CHARACTERIZATION OF FUNCTIONALIZED POLYMER NANOSTRUCTURE THIN FILMS USING ANGULAR POLARIMETRIC MEASUREMENTS

A Thesis

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ABSTRACT

Optical polarimetry is of paramount significance for efficient detection, discrimination, characterization and analysis of the optical properties of materials.

This study introduces a novel approach of characterization of functionalized polymer nanostructures thin films, based on their optical polarization properties. By performing polarimetric angular measurements of the back scattered signals from the samples, the Stokes parameters and the Muller Matrix of the samples were estimated, using mathematical algorithms implemented by Matlab subroutines. Additional information regarding the characterization of the materials was obtained through Mueller matrix decomposition analysis.

The work in this thesis was performed using the Air Force Research Laboratory (AFRL) polarimetric multifunctional imaging platform, designed in-house, for remote characterization of materials. The AFRL polarimetric system is a fully automated, auto calibrated, scalable, and reconfigurable electro-optical imaging system, consisting of a 1065 nm laser source coupled through liquid crystal (LC) polarimetric components to a single- Femtowatt photodetector operating under backscattered geometry. To achieve automation of the system, all the LC components and the femtowatt photodetector are controlled by means of a Labview developed GUI. Specifically, the polarimetric state intensities are detected by the photoreceiver and then sent to the computer via a data
acquisition unit (DAQ) with a sampling frequency of 100 KHz, finally, processed using Excel and Matlab subroutines. Six set of measurements were acquired, for increased statistical accuracy, and then averaged.

The outcome of this thesis indicates that polarimetric characterization of functionalized polymer nanostructures thin films may provide important discriminant signatures and figure-of-Merits (FOM)’s, leading to enhanced characterization of the materials.
DEDICATION

To Farzaneh Begligi and Manouchehr Farrahi my loving parents and my foundation for making me be who I am.

To Amir Farrahi, my source of inspiration, the best friend and beloved brother.
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Last but not least I wish to thank my parents, my brother and my family for their love and support throughout my life.
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CHAPTER I

INTRODUCTION

1.1. Overview

The objective of this study is to characterize polymer based nanostructure materials using Muller matrix and Stokes parameters analysis. Specifically gold nanoparticle where added to the composition of polymer samples and the behavior of them were examined using the Infrared light. This polarimetric multifunctional imaging platform utilized in this study was developed as part of a contract with Air Force Research Laboratory (AFRL) [40]. Several other platforms have been developed previously [2], [4], [5], [6], [7], [8], [9].

Baba developed a polarimetric testbed. In this testbed he used the crystal optical components [4], [5]. Calibration of the polarimetric system was done using known samples like linear polarizers and air. His work is used to calibrate the polarimetric system which we utilized in this thesis. The other polarimetric testbed which was developed later by Bueno [1], [2] used liquid crystal optical component but compare to Baba calibration which was fully automated, the optical components were inserted manually for the calibration of this platform.
One of the unique characteristics of the optical platform which is developed for this study is the ability of detection of backscattered lights using single pixel detector with high specificity, and high scatter rejection, under varying the aspect angles of the object. Detection of objects using single-pixel detection technique and changing object aspect angles provides enhanced information for characterization and discrimination. The backscattered polarimetric signals obtained by varying polarimetric states of laser light, can provide relative information of the object material composition and characteristic of their surface aimed at analyzing the behavior of the polymer nano-composites. Unusual physical and chemical properties of metal nanoparticles make them desirable to be used for sensing, electronics, medicine, and biology applications. Integration of gold nanoparticle in to polymers will enhance their electrical, thermal and physical properties and their application is useful for biosensors and optoelectronic devices [3]. The work in this thesis was performed using the Air Force Research Laboratory (AFRL) polarimetric multifunctional imaging platform, designed in-house, for remote characterization of materials. The AFRL polarimetric system is a fully automated, auto calibrated, scalable, and reconfigurable electro-optical imaging system, consisting of a 1060 nm laser source coupled through liquid crystal (LC) polarimetric components to a single-Femtowatt photodetector operating under backscattered geometry. To achieve automation of the system, all the LC components and the femtowatt photodetector are controlled by means of a Labview developed GUI. Specifically, the polarimetric state intensities are detected by the photoreceiver and then sent to the computer via a data acquisition unit (DAQ) with a sampling frequency of 100 KHz, finally, processed using Excel and Matlab subroutines.
Six set of measurements were acquired, for increased statistical accuracy, and then averaged.

The increasing interest in deploying high performance materials has brought considerable study for hybrid materials, especially polymer nanoparticle composites. Combining nanoparticles in polymer domain will result in increasing the mechanical, electrical, optical and magnetic properties of materials [32].

Morphology of nanocomposite systems depends on characteristic of the copolymer and also properties of the nanoparticles. The distribution of nanoparticles within the block copolymer matrices depends on the polymer/nanoparticle interactions and also it is related to size ratio of particle to polymer [33].

Several methods have been proposed for the preparation of the polymer nanoparticle composites such as in situ method and ex situ method. In the in situ method the nanoparticles are produced in the matrix of polymer while, in ex situ method, previously generated nanoparticles, will incorporate and integrate within the matrix of polymer [34]. Last method is suitable for flexible selection of the broad range of host BCPs and for wide range of high-quality nanoparticles. In order to manage the NP locations, various techniques have been developed. Chiu et al. [33], reported that the location of ligands can be efficiently adjusted by changing their composition on the surfaces of the particle. 1) For instance, particles which are concatenated to the surface of mixture of PS and PVP thiols adsorb at the interface of PS and PVP blocks while segregation of particles will occur within just PS or PVP thiol and close to the center region of compatible domains. 2) Location of particles in PS-P2VP [35] can be controlled efficiently by adjusting the areal chain density of thiol terminated polystyrene [PS-SH]
ligands. In the case that the chain density of ligands decreases, more particles prone to move to the microdomain interface of PS and P2VP. In addition, the interfacial tension and domain spacing are the result of the presence of nanoparticles at the interface of a diblock copolymer. These effects will result in morphology transition to bicontinuous phase. 3) Relative size of BCPs and NPs are also important factors. A ternary hieratical structure has been reported by Bockstaller et al. [36]. This structure consists of PS-PES, gold nanoparticles (Au NP) and silicia nanoparticles. Silica nanoparticles concentrated at the center of PEP domains and Au NPs isolated at the interface of PS and PES domains. This structure is shown in Figure.1.1. 4) The emergence of several hydrogen bounds among the hydroxyl groups in the coronal [PS-r-PVPh-SH] of NPs and pyridine group in the matrix of PS-P2VP leads to localization of gold nanoparticles in PS-P2VP domains. In this process, co-assembly of block copolymer and gold nanoparticles produces novel transition from lamellae to cylindrical PS morphologies and spherical to cylindrical P2VP morphologies [37]. Furthermore, morphologies of BCPs can be influenced by the incorporation of NPs. Also nanoparticles are able to change the orientation and morphology of domains whit in a diblock copolymer.

![Figure.1.1 Schematic of particle distribution (electron micrograph of a ternary blend of PS-PEP and AuR1 and SiO2R2) [36].](image)
The optical characteristics of the polymers, such as contrast, index of refraction can be increased by the incorporation of nanoparticles. Bockstaller et. al, reported that a repetitive metallodielectric structure can be produced by co-assembly of diblock copolymers and gold nanoparticles. This structure is suitable for fabrication of photonic bandgap materials for near infrared or optical frequencies [20]. Dielectric contrast can be increased by selective isolation of gold nanoparticles within one domain among adjacent block copolymer microdomains. The output photonic structure has high reflectivity in the visible region which expresses that absorption losses can be reduced in periodic microstructures [38].

Different block copolymer samples were cast on silicon substrate. In the processes of fabricating the polymer samples the thermal annealing was used to induce micro phase separation. In this study we used Atomic Force Microscopy to find the orientation of polymer blocks within the casted samples and also to observe the separation of micro phases. AFM or atomic force microscopy is a useful tool for analyzing the surface structure of materials. The technique applied in this study is called tapping mode atomic force microscopy. In this method a sharp tip (probe) which is usually a silicon nitride crystal or asilicon, oscillates above the specimen surface. Figure.1.2 depicts the fundamental of AFM process.

While the probe scans over the surface of the sample, the tip will rise and fall on the surface with different features. The laser beam which is pointed to the probe will be reflected to a sensor. As the probe goes up and down the laser beam will hit different portions of the sample and consequently it will hit different sections of the sensor. Oscillation frequency of the probe will change by the harder or softer features of the
sample surface and will cause the phase contrast images. AFM measurements are mostly done in the room temperature and in air on films cast on flat wafers like silicon.

Surface topography of the sample nanocomposites was imaged in this study using a Dimension Icon atomic force microscope (AFM) (Bruker AXS) in the Peak Force Quantitative Nanomechanical Property mapping mode [20]. Pre annealing and post annealing backscattered measurements were done for the samples.

Polystyrene-b-methylmethacrylate (PS-PMMA) diblock copolymer was flow-coated on ultraviolet–ozone-cleaned Silicon substrates. One set of experiments was performed on the pure as-cast thin film, which means there was just block copolymer and the sample doesn’t contain any nanoparticles. Other set of experiments were performed on the samples of PS-PMMA solutions which were admixed with appropriate amount of synthesized AuNPs. Two different thickness of this combination were considered for
optical measurements. In this experiment measurements were performed on the as-cast sample.

Other study was done to characterize the specific thickness (183nm) of pure PS-PMMA sample. The experimental measurements were performed on as-cast and oven annealed sample. PS-P2VP thin films are the other block copolymer samples which were studied in this thesis. Several thicknesses of this block copolymer contains Au NPs were cast and optical experiments were done but one case of the results are provided in this thesis which is the comparison of two different thicknesses of oven annealed samples. Complete information of the samples is provided in the chapter 3. Typically, the material characteristics of an object are defined by it Muller matrix (MM) [1]. Specific elements of MM or a group of elements contain material information such as isotropic absorption. Muller matrix decomposition will provide more specific information to characterize the materials. One of these decomposed elements is depolarization coefficient which is defined as the ability of transformation of the polarized light into unpolarized light. Degree of polarization which is used as the measure the randomness of the polarization of light is one of the factors that utilized to characterize the polymer samples. Other key elements such as diattenuation and retardance were tested not only for the fixed normal incidence of light but also for small angular rotation of object. Stokes vector and polarizance coefficient are other figure of merits which have been studied to characterize the materials and utilized for our analysis in this work.

Nanostructured materials have the dimension in the range of 1-100 nm and they exhibit unique physical, chemical, electrical, mechanical properties which are different from their bulk counterparts due to the quantum effect. Regarding these properties they
have tremendous applications in medical, aerospace, sensing and biology fields [14], [15]. Soft materials like colloids, biomaterials, polymers and their composites, which have fluidlike disorder, have gained high interest by scientists recently. They show the equilibrium behavior and can be deformed easily by applying external pressure. One important behavior which these materials have is their inherent capacity of self-assembly into nanostructures. Self-assembly is the feature of supramolecular chemistry in which the components are connected together naturally and using covalent interactions such as molecular surface forces, van der Waals interactions, electrostatic interactions, Self-organization is repeatedly retained in natural systems and it is a significant tool to fabricate useful mesostructured materials [28]. Self-assembly have several advantages. It is fast and not expensive and scalable. Self-assembly works using weak forces [27].

Block copolymers have been known as a promising candidate for providing self-assembled nanostructure for a long time and recently they have gained an interest due to their ability of self-organization into periodic nanostructures. Composites of BCP/NP are desirable due to their unique properties to build new materials [29].

A copolymer is a polymer which is derived from two or more repeating monomeric spices. A Block copolymer is a special type of polymers which are composed of two (diblock copolymers) or more (multiblock copolymers) chemically different blocks of polymer. These blocks are covalently bound together. The thermodynamics of the block copolymers (BCP) can be expressed using entropy and enthalpy effects. Enthalpy dominates when the temperature becomes less than the order-to-disorder transition temperature, $T_{odt}$. Order to disorder transition is a transition to less ordered states of systems and in this transition system undergoes several phase transitions.
Example of such transition is melting of ice. When the enthalpy effect dominates, owe to the covalent binding of blocks and their incompatibility, these blocks will be organized in periodic nanostructures [30]. Microphase separation can decrease the interfacial energy and increase chain conformation entropy [20]. When the temperature goes higher than $T_{ODT}$ the entropy effect dominates the enthalpy effect and homogeneous phase separation is the result. $T_{ODT}$ temperature depends on three factors:

- $N$, the degree of polymerization
- $f$, volume fraction of one block
- $\chi$, the Flory-Huggins interaction parameter

Segregation power is defined by the product of $\chi$ and $N$ and it represents contribution of entropy and enthalpy. If this product for a given composition is below a specific level, morphology will get disordered. The critical value of $\chi N$ for diblock polymer with the symmetric chain length is 10.5. Strong segregation limit or SSL is defined for the case that segregation power is higher than 10.5, and weak segregation limit or WSL is defined for the case that $\chi N \sim 10.5$. The morphology of the structure, changes with the volume fraction of the blocks. Furthermore, molecular weight of the block copolymer defines dimension of these structures. Phase diagram of a diblock copolymer is depicted in Figure.1.3 The common periodic morphologies by increasing volume fracture are bodycentered cubic, hexagonally, to bicontinuousgyroid, and lamellae. Figure.1.4 depicts these morphologies with the molecules of diblock using two-color chains [31], [20].
Figure 1.3 Phase diagram of diblock copolymer. Regions of stability of disordered (dis), lamellar (lam), gyroid (gyr), hexagonal (hex) and body-centered cubic (bcc) phases are illustrated.

Figure 1.4 Common periodic morphologies of block copolymers [27].

One of the block copolymers used as the sample in this work is PS-b-PMMA which is short term for polystyrene-poly (methyl methacrylate). This block copolymer is made
by first polymerizing styrene and then PMMA is polymerized from the reactive end of
the polystyrene chains [14], [15], [16]. One of the interesting properties of the block
copolymers is the microphase separation in thin film geometry which can result in the
formation of periodic nanostructures with length scales on the order of tens of
nanometers. Based on the relative length of each block several morphologies can be
obtained. Due to the incompatibility of two blocks in an AB diblock copolymer,
microphase separation usually occurs. If the length of the both A and B blocks are the
same a lamellar structure will be achieved. Otherwise when one of the blocks is
considerably longer than others in order to maintain the equal stretching of blocks their
interface begins to curve and will led to the collection of cylinder or spherical micelles of
the shorter blocks embedded into the matrix of longer blocks [17]. A Morphology that a
diblock copolymer can adopt is detectable by variety of imaging and scattering
techniques such as Atomic Force Microscopy (AFM). AFM is a popular technique and is
suitable for directly collecting image of the surface contains tens nanometers lamellar
structures or spherical micelles. Chemical structure of PS-b-PMMA is depicted
in Figure.1.5.

![Chemical structure of PS-b-PMMA](image)

Figure.1.5 Chemical structure of PS-b-PMMA
1.2. Publications Related to This Study


1.3. Thesis Outline

The reminder sections of this thesis have been organized as following. In chapter 2, theory behind the study of characterization of polymer samples is presented. Properties of light and definition of Muller Matrix and reduced decomposition data reduction technique are discussed. Chapter 3 presents the sample preparation and experimental arrangements and discusses the properties of polymer samples. Also in this chapter the calibration data is provided. Chapter 4, presents results and discussion of acquired backscattered signals, Muller Matrix and Stokes vector analysis of the sample. Muller Matrices of the samples have been decomposed and depolarization, diattenuation, retardance coefficient sand polarizance comparison have been discussed. Finally, Chapter 5 provides the conclusion of studies and some future enhancement are proposed.
CHAPTER II

THEORY

The theory that has been used for this study is provided in this chapter. Section 2.1 discusses the basic polarimetric phenomena of light, properties of light propagation and its interaction with materials and different polarization of light. Section 2.2 discusses Stokes vector parameters for different polarization states. In section 2.3 Muller Matrix studies of the objects are done and section 2.4 contains the data reduction technique to calculate Muller matrices from the intensity values obtained from the experiments and finally, section 2.5 provides the decomposition of Muller matrix and Stokes vector analysis is provided in section 2.6.

2.1. Polarimetric Principles

In order to have the more precise discussion of the results of this study it is essential to have the better understanding about the fundamental of light and its interaction with matter [1]. Light is basically an electromagnetic wave and its propagation can be described by Maxwell theory. Analysis of light in this context is
called electromagnetic optics. “Photon optic” or “quantum optic” describes the lights in terms of energy levels [11]. An electromagnetic wave consists of electric and magnetic fields which are perpendicular to its propagation axis. Both of these fields have an amplitude and direction and they vary sinusoidally with time. Electric and magnetic fields reach their highest pick at the same time which means they oscillates in phase. Frequency of a wave is described by the rate of its oscillation and wavelength of a wave is described by the distance a beam travels during one period of the oscillation [12] and they are related to the speed of light where

\[ v = \lambda f \]  \hspace{1cm} (2.1)

For an electromagnetic wave travelling through air or vacuum with a good approximation \( v = c \), where \( c \) is the speed of light.

2.1.1. Polarization of Light

Polarization is an interesting property of light. When the light interacts with the matter the polarization can be induced through the transmission, reflection or scattering. Polarization of light is the key methodology used in this work to study the light interaction with matter. In general, there are three forms of polarization of light: linear polarization, elliptical polarization and circular polarization. If the light propagated through the z axis and the electric field lies on the y axis this light is vertically polarized and if the propagation axis of the light is z axis and the electric field lies on x axis light is horizontally polarized.

Circular polarized light consists of two equal amplitude plane waves with 90° degrees phase difference. If the relative phase difference is more than 90° or the
amplitude of the plane waves are not equal the light is said to be elliptically polarized. Figure.2.1 to Figure.2.3 illustrate these concepts.

Figure.2.1 Linearly polarized light in vertical direction

Figure.2.2 Circularly polarized light

Figure.2.3 Elliptically polarized light
Equation 2.2 describes lights in term of amplitude and phase:

\[ E_x(z,t) = E_{0x} \cos(\omega t + \delta_x) \]  
\[ E_y(z,t) = E_{0y} \cos(\omega t + \delta_y) \]

Where \( E_{0x} \) and \( E_{0y} \) are the amplitude in the x and y plane and \( \delta = \delta_y - \delta_x \) is phase shift of the wave between electrical and magnetic fields. These components (magnitude and phase) determine the polarization of light.

In general, polarization pattern follows an ellipse Equation. A rotated ellipse by an angle \( \psi \) from the major axis X and Y [2], [10], is shown in Figure.2.4

![Rotated Polarization ellipse](image)

Figure.2.4 Rotated Polarization ellipse [10].

Table 2.1 lists some degenerate forms of the polarization ellipse which in this table, the electric filed amplitudes are normalized to unity and the phase difference is represented in multiples of radians for one wavelength [1], [10], [13].
Table 2.1 Degenerated forms of the polarization ellipse.

<table>
<thead>
<tr>
<th>Polarization</th>
<th>$E_{0x}$</th>
<th>$E_{0y}$</th>
<th>$\delta = \delta_y - \delta_x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear Horizontal</td>
<td>1</td>
<td>0</td>
<td>Any</td>
</tr>
<tr>
<td>Linear Vertical</td>
<td>0</td>
<td>1</td>
<td>Any</td>
</tr>
<tr>
<td>Linear +45°</td>
<td>1</td>
<td>1</td>
<td>$\pi$</td>
</tr>
<tr>
<td>Linear -45°</td>
<td>1</td>
<td>1</td>
<td>$0$</td>
</tr>
<tr>
<td>Right Circular</td>
<td>1</td>
<td>1</td>
<td>$\frac{\pi}{2}$</td>
</tr>
<tr>
<td>Left Circular</td>
<td>1</td>
<td>1</td>
<td>$\frac{\pi}{3}$</td>
</tr>
</tbody>
</table>

2.2. Stokes Parameters

Light can be characterized in terms of polarization using Stokes vector. In 1852 George Gabriel Stokes discovered that any polarization state of a light beam could be completely characterized by four quantities called Stokes parameters [10]. The first element of these parameters shows the total intensity of the light while other elements describe the polarization of the light beam [2]. As stated previously, the polarization of light is related to the field quantities, hence Stokes parameters could be derived from electric field of the beam. Prior to this theory, polarization properties of light were studied by wave theory.

To derive Stokes vector parameters, consider a pair of plane waves which are orthogonal to each other at a point in space, $z = 0$, to be represented by Equations (2.3a) and (2.3b).
\[ E_x(t) = E_{0x}(t) \cos(\omega t + \delta_x(t)) \] (2.3a)

\[ E_y(t) = E_{0y}(t) \cos(\omega t + \delta_y(t)) \] (2.3b)

where \( E_{0x}(t) \) and \( E_{0y}(t) \) are the instantaneous amplitudes, \( \omega \) is the instantaneous angular frequency, and \( \delta_x(t) \), \( \delta_y(t) \) are the instantaneous phase factors. Rewriting Equations (2.3a) and (2.3b) using the identity \( \cos(\alpha + \beta) = \cos(\alpha)\cos(\beta) - \sin(\alpha)\sin(\beta) \) will result in (2.4a) and (2.4b) Equations:

\[ \frac{E_x(x)}{E_{0x}(t)} = \cos(\omega t) \cos(\delta_x(t)) - \sin(\omega t) \sin(\delta_x(t)) \] (2.4a)

\[ \frac{E_y(x)}{E_{0y}(t)} = \cos(\omega t) \cos(\delta_y(t)) - \sin(\omega t) \sin(\delta_y(t)) \] (2.4b)

Equations (2.4a) and (2.4b) are solved for \( \cos(\omega t) \) and \( \sin(\omega t) \) using the identities \( 2 \cos(X)\sin(Y) = \sin(X + Y) \sin(X - Y) \) and \( \sin(-X) = -\sin(X) \). The derived Equations (2.5) are as follow

\[ \frac{E_x(x)}{E_{0x}(t)} \sin \delta_y(t) - \frac{E_y(x)}{E_{0y}(t)} \sin \delta_x(t) = \cos(\omega t) \sin(\delta(t)) \] (2.5a)

\[ \frac{E_x(x)}{E_{0x}(t)} \cos \delta_y(t) - \frac{E_y(x)}{E_{0y}(t)} \cos \delta_x(t) = \sin(\omega t) \sin(\delta(t)) \] (2.5b)

Squaring the both sides of Equations (2.5a) and (2.5b) and summing them together will result in

\[ \frac{E_x^2(t)}{E_{0x}^2(t)} + \frac{E_y^2(t)}{E_{0y}^2(t)} - \frac{2E_x(t)E_y(t)}{E_{0x}(t)E_{0y}(t)} \cos \delta(t) = \sin^2 \delta(t) \] (2.6)
which is familiar polarization ellipse. For monochromatic radiation, the amplitude
and phase are constant all the time. The Equation will reduce to

\[
\frac{E_x^2(t)}{E_{0x}^2} + \frac{E_y^2(t)}{E_{0y}^2} - \frac{2E_x(t)E_y(t)}{E_{0x}E_{0y}} \cos \delta(t) = \sin^2 \delta(t) \quad (2.7)
\]

Equation (2.7) is called the polarization ellipse. \(E_{0x}, E_{0y}\) and \(\delta\) are constant while
\(E_x, E_y\) are dependent on time. In order to represent (2.7) in terms of the observables of
the optical field, an average over the time of observation should be taken. The average
only over a single period of oscillation is needed. Symbol \(<\ldots>\) represents the time
average so

\[
\frac{\langle E_x^2(t) \rangle}{E_{0x}^2} + \frac{\langle E_y^2(t) \rangle}{E_{0y}^2} - \frac{2\langle E_x(t)E_y(t) \rangle}{E_{0x}E_{0y}} \cos \delta = \sin^2 \delta \quad (2.8)
\]

where

\[
\langle E_i(t)E_j(t) \rangle = \lim_{T \to \infty} \frac{1}{T} \int_0^T E_i(t)E_j(t)dt \quad i, j = x, y \quad (2.9)
\]

Multiplying the Equation (2.8) by \(4E_{0x}^2E_{0y}^2\) gives

\[
4E_{0y}^2\langle E_x^2(t) \rangle + 4E_{0x}^2\langle E_y^2(t) \rangle - 8E_{0x}E_{0y}\langle E_x(t)E_y(t) \rangle \cos \delta = (2E_{0x}E_{0y} \sin \delta)^2 \quad (2.10)
\]

Average values of Equation 2.8 using the Equation 2.9 are

\[
\langle E_x^2(t) \rangle = \frac{1}{2} E_{0x}^2 \quad (2.11a)
\]

\[
\langle E_y^2(t) \rangle = \frac{1}{2} E_{0y}^2 \quad (2.11b)
\]

\[
\langle E_x(t)E_y(t) \rangle = \frac{1}{2} E_{0x}E_{0y} \cos \delta \quad (2.11c)
\]

If we substitute the Equations (2.11a), (2.11b), (2.11c) into Equation 2.10 the
following Equation will be yielded
\[2E_{0x}^2 E_{0y}^2 + 2E_{0x}^2 E_{0y}^2 - (2E_{0x} E_{0y} \cos \delta)^2 = (2E_{0x} E_{0y} \sin \delta)^2\]  

(2.12)

We wish to express the final result in term of intensity, so by adding and subtracting the \((E_{0x}^4 + E_{0y}^4)\) quantity to the left hand side of the Equation (2.12) will lead to the perfect squares. Grouping the squares, will result in Equation (2.13)

\[(E_{0x}^2 + E_{0y}^2)^2 - (E_{0x}^2 - E_{0y}^2)^2 - (2E_{0x} E_{0y} \cos \delta)^2 = (2E_{0x} E_{0y} \sin \delta)^2\]  

(2.13)

The Equation (2.13) could be express as the

\[S_0^2 = S_1^2 + S_2^2 + S_3^2\]  

(2.14)

Where

\[
S_0 = E_{0x}^2 + E_{0y}^2 \\
S_1 = E_{0x}^2 - E_{0y}^2 \\
S_2 = 2E_{0x} E_{0y} \cos \delta \\
S_3 = 2E_{0x} E_{0y} \sin \delta
\]  

(2.15)

Four Equations which are introduced in 2.15 are the Stokes polarization parameters for a plane wave. These parameters were discovered by Sir Stokes in 1982. Stokes parameters are observables of the optical field.

- \(S_0\) represents the total intensity of the light beam.
- \(S_1\) represents the amount of linear horizontal or vertical polarization.
- \(S_2\) represents the amount of linear +45 or -45 polarization of the light beam.
- \(S_3\) represents the amount of right or left circular polarization of the light beam.

These parameters are represented in term of quantities and all of them are always real quantities [10].
Since the amplitudes and phases fluctuate slowly for partially polarized light beam so the Equation (2.14) is valid for very short time intervals. For any state of polarized light using the Schawrz’s inequality the Stokes parameters always satisfy the following relation:

\[ S_0^2 \geq S_1^2 + S_2^2 + S_3^2 \]  

(2.16)

The equality applies for the completely polarized light and inequality applies for partially polarized or unpolarized light.

Stokes vector representation for a plane wave can be written like Equation (2.17).

\[
\begin{bmatrix}
S_0 \\
S_1 \\
S_2 \\
S_3
\end{bmatrix}
\]  

(2.17)

The Stokes vectors for some degenerate forms of polarized ellipse are listed below where in these vectors, subscripts H, V, P, M, R, L represent Horizontal, Vertical, +45°, -45°, Right- Circular, Left-Circular respectively [1].

- **Linear Horizontal Polarized Light**

\[
S_H = \frac{1}{2} \begin{bmatrix} 1 \\ 1 \\ 0 \\ 0 \end{bmatrix}
\]  

(2.18)

- **Linear Vertical Polarized Light**

\[
S_V = \frac{1}{2} \begin{bmatrix} 1 \\ -1 \\ 0 \\ 0 \end{bmatrix}
\]  

(2.19)
• Linear +45° Polarized Light

\[
S_p = \begin{pmatrix}
\frac{1}{2} \\
0 \\
1 \\
0
\end{pmatrix}
\] (2.20)

• Linear -45° Polarized Light

\[
S_M = \begin{pmatrix}
\frac{1}{2} \\
0 \\
-1 \\
0
\end{pmatrix}
\] (2.21)

• Right Circularly Polarized Light

\[
S_r = \begin{pmatrix}
1 \\
0 \\
0 \\
1
\end{pmatrix}
\] (2.22)

• Left Circularly Polarized Light

\[
S_L = \begin{pmatrix}
1 \\
0 \\
0 \\
-1
\end{pmatrix}
\] (2.23)

2.3. Muller Matrix

In the previous section we provided information about the Stokes parameters. As stated if polarized light interacts with the elements, it can change the state polarization of the light and Stokes parameters are the powerful tool to study this interaction. This study will lead to representing objects by Muller matrix. For any
polarizing device Muller matrix is represented by $M$, and it is defined as the matrix which transforms the light incident Stokes vectors to the resulting Stokes vector. Suppose the Stokes vector of the incident light as $S$, after it interacts with a polarizing medium with Muller Matrix, $M$, some part of the light may be reflected, scattered or transmitted. The input Stokes parameters $S$ will change and the exiting light could be characterized by $S'$ which are the Stokes parameters of the reflected, transmitted or scattered light. Equation (2.24) describes this transformation.

$$S' = MS$$  \hspace{1cm} (2.24)

The Muller Matrix is a 4x4 matrix contains real valued elements. It was introduced by Hans Muller and it is a function of the propagation and wavelength of the incident light.

The Equation (2.24) can be written as,

$$\begin{bmatrix}
S_0' \\
S_1' \\
S_2' \\
S_3'
\end{bmatrix} =
\begin{bmatrix}
m_{11} & m_{12} & m_{13} & m_{14} \\
m_{21} & m_{22} & m_{23} & m_{24} \\
m_{31} & m_{32} & m_{33} & m_{34} \\
m_{41} & m_{42} & m_{43} & m_{44}
\end{bmatrix}
\begin{bmatrix}
S_0 \\
S_1 \\
S_2 \\
S_3
\end{bmatrix}$$ \hspace{1cm} (2.25)

$W_q = [A_{q,1}G_{q,1}, A_{q,1}G_{q,2}, A_{q,1}G_{q,3}, ..., A_{q,1}G_{q,4}]^T$

And the schematic of the transmission is shown in Figure.2.5
Figure 2.5 Polarization state of the light changes after interacting with object

For actual applications there may be more than one polarizing component which each of them has their own Muller matrix. In this case the Muller matrix of all the components need to be multiplied to get the total transformation as depicted in Figure 2.6

![Diagram showing polarization state changes](image)

Figure 2.6 Elements with different Muller matrices

In this fig, the Stokes vector of incident light, $S$, after interaction with the first polarizing object, Muller matrix $M_1$, will be transformed to Stokes vector $S'$. Thus the Equation (2.24) can be written as,

$$S' = M_1 S$$  \hspace{1cm} (2.26)

$S'$, emerges from the first polarizing element and interacts with the second object (M2) and the $S'$ will be transformed to $S''$. Referring to Equation (2.24)

$$S'' = M_2 S$$  \hspace{1cm} (2.27)
Combining Equations (2.26) and (2.27) gives the total transformation of light from the input light to the output light. Output Stokes vector is defined by $S_{\text{out}}$ and the resulting Equation can be written as

$$S_{\text{out}} = M_{\text{2}}M_{\text{1}}S$$  \hspace{1cm} (2.28)

Several conditions have been developed to ensure that experimentally founded Muller matrices are physically realizable. Between these conditions, following three conditions are the most common conditions:

1) $T_r(MM^T) \leq 4m_{11}^2$  \hspace{1cm} (2.29)

2) $m_{11} \geq |m_j|$  \hspace{1cm} (2.30)

3) $m_{11}^2 \geq m_{12}^2 + m_{13}^2 + m_{14}^2$  \hspace{1cm} (2.31)

Note that $T_r$ is the trace of matrix.

As it is shown in Figure.2.6, each element of the Muller matrix of a specific material describes the optical properties of that material.

$m_{11}$ is called isotropic absorption and it is the amount of the attenuation of light’s intensity after interacting with the sample. Dichorhisim refers to the differences in the absorption of orthogonal polarization the light which arises from the structural symmetry. Linear Dichorhism represents the differential absorption between the two orthogonal, linearly polarized lights while the circular dichorhism refers to the differential absorption of the two orthogonal, circularly polarized lights. When the light passes through certain kind of materials it decomposes in to two rays, this phenomenon is called birefringence. Linear birefringence is the difference in speed of propagation of two orthogonal, linearly
polarized light [1], [2], [17], [18]. The circular birefringence is the difference in speed of the two orthogonal, circularly polarized lights after interacting with the matter.

<table>
<thead>
<tr>
<th>$m_{11}$</th>
<th>$m_{32}$</th>
<th>$m_{43}$</th>
<th>$m_{44}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isotropic Absorption</td>
<td>-(Linear Dichroism(0))</td>
<td>-(Linear Dichroism(45))</td>
<td>Isotropic Absorption</td>
</tr>
<tr>
<td>$m_{21}$</td>
<td>$m_{22}$</td>
<td>$m_{23}$</td>
<td>$m_{24}$</td>
</tr>
<tr>
<td>-(Linear Dichroism(0))</td>
<td>Isotropic Absorption</td>
<td>+( Circular Birefringence)</td>
<td>+(Linear Birefringence(45))</td>
</tr>
<tr>
<td>$m_{31}$</td>
<td>$m_{32}$</td>
<td>$m_{33}$</td>
<td>$m_{34}$</td>
</tr>
<tr>
<td>-(Linear Dichroism(45))</td>
<td>-(Circular Birefringence)</td>
<td>Isotropic Absorption</td>
<td>+(Linear Birefringence(0))</td>
</tr>
<tr>
<td>$m_{41}$</td>
<td>$m_{42}$</td>
<td>$m_{43}$</td>
<td>$m_{44}$</td>
</tr>
<tr>
<td>Circular Dichroism</td>
<td>+(Linear Birefringence(45))</td>
<td>-(Linear Birefringence(0))</td>
<td>Isotropic Absorption</td>
</tr>
</tbody>
</table>

| Table 2.2 Muller matrix elements and their optical properties |

2.4. Data Reduction Technique

Generally, the Muller matrix of a sample which is under the polarimetric experiment is unknown and it should be solved. Only the input and output Stokes vectors are known. To find the value of 16 Muller matrix elements a minimum of sixteen linearly
Equations are essential. The detector typically will measure $S_0$, which is the first element of the Stokes vector and it represents the total intensity of the light. In order to find the 16 unknown values sixteen measurements will need to be taken. Data reduction technique is the term used for this calculation process and finding the sixteen unknown Muller matrix elements.

The experimental setup which contains optical components can be divided into two sections. Generator arm and the analyzer arm. The generator arm consists of the components from the laser source to the sample and the analyzer arm consists of the components after the sample including the detector. Each arm has its own Stokes vector. By changing the configuration of the generator and analyzer arm sixteen different combinations would be achieved (four on each arm). These combinations are called the states of the experiments. By changing the polarization of the generator and analyzer arm components to the known states, sixteen different measurements could be taken and as a result different Equations could be yield. The schematic of the experimental setup is shown in Figure.2.7.
The generator arm consists of the source and G1, G2 optical components and the analyzer arm consists of the detector and A1 and A2 optical components. Consider $G_q$ as the Stokes vectors of the generator side and $A_q$ as the Stokes vector of the analyzer side and $q$ as the representative of the states of experiment. Consider $M$ as the Muller matrix of the object and $p_q$ as the measured intensity of each state. Note that $p_q$ refers to the intensity or $S_0$. The total system can be shown in Equations (2.32) and (2.33).

$$P_q = A_q^T M S_q = \begin{bmatrix} A_{q,1} & A_{q,2} & A_{q,3} & A_{q,4} \end{bmatrix} \begin{bmatrix} m_{11} & m_{12} & m_{13} & m_{14} \\ m_{21} & m_{22} & m_{23} & m_{24} \\ m_{31} & m_{32} & m_{33} & m_{34} \\ m_{41} & m_{42} & m_{43} & m_{44} \end{bmatrix} \begin{bmatrix} G_{q,1} \\ G_{q,2} \\ G_{q,3} \\ G_{q,4} \end{bmatrix}$$ (2.32)

$$P_q = \sum_{j=1}^{4} \sum_{k=1}^{4} A_{q,j} M_{j,k} G_{q,k}$$ (2.33)

In Equation (2.33), the analyzer and generator matrices have been expressed in the format of 16x1 measurement vector for the $q^{th}$ state [19].

$$W_q = \begin{bmatrix} A_{q,1} G_{q,1} & A_{q,1} G_{q,2} & A_{q,1} G_{q,3} & \ldots & A_{q,4} G_{q,4} \end{bmatrix}^T$$ (2.34)

The Muller matrix is written in the form of 16x1 vector and represents the intensity of sixteen different states, $p_q$. As the detector only measures $S_0$ thus the Equation (2.33) can be written as,
The value of $q$ is equal to 16 since sixteen measurements are taken. Therefore, $W_q$ will be equal to 16x16 matrix. The multiplication of $W_q$ and Muller vector which is a 16x1 vector will give 16x1 intensity vector. Each element of the resulting vector represents the intensity of each state.

The Muller matrix of the object can be determined using the inverse of $W$, there if $W$ contains sixteen linearly independent rows, thus Muller matrix of the object can be achieved using Equation (2.36),

$$M = W^{-1}P$$

If the number of Equations is more than 16 or in the other word if $q > 16$ and the system is over-determined the pseudo-inverse can be taken as Equation (2.37).

$$M = [W^TW]^{-1}W^TP = W^{-1}_pP$$

Data reduction method has several advantages such as:

- It is easy to understand and implement.
- This method is general and independent of the source and detectors. It can be calculated using the Stokes vectors associated with the generator and analyzer arms which are either ideal or non-ideal and obtained by calibration process.
• It is not restricted by the number of the states and can be used for over determined states, i.e. \( q > 16 \) and may improve the measurements.

2.5. Decomposition of Muller Matrices

Since the Muller matrix of an object represents various optical properties, decomposition of that matrix to three constituent matrices has further advantages in characterization of the materials. These three matrices are named: depolarization, diattenuation and retardance. Lu-Chipman is the name of the algorithm used in decomposing the Muller matrix into three matrices which stated previously. This algorithm is represented by Equation (2.38)

\[
M_{\text{object}} = M_\Delta M_R M_D
\]  
(2.38)

Where \( M_\Delta \) represents the depolarization matrix, \( M_R \) represents the retardance matrix and \( M_D \) represents the diattenuation matrix [18].

The diattenuation magnitude is defined in Equation (2.39) using the transmittance

\[
D = \frac{T_{\text{max}} - T_{\text{min}}}{T_{\text{max}} + T_{\text{min}}} \quad 0 \leq D \leq 1
\]  
(2.39)

where \( T_{\text{max}} \) is the maximum transmittance and \( T_{\text{min}} \) is the minimum transmittance.

Transmittance is defined by Equation (2.40) and it is related to the first row of the Muller matrix and the Stokes vectors.

\[
T = \frac{S_0}{S_0} = \frac{S_0 m_{11} + S_1 m_{12} + S_2 m_{13} + S_3 m_{14}}{S_0} \quad (2.40)
\]

\[
T = m_{11} + \frac{m \bar{S}}{S_0}
\]
Where \( \mathbf{S} = [S_1, S_2, S_3] \) and \( \mathbf{m} = [m_{12}, m_{13}, m_{14}] \).

Since the numerator operation is a dot product, the minimum and maximum transmittance can be achieved using \( |\mathbf{m}|(-S_0) \) and \( |\mathbf{m}|(S_0) \) respectively. By substituting these values in the diattenuation magnitude, Equation (2.39), and rearranging them, \( D \) will be achieved in terms of the Muller matrix elements, as it is shown in Equation (2.41)

\[
D = \sqrt{\frac{m_{12}^2 + m_{13}^2 + m_{14}^2}{m_{11}}} \quad (2.41)
\]

The diattenuation magnitude value is a significant parameter to describe the characteristic of a matter [18], [21]. The diattenuation can be written as column vector,

\[
\mathbf{D} = \begin{bmatrix} D_H \\ D_{45} \\ D_C \end{bmatrix} = \begin{bmatrix} \frac{1}{m_{11}} \\ m_{12} \\ m_{13} \end{bmatrix} \begin{bmatrix} m_{12} \\ m_{13} \\ m_{14} \end{bmatrix} \quad (2.42)
\]

where in this Equation the diattenuation is represented with specific polarization states.

The polarizance vector is needed to calculate the complete diattenuation matrix. Polarizance is defined as the behavior of object to change the completely unpolarized incident light into polarized light and it is given by vector \( \mathbf{P} \) as it is shown in Equation (2.43a)

\[
\mathbf{P} = \begin{bmatrix} P_H \\ P_{45} \\ P_C \end{bmatrix} = \begin{bmatrix} \frac{1}{m_{11}} \\ m_{21} \\ m_{31} \end{bmatrix} \begin{bmatrix} m_{21} \\ m_{31} \\ m_{41} \end{bmatrix} \quad (2.43a)
\]

A normalized polarizance vector can be expressed as Equation (2.43b).
Polarizance range is between 0 and 1. Higher values of $P$ indicate higher polarizing power (because of the target characteristics).

The diattenuation matrix can be written in general form of Equation (2.44)

$$
M_D = \begin{bmatrix}
1 & \bar{\vec{D}}^T \\
\bar{\vec{P}} & m_D
\end{bmatrix}
$$

(2.44)

where $m_D = aI_3 + b(\bar{\vec{D}}\bar{\vec{D}}^T)$ and is a 3x3 matrix. Thus, the full diattenuation matrix is equal to

$$
D = \begin{bmatrix}
m_{11} & m_{12} & m_{13} & m_{14} \\
m_{21} & a + bm_{12}^2 & bm_{12}m_{13} & bm_{12}m_{14} \\
m_{31} & bm_{13}m_{12} & a + bm_{13}^2 & bm_{13}m_{14} \\
m_{41} & bm_{14}m_{12} & bm_{14}m_{13} & a + bm_{14}^2
\end{bmatrix}
$$

(2.45)

where

$$
D = \left| \bar{\vec{D}} \right|
$$

$$
a = \sqrt{1 - D^2}
$$

$$
b = \frac{1 - \sqrt{1 - D^2}}{D^2}
$$

(2.46)

The retardance matrix $M_R$ can be calculated by Equation (2.47).
\[ M_R = \begin{bmatrix} 1 & 0^T \\ 0 & m_R \end{bmatrix} \] (2.47)

\[ M_R = \frac{1}{a} \begin{bmatrix} a & 0 & 0 & 0 \\ 0 & m_{22} - b(m_{12}) & m_{23} - b(m_{13}) & m_{24} - b(m_{14}) \\ 0 & m_{32} - b(m_{12}) & m_{33} - b(m_{13}) & m_{34} - b(m_{14}) \\ 0 & m_{42} - b(m_{12}) & m_{43} - b(m_{13}) & m_{44} - b(m_{14}) \end{bmatrix} \]

The total retardance is a valuable parameter in characterizing a material which is defined in Equation (2.48).

\[
R = \left| \bar{R} \right| = \cos^{-1}\left( \frac{Tr(m_R) - 1}{2} \right) \quad 0 \leq R \leq \pi
\]

\[
R = \left| \bar{R} \right| = 2\pi - \cos^{-1}\left( \frac{Tr(m_R) - 1}{2} \right) \quad 0 \leq R \leq 2\pi \tag{2.48}
\]

By rearranging the Equation (2.38) we will obtain Equation (2.49) which represents the behavior of depolarization and retardance together.

\[ M' = MM_D^{-1} = M_A M_R \tag{2.49} \]

\[ M' \], can be decomposed by using Equation (2.50)

\[
M' = \begin{bmatrix} 1 & 0^T \\ \overrightarrow{P_A} & \overrightarrow{m_A} \end{bmatrix} \begin{bmatrix} 1 & 0^T \\ 0 & m_R \end{bmatrix} = \begin{bmatrix} 1 & 0^T \\ \overrightarrow{P_A} & m_A m_R \end{bmatrix} = \begin{bmatrix} 1 & 0^T \\ \overrightarrow{P_A} m' \end{bmatrix} \tag{2.50}
\]

where

\[
\overrightarrow{P_A} = \frac{\overrightarrow{P} - mD}{1 - D^2} \tag{2.51}
\]

\[
m' = m_A m_R \tag{2.52}
\]

In Equation (2.52) \( m \) is the lower 3x3 sub-matrix of the Muller matrix \( M \) and \( m' \) is the lower 3x3 sub-matrix of \( M' \) which is defined in Equation (2.49) \cite{19},\cite{21}.
Equation (2.53) represents the net depolarization definition.

\[
\Delta = 1 - \frac{\left| \text{tr}M_\Delta - 1 \right|}{3} 
\]

(2.53)

The other way of calculation this parameter is provided in Equation (2.54).

\[
\Delta = 1 - \sqrt{\frac{\sum MM_{ij}^2 - M_{11}^2}{(M_{11})(\sqrt{3})}} 
\]

(2.54)

Consider \( \lambda_1, \lambda_2, \lambda_3 \) to be the eigenvalues of \( m^T m \), so the eigenvalues of \( m_\Delta \) are \( \sqrt{\lambda_1}, \sqrt{\lambda_2}, \sqrt{\lambda_3} \).

\[
m^T m = m_\Delta m_R (m_\Delta m_R)^T = m_\Delta^2
\]

(2.55)

where in Equation (2.55), \( m_R \) is the rotation matrix. \( m_\Delta \) can be expressed using the Cayley-Hamilton theorem [10],

\[
m_\Delta = \pm \left[ m^T m + f_3 I \right]^{-1} \left[ f_2 m^T m + f_3 I \right]
\]

(2.56)

where

\[
f_1 = \sqrt{\lambda_1} + \sqrt{\lambda_2} + \sqrt{\lambda_3}
\]

\[
f_2 = \sqrt{\lambda_1 \lambda_2} + \sqrt{\lambda_2 \lambda_3} + \sqrt{\lambda_3 \lambda_1}
\]

(2.57)

\[
f_3 = \sqrt{\lambda_1 \lambda_2 \lambda_3}
\]

Thus, all three decomposed constituent matrices have been calculated. Complete details of the full derivations can be found in [10], [19], [21], [22].

Mueller matrix decomposition into a sequence of three matrix factors, namely, depolarization, retardance, and diattenuation, was originally proposed by Shih-Yau Lu, et al. 32. This concept can be expanded for Bidirectional Reflectance Distribution Function
(BRDF) applications by expressing them in terms of the aspect angle of an object, $\theta$, so that

$$M(\theta) = M_{\text{depol}}(\theta) M_{\text{ret}}(\theta) M_{\text{diat}}(\theta)$$  \hspace{1cm} (2.58)

$M_{\text{depol}}(\theta)$ accounts for the depolarizing effects of the medium, $M_{\text{ret}}(\theta)$ accounts for the retardance effects of linear birefringence and optical activity, and $M_{\text{diat}}(\theta)$ describes the effects of linear and circular dichroism. From these matrices the diattenuation, retardance, and depolarization characteristics of the medium are readily determined.

The depolarization is quantified in terms of the depolarization index, $P_D$, according to

$$P_D(\theta) = \text{Dep}(M(\theta)) = 1 - \sqrt{\frac{\sum_{i,j} m_{ij}^2(\theta) - m_{00}^2(\theta)}{3m_{00}^2(\theta)}}$$  \hspace{1cm} (2.59)

where $m_{ij}(\theta)$ are the MM elements as a function of the aspect angle. From the decomposed retardance matrix, $M_{\text{ret}}(\theta)$, the total retardance, $R$, which includes the effects of both linear and circular birefringence, can be expressed as

$$R(\theta) = \cos^{-1}\left(\frac{\text{tr}(M_{\text{ret}}(\theta))}{2} - 1\right)$$  \hspace{1cm} (2.60)

where $\text{tr}(M_{\text{ret}}(\theta))$ is the trace of the retardance matrix. The diattenuation, $d$, is dependent on the first row vector of the MM [41]. This vector describes differential attenuation for both linear and circular polarization states and the diattenuation can be expressed in terms of it as
\[ d(\theta) = \frac{1}{m_{00}(\theta)} \times \sqrt{m_{01}^2(\theta) + m_{02}^2(\theta) + m_{03}^2(\theta)} \]  

(2.61)

2.6. Stokes Analysis

The polarimetric system developed in this study is able to calculate the Muller matrix of the object and derive all sixteen elements. Incomplete systems are not able to calculate all sixteen Muller matrix elements of the object. The purpose of those systems is to derive particular elements or a portion of the Stokes vectors as the figure of merit to characterize an object and consequently they are less expensive and simpler. Whatever the case, the Stokes vector itself contains valuable information since it describes the polarization ellipse. Earlier, the Equation of Stokes vector was derived in the form of,

\[
S = \begin{bmatrix}
S_0 \\
S_1 \\
S_2 \\
S_3
\end{bmatrix}
\]  

(2.62)

Several figures of merit can be derived using Stokes analysis. In Equation (2.62) \( S_0, S_1, S_2, S_3 \) are the Stokes vector elements and each of them has their own physical meaning in term of light intensity[19], [23].

Degree of polarization (DOP) represents the polarization of light as the ratio of Stokes parameters \( (S_1, S_2, S_3) \) and \( S_0 \). Stokes vector is applicable for both completely polarized light and unpolarized light. Equation (2.63) defines DOP in terms of Stokes parameters:

\[
DOP = \frac{\sqrt{S_1^2 + S_2^2 + S_3^2}}{S_0}
\]  

(2.63)
Degree of polarization can be calculated for particular polarization such as linear polarization and circular polarization. Degree of linear polarization (DOCP) is given by Equation (2.64)

\[
DOLP = \frac{\sqrt{S_1^2 + S_2^2}}{S_0}
\]  

(2.64)

DOLP or degree of circular polarization is given by Equation (2.65)

\[
DOCP = \frac{S_1}{S_0}
\]

(2.65)

As it is shown earlier in Figure 2.4, polarization forms an ellipse rotated by an angle \(\Psi\), which is adapted from the Goldstein [10]. The ellipticity is described as the ratio of minor axis to the major axis of this ellipse and it is represented in terms of Stokess parameters in Equation (2.66). The other parameter, eccentricity, which is closely related parameter to ellipticity is shown in Equation (2.67) where in this Equation “\(e\)” represents the ellipticity. Another figure if merit is the orientation of major axis is given by Equation (2.68).

\[
e = b = \frac{S_1}{S_0 + \sqrt{S_1^2 + S_2^2}}
\]  

(2.66)

\[
Eccentricity = \sqrt{1 - e^2}
\]

(2.67)

\[
\Psi = \frac{1}{2} \arctan \left( \frac{S_2}{S_1} \right)
\]

(2.68)

Ellipticity values change from 0 to 1, where 0 is considered as linearly polarized light and 1 considered as circularly polarized light. Eccentricity has the similar range.
The output Stokes vector can be achieved easily using Equation (2.69), once the Muller matrix of an object is known. In this Equation $S$ represents the Stokes vector of the incident light and $M$ is the Muller matrix of the object. As a result, $S'$ is the output Stokes vector and can be calculated by

$$S' = MS$$ \hspace{1cm} (2.69)

In a complete polarimetric system each of 16 states has different input Stokes vector so each of them will have different output Stokes vector. In addition to the “classical method”, which has been described in this thesis, there are other techniques used for characterization of an object and find its Stoke vector such as “Fourier Analysis with a Rotating Quarter Wave Retarder”, “Dual Rotating Retarder Polarimetry” and “The Quarter Wave Retarder Polarizer Method” which are described in detail in [10],[24],[25].
CHAPTER III

EXPERIMENTAL DESCRIPTION

This chapter consists of three parts which are 1) Polymer Sample Properties and Fabrication Techniques, 2) System Components and Calibration of Optical Devices and 3) Experimental Arrangement.

In this chapter the preparation and fabrication of polymer samples and their properties are described. In addition, the calibration procedures of the electro-optical system design and the experimental arrangement of the system used in this study is adequately described.

3.1. Polymer Sample Properties and Fabrication Procedures

The polymers for this study were purchased from the Polymer Source Inc. with the following properties and used as obtained.

3.1.1. PS-PMMA and PS-PMMA/AuNP

The first block copolymer is PS-b-PMMA or Poly (styrene-block-methyl methacrylate) with molecular weight of PS $57kg/mol^{-1}$, PMMA $25kg/mol^{-1}$ (total molecular weight $82kg/mol^{-1}$). Thiol- terminated polystyrene (PS-SH) Au NPs with
average core diameter \( < d > = 3.61 \pm 1.29 \text{nm} \) and degree of polymerization of surface-grafted chains \( N = 9 \) were synthesized by phase transfer reduction of \([\text{AuCl}_4^-]\) in the presence of the thiol ligands. Appropriate amount of AuNPs were mixed with the PS-PMMA solutions. The concentration of PS-b-PMMA in toluene is 3wt%. The concentration of Au NP with respect to PS-b-PMMA is 10%. Thins films (120nm and 180nm) were flow-coated on ultraviolet-zone-cleaned silicon substrates.

Surface topography was imaged using a Dimension Icon atomic force microscope (Bruker AXS) in the Peak Force Quantitative Nanomechanical Property mapping mode [39].

From the above mentioned block copolymer three samples were fabricated over bare silicon in different thicknesses, listