(\lambda)}{2} (\cosh \nu + \sinh \nu \sin 2\phi_d) \\ V_2^\omega &= 0 \\ V_2^{2\omega} &= c_2 I_0(\lambda) J_2(\delta_0) (\sinh \nu \cos 2\phi_d - (\cosh \nu - 1) \sin 2\phi_d \cos 2\phi_d) \end{aligned} \quad \text{B.22}$$

Using equations B.21 and B.22 we can write

$$R^{DC} = \frac{V_1^{DC}}{V_2^{DC}} = \frac{c_1 (\cosh \nu - \sinh \nu \sin 2\phi_d)}{c_2 (\cosh \nu + \sinh \nu \sin 2\phi_d)}$$

The procedure for obtaining the ratio c_1/c_2 is given in B.7. We get

$$R_c^{DC} = R^{DC} \frac{c_2}{c_1} = \frac{(\cosh \nu - \sinh \nu \sin 2\phi_d)}{(\cosh \nu + \sinh \nu \sin 2\phi_d)}$$

We can simplify the above to write

$$R_1 = \frac{1 + R_c^{DC}}{1 - R_c^{DC}} = \frac{\cosh \nu}{\sinh \nu \sin 2\phi_d} \quad \text{B.23}$$

Similarly, using equations B.21 and B.22 we get

$$R_2 = \frac{R_c^{2\omega} + 1}{R_c^{2\omega} - 1} = \frac{\sinh \nu}{(\cosh \nu - 1) \sin 2\phi_d} \quad \text{B.24}$$

Where

$$R_c^{2\omega} = \frac{c_2}{c_1} \frac{V_1^{2\omega}}{V_2^{2\omega}}$$

We obtain the values of linear dichroism and its orientation angle using equations B.23 and B.24 as shown below

$$\sin 2\phi_d = \frac{\cosh \nu}{R_1 \sinh \nu} \quad \text{B.25}$$

Substituting equation B.25 in equation B.24 we get

$$\begin{aligned} R_2 &= \frac{\sinh \nu}{(\cosh \nu - 1) \frac{\cosh \nu}{R_1 \sinh \nu}} \\ \frac{R_2}{R_1} &= \frac{\sinh^2 \nu}{\cosh \nu (\cosh \nu - 1)} \\ \frac{R_2}{R_1} &= \frac{\cosh \nu + 1}{\cosh \nu} \\ \cosh \nu &= \frac{R_1}{R_2 - R_1} \end{aligned} \quad \text{B.26}$$

Once the relative absorption coefficient of the sample is obtained using equation B.26, we use equation B.25 to obtain its orientation angle. If necessary, relative absorption coefficient can be converted to linear dichroism using equation 3.24. Since $\cosh(\nu)$ is a monotonically increasing function we do not have to add multiples of $\pi/2$ radians as required when we solved for linear birefringence.

B.3.4 Optical sample with coaxial linear birefringence and linear dichroism

The Mueller matrix for an optical sample containing simultaneously coaxial linear birefringence and linear dichroism was derived in appendix A. Substituting the appropriate elements of the Mueller matrix from equation A.42 in equation B.15 we get equation B.27.

$$\begin{aligned} V_1^{DC} &= \frac{c_1 I_0(\lambda)}{2} (\cosh \nu - \sinh \nu \sin 2\theta) \\ V_1^\omega &= c_1 I_0(\lambda) J_1(\delta_0) (\sin \mu \cos 2\theta) \\ V_1^{2\omega} &= c_1 I_0(\lambda) J_2(\delta_0) (-\sinh \nu \cos 2\theta + \sin 2\theta \cos 2\theta (\cosh \nu - \cos \mu)) \end{aligned} \quad \text{B.27}$$

And similarly substituting equation A.42 in equation B.16 we get equation B.28.

$$\begin{aligned} V_2^{DC} &= \frac{c_2 I_0(\lambda)}{2} (\cosh \nu + \sinh \nu \sin 2\theta) \\ V_2^\omega &= -c_2 I_0(\lambda) J_1(\delta_0) (\sin \mu \cos 2\theta) \\ V_2^{2\omega} &= -c_2 I_0(\lambda) J_2(\delta_0) (\sinh \nu \cos 2\theta + \sin 2\theta \cos 2\theta (\cosh \nu - \cos \mu)) \end{aligned} \quad \text{B.28}$$

A new technique based on spectroscopic referencing methods is presented here to solve equations B.27 and B.28. The voltage signal obtained at the two sample detectors in the absence of the optical sample and PEM is derived in B.7. The voltage signal is presented here in equations B.29.

$$\begin{aligned} V_1 &= \frac{c_1 I_0(\lambda)}{2} \\ V_2 &= \frac{c_2 I_0(\lambda)}{2} \end{aligned} \quad \text{B.29}$$

From equations B.27 and B.29 we get equation B.30

$$\frac{V_1^{DC}}{V_1} = \cosh \nu - \sinh \nu \sin 2\theta \quad \text{B.30}$$

Similarly, from equations B.28 and B.29 we get equation B.31.

$$\frac{V_2^{DC}}{V_2} = \cosh \nu + \sinh \nu \sin 2\theta \quad \text{B.31}$$

Using equations B.30 and B.31 we get

$$\frac{V_1^{DC}}{V_1} + \frac{V_2^{DC}}{V_2} = 2 \cosh \nu$$

And simplifying we have

$$\nu = \cosh^{-1} \left(\frac{V_1^{DC}}{2V_1} + \frac{V_2^{DC}}{2V_2} \right) \quad \text{B.32}$$

Using equations B.30 and B.31 we now obtain the orientation angle for both linear birefringence and linear dichroism as shown below.

$$\begin{aligned} \frac{V_1^{DC}}{V_1} &= \cosh \nu - \sinh \nu \sin 2\theta \\ \sin 2\theta &= \frac{1}{\sinh \nu} \left(\cosh \nu - \frac{V_1^{DC}}{V_1} \right) \\ \theta &= \frac{1}{2} \sin^{-1} \left[\frac{1}{\sinh \nu} \left(\cosh \nu - \frac{V_1^{DC}}{V_1} \right) \right] \end{aligned} \quad \text{B.33}$$

Where ν required in equation B.33 is given by equation B.32. Using equations B.27 and B.29 we get

$$\begin{aligned} \frac{V_1^{\omega}}{V_1} &= 2J_1(\delta_0) \sin \mu \cos 2\theta \\ \sin \mu &= \frac{V_1^{\omega}}{2V_1 J_1(\delta_0) \cos 2\theta} \\ \mu &= \sin^{-1} \left(\frac{V_1^{\omega}}{2V_1 J_1(\delta_0) \cos 2\theta} \right) \end{aligned} \quad \text{B.34}$$

Where θ required in equation B.34 is given by equation B.33. The procedure for obtaining the calibration constant $J_1(\delta_0)$ is given in B.6.

A problem during the use of such a reference technique is the lamp intensity fluctuations over time. These can be overcome with the use of a reference detector in the spectropolarimeter. Let voltage signal obtained from the reference detector is V_r . Then division with V_r modifies equations A.1, A.2, and A.3. All further ratios are the same. This is again similar to ordinary spectroscopic techniques. We can use equations 3.23 and 3.24 to convert the linear retardance and relative absorption coefficient to linear birefringence and linear dichroism respectively.

B.3.5 Optical sample with isotropic absorbance, isotropic retardance, and coaxial linear birefringence and linear dichroism

The Mueller matrix for such a sample is given in equation A.43. Substituting the appropriate elements in equation B.15 we get equation B.35.

$$\begin{aligned} V_1^{DC} &= \frac{c_1 I_0(\lambda)}{2} e^{-A_c} (\cosh \nu - \sinh \nu \sin 2\theta) \\ V_1^\omega &= c_1 I_0(\lambda) J_1(\delta_0) e^{-A_c} (\sin \mu \cos 2\theta) \\ V_1^{2\omega} &= c_1 I_0(\lambda) J_2(\delta_0) e^{-A_c} (-\sinh \nu \cos 2\theta + \sin 2\theta \cosh \nu (\cosh \nu - \cos \mu)) \end{aligned} \quad \text{B.35}$$

And similarly substituting equation A.43 in equation B.16 we get equation B.36.

$$\begin{aligned} V_2^{DC} &= \frac{c_2 I_0(\lambda)}{2} e^{-A_c} (\cosh \nu + \sinh \nu \sin 2\theta) \\ V_2^\omega &= -c_2 I_0(\lambda) J_1(\delta_0) e^{-A_c} (\sin \mu \cos 2\theta) \\ V_2^{2\omega} &= -c_2 I_0(\lambda) J_2(\delta_0) e^{-A_c} (\sinh \nu \cos 2\theta + \sin 2\theta \cosh \nu (\cosh \nu - \cos \mu)) \end{aligned} \quad \text{B.36}$$

Attempting to solve equations B.35 and B.36 in a manner similar to equations B.27 and B.28 leads us to equation B.37.

$$\frac{V_1^{DC}}{V_1} + \frac{V_2^{DC}}{V_2} = 2e^{-A_c} \cosh v \quad \text{B.37}$$

The terms V_1 and V_2 in equation B.37 are defined in equation B.29. Equation B.37 involves isotropic absorbance. It is not possible to eliminate the isotropic absorbance and solve for linear dichroism. An alternative is thus necessary.

During film stretching it can be assumed that isotropic absorbance remains the same and linear dichroism and linear birefringence increase monotonically from zero. Using a procedure followed in appendix A, we can show that the Mueller matrix for an optical sample containing only isotropic absorbance is given by equation B.38.

$$\mathbf{M} = e^{-A_c} \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \quad \text{B.38}$$

Substituting appropriate elements from equation B.38 in equation B.15 we get equation B.39

$$\begin{aligned} V_1^{DC} \Big|_{IA} &= \frac{c_1 I_0(\lambda)}{2} e^{-A_c} \\ V_1^{\omega} \Big|_{IA} &= 0 \\ V_1^{2\omega} \Big|_{IA} &= 0 \end{aligned} \quad \text{B.39}$$

Similarly, substituting appropriate elements from equation B.38 in equation B.16 we get equation B.40. In equation B.39 IA stands for isotropic absorbance.

$$\begin{aligned}
V_2^{DC} \Big|_{IA} &= \frac{c_2 I_0(\lambda)}{2} e^{-A_c} \\
V_2^{\omega} \Big|_{IA} &= 0 \\
V_2^{2\omega} \Big|_{IA} &= 0
\end{aligned}
\tag{B.40}$$

Using equations B.35 and B.39 we get equation B.41

$$\frac{V_1^{DC}}{V_1^{DC} \Big|_{IA}} = \cosh \nu - \sinh \nu \sin 2\theta
\tag{B.41}$$

Similarly, using equation B.36 and B.40 we get equation B.42

$$\frac{V_2^{DC}}{V_2^{DC} \Big|_{IA}} = \cosh \nu + \sinh \nu \sin 2\theta
\tag{B.42}$$

Using equations B.41 and B.42 we obtain the relative absorption coefficient of the sample presented here in equation B.43

$$\nu = \frac{1}{2} \cosh^{-1} \left(\frac{V_1^{DC}}{V_1^{DC} \Big|_{IA}} + \frac{V_2^{DC}}{V_2^{DC} \Big|_{IA}} \right)
\tag{B.43}$$

We can then use equations B.41 and B.43 to obtain the coaxial orientation angle presented here in equation B.44.

$$\theta = \frac{1}{2} \sin^{-1} \left[\frac{1}{\sinh \nu} \left(\cosh \nu - \frac{V_1^{DC}}{V_1^{DC} \Big|_{IA}} \right) \right]
\tag{B.44}$$

The linear retardance can then be obtained from equations B.35, B.39 and B.44 as follows

$$\frac{V_1^{\omega}}{V_1^{DC} \Big|_{IA}} = 2J_1(\delta_0) \sin \mu \cos 2\theta$$

$$\mu = \sin^{-1} \left(\frac{1}{2J_1(\delta_0) \cos 2\theta} \frac{V_1^\omega}{V_1^{DC} |_{IA}} \right) \quad \text{B.45}$$

B.3.6 Optical sample with circular birefringence

Fuller [58] has reported the Mueller matrix for circular birefringence given here in equation B.46.

$$M_{CB} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos 2\delta_{CB} & \sin 2\delta_{CB} & 0 \\ 0 & -\sin 2\delta_{CB} & \cos 2\delta_{CB} & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \quad \text{B.46}$$

Where

$$\delta_{CB} = \frac{2\pi \Delta n_{CB} d}{\lambda} \quad \text{B.47}$$

In equation B.47, Δn_{CB} is the circular birefringence for an optical sample of thickness d . Substituting appropriate elements of equation B.46 in equation B.15 we get

$$\begin{aligned} V_1^{DC} &= \frac{c_1 I_0(\lambda)}{2} \\ V_1^\omega &= 0 \\ V_1^{2\omega} &= -c_1 I_0(\lambda) J_2(\delta_0) \sin 2\delta_{CB} \end{aligned} \quad \text{B.48}$$

Using equation B.48 the circular birefringence of an optical sample is obtained as given in equation B.49.

$$\delta_{CB} = \frac{1}{2} \sin^{-1} \left(-\frac{V_1^{2\omega}}{2V_1^{DC} J_2(\delta_0)} \right) \quad \text{B.49}$$

B.3.7 Optical sample with circular dichroism

Fuller [58] has reported the Mueller matrix for circular dichroism given here in equation B.50.

$$M_{CB} = \begin{bmatrix} \cosh \delta_{CD} & 0 & 0 & \sinh \delta_{CD} \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ \sinh \delta_{CD} & 0 & 0 & \cosh \delta_{CD} \end{bmatrix} \quad B.50$$

Where

$$\delta_{CD} = \frac{2\pi\Delta n_{CD}d}{\lambda} \quad B.51$$

In equation B.51, Δn_{CD} is the circular birefringence for an optical sample of thickness d . Substituting appropriate elements of equation B.50 in equation B.15 we get

$$\begin{aligned} V_1^{IX} &= \frac{c_1 I_0(\lambda)}{2} \cosh \delta_{CD} \\ V_1^\omega &= -c_1 I_0(\lambda) J_1(\delta_0) \sinh \delta_{CD} \\ V_1^{2\omega} &= 0 \end{aligned} \quad B.52$$

Using equation B.52 the circular dichroism of an optical sample is obtained as given in equation B.53.

$$\delta_{CD} = \tanh^{-1} \left(-\frac{V_1^\omega}{2V_1^{IX} J_1(\delta_0)} \right) \quad B.53$$

B.4 Alignment of the polarizing beam-splitter

The polarizing beam-splitter is aligned such that the two faces are at 45° and 135° during the course of the experiment. For alignment and calibration of PEM the

two faces of the polarizing beam-splitter are at 0° and 90° respectively. The following procedure details the alignment of the polarizing beam-splitter.

- 1) Start the AOTF monochromator at some wavelength.
- 2) Introduce the linear polarizer. Rotate the linear polarizer till we observe maximum intensity of light emerging out. Define the angle of the linear polarizer to be 0° .
- 3) Introduce the polarizing beam-splitter at some angle. Rotate the polarizing beam-splitter till we observe maximum intensity of light emerging from one face and zero intensity of light emerging from the second face of the polarizing beam-splitter. At this angle the face with maximum intensity is aligned at 0° and the face with zero intensity is aligned at 45° .
- 4) Rotate the beam-splitter by 45° . By this rotation the two faces of the beam-splitter are aligned at 45° and 135° respectively.

The polarizing beam-splitter has to be used in one of two orientations. It has to be used with the two faces at 0° and 90° or with the two faces at 45° and 135° . As explained in chapter 4, a plate was built such that these changes could be carried out without the need of rotation. This is necessary, as a rotary mount that can simultaneously rotate the polarizing beam-splitter and the sample detectors is difficult to construct.

B.5 Alignment procedure for the PEM

A generalized alignment procedure for the PEM is presented in this section. The PEM is to be aligned at an angle 45° with respect to the linear polarizer. The PEM is initially introduced between the linear polarizer and the polarizing beam-splitter at some unknown angle. The polarizing beam-splitter is aligned such that the two faces are at 0° and 90° respectively. The alignment procedure for the polarizing beam-splitter is given in section B.4. The Stokes vector for light emerging from the linear polarizer at 0° is given in equation B.2. The PEM acts as a linear retarder aligned at some angle θ° and its Mueller matrix is given in table 3.3. The Stokes vector of light emerging from the PEM can be determined as follows

$$\mathbf{S} = I_0(\lambda) \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos^2 2\chi + \cos \mu_{PEM} \sin^2 2\chi & (1 - \cos \mu_{PEM}) \sin 2\chi \cos 2\chi & \sin \mu_{PEM} \sin 2\chi \\ 0 & (1 - \cos \mu_{PEM}) \sin 2\chi \cos 2\chi & \sin^2 2\chi + \cos \mu_{PEM} \cos^2 2\chi & -\sin \mu_{PEM} \cos 2\chi \\ 0 & -\sin \mu_{PEM} \sin 2\chi & \sin \mu_{PEM} \cos 2\chi & \cos \mu_{PEM} \end{bmatrix} \cdot \begin{bmatrix} 1 \\ 1 \\ 0 \\ 0 \end{bmatrix}$$

$$\mathbf{S} = I_0(\lambda) \begin{bmatrix} 1 \\ \cos^2 2\chi + \cos \mu_{PEM} \sin^2 2\chi \\ (1 - \cos \mu_{PEM}) \sin 2\chi \cos 2\chi \\ -\sin \mu_{PEM} \sin 2\chi \end{bmatrix}$$

Light emerging from the PEM is incident on the polarizing beam-splitter. We will only work with the light emerging from the face of the polarizing beam-splitter aligned at an angle 90° to the linear polarizer. The Mueller matrix for this face can be obtained from table 3.3. The Stokes vector of light emerging from this face is calculated as follows

$$\begin{aligned}
S &= I_0(\lambda) \cdot \frac{1}{2} \begin{bmatrix} 1 & -1 & 0 & 0 \\ -1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \cdot \begin{bmatrix} 1 \\ \cos^2 2\chi + \cos \mu_{PEM} \sin^2 2\chi \\ (1 - \cos \mu_{PEM}) \sin 2\chi \cos 2\chi \\ -\sin \mu_{PEM} \sin 2\chi \end{bmatrix} \\
S &= \frac{I_0(\lambda)}{2} \begin{bmatrix} 1 - \cos^2 2\chi - \cos \mu_{PEM} \sin^2 2\chi \\ -1 + \cos^2 2\chi + \cos \mu_{PEM} \sin^2 2\chi \\ 0 \\ 0 \end{bmatrix} \tag{B.54}
\end{aligned}$$

The first element of the Stokes vector given in equation B.54 is the intensity of light incident on the detector. The voltage signal produced by the detector is given in equation B.55.

$$V = \frac{cI_0(\lambda)}{2} (1 - \cos^2 2\chi - \cos \mu_{PEM} \sin^2 2\chi) \tag{B.55}$$

As explained in equation B.10 the retardance of the PEM is a sinusoidal function. Substituting equations B.10 and B.12 in equation B.55 we get equation B.56.

$$V = \frac{cI_0(\lambda)}{2} \{1 - \cos^2 2\chi - J_0(\delta_0) \sin^2 2\chi - 2J_2(\delta_0) \sin^2 2\chi \sin 2\omega t\} \tag{B.56}$$

The PEM is now adjusted for some non-zero value of δ_0 and rotated axially. At $\chi = 0^\circ$ we get

$$V = 0$$

Once the angle 0° is obtained we rotate the PEM exactly by 45° . The alignment procedure for the PEM is listed below.

- 1) Align the polarizing beam-splitter such that the two faces are at 0° and 90° respectively using the procedure detailed in section B.4.

- 2) Introduce the PEM at some angle between the linear polarizer and the beam-splitter. Adjust the PEM to the wavelength of the AOTF and to some non-zero value of maximum retardance δ_0 .
- 3) Rotate the PEM so that the voltage signal obtained from the face in the beam-splitter at 90° with respect to the linear polarizer is zero. At this angle the PEM is set at 0° .
- 4) Rotate the PEM by 45° .

B.6 Determination of the calibration constants

The calibration constants $J_1(\delta_0)$ and $J_2(\delta_0)$ are determined with the PEM at 45° between the linear polarizer and the polarizing beam-splitter. The polarizing beam-splitter is aligned such that the two faces are at 0° and 90° respectively. Only the signal from the face at 90° is to be used. In this setup, the voltage signal produced by the sample detector is obtained from equation B.48 by substituting $\chi = 45^\circ$. The voltage output is given in equation B.57.

$$V = \frac{cI_0(\lambda)}{2} [1 - J_0(\delta_0) - 2J_2(\delta_0) \sin 2\omega t] \quad \text{B.57}$$

We measure the Fourier coefficients of voltage that are composed of the direct current part and the alternating current part at frequency 2ω . We get

$$V^{DC} = \frac{cI_0(\lambda)}{2} [1 - J_0(\delta_0)]$$

$$V^{2\omega} = -cI_0(\lambda)J_2(\delta_0)$$

Taking the ratio of the Fourier coefficient at frequency 2ω to the direct current Fourier coefficient we get equation B.58.

$$\frac{V^{2\omega}}{2V^{DC}} = -\frac{J_2(\delta_0)}{1 - J_0(\delta_0)} \quad \text{B.58}$$

A plot of the measured ratio $V^{2\omega}/2V^{DC}$ versus δ_0 should have appearance given in figure B.1. The desired setting is $\delta_0 = 2.405$ radians. At this value the measured ratio has the value -0.4318. The PEM amplitude is set such that the measured ratio is equal to the desired ratio. The following list is the procedure for setting the PEM amplitude.

- 1) Align the PEM at 45° between the linear polarizer and the beam-splitter with one face at 90° using the procedures given in sections B.4 and B.5.
- 2) Change the PEM maximum amplitude in steps. At each step record the experimental ratio $V^{2\omega}/2V^{DC}$.
- 3) Plot $V^{2\omega}/2V^{DC}$ versus δ_0 . This figure should resemble figure 2. Determine the location at which the ratio $V^{2\omega}/2V^{DC} = -0.4318$. Read the value of PEM maximum amplitude at which we observe this value of the experimental ratio.
- 4) At this PEM maximum amplitude setting we have $J_1(\delta_0) = 0.5191$ and $J_2(\delta_0) = 0.4318$.

B.7 The ratio c_1/c_2

The ratio c_1/c_2 is determined with only the linear polarizer and the polarizing beam-splitter in the system. The polarizing beam-splitter is aligned such that the two

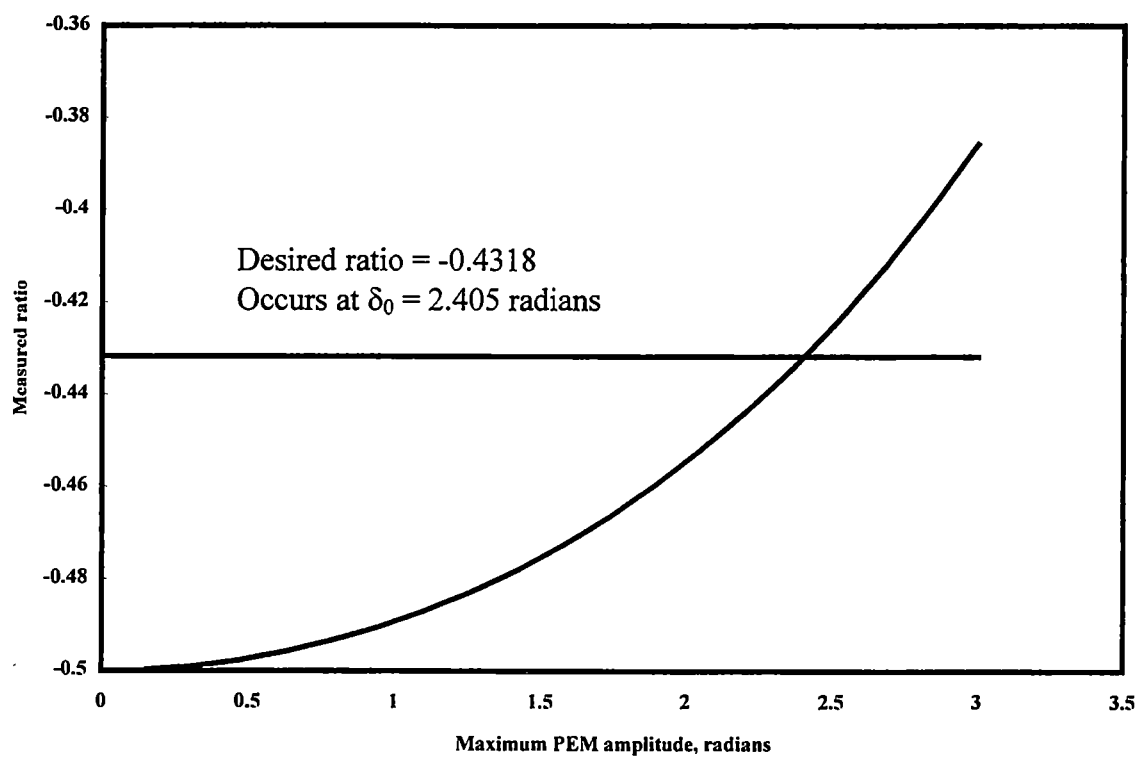


Figure B.1 PEM amplitude setting

faces are at 45° and 135° with respect to the linear polarizer. This alignment procedure is given in B.4. Equation B.2 gives the Stokes vector of light emerging from the linear polarizer. The Mueller matrices for the two faces of the polarizing beam-splitter are obtained by substituting $\theta_{LP} = 45^\circ$ and $\theta_{LP} = 135^\circ$ in the Mueller matrix of a polarizer in table 3.3. The Stokes vector of light emerging from the face at 45° is given in equation B.59.

$$\mathbf{S}_1 = I_0(\lambda) \cdot \frac{1}{2} \begin{bmatrix} 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \\ 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \cdot \begin{bmatrix} 1 \\ 1 \\ 0 \\ 0 \end{bmatrix} = \frac{I_0(\lambda)}{2} \begin{bmatrix} 1 \\ 0 \\ 1 \\ 0 \end{bmatrix} \quad \text{B.59}$$

Similarly, the Stokes vector of light emerging from the face at 135° is given in equation B.60.

$$\mathbf{S}_2 = I_0(\lambda) \cdot \frac{1}{2} \begin{bmatrix} 1 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 \\ -1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \cdot \begin{bmatrix} 1 \\ 1 \\ 0 \\ 0 \end{bmatrix} = \frac{I_0(\lambda)}{2} \begin{bmatrix} 1 \\ 0 \\ -1 \\ 0 \end{bmatrix} \quad \text{B.60}$$

The light emerging from the two detectors is incident on two detectors where light intensity is linearly converted to voltage signals. A constant is introduced during the linear conversion and due to any effects of detector electronics. The constant may be different for the two detectors based on unequal linearity and electronic effects. The first element of the Stokes vector is light intensity. The voltage signals produced by the two detectors are given in equation B.61.

$$\begin{aligned} V_1 &= \frac{c_1 I_0(\lambda)}{2} \\ V_2 &= \frac{c_2 I_0(\lambda)}{2} \end{aligned} \quad \text{B.61}$$

Taking the ratio of the two measured quantities given in equation B.61, the required ratio c_1/c_2 is given in equation B.62.

$$\frac{c_1}{c_2} = \frac{V_1}{V_2} \quad \text{B.62}$$

The following list is the procedure for determining the ratio c_1/c_2

- 1) Align the linear polarizer in the system and the polarizing beams-splitter such that the two faces are at 45° and 135° with respect to the linear polarizer. This alignment procedure is given in B.4.
- 2) At a given wavelength record the voltage signals produced by the two detectors. Obtain its ratio. This ratio is the desired value.
- 3) Repeat at all wavelengths of interest.

VITA

Bhushan Janardan Deshpande was born in Mumbai, India on March 6, 1974. He received his Bachelors degree in Chemical Engineering from the Department of Chemical Technology at the University of Bombay in 1995. He entered the University of Tennessee at Knoxville in August 1995.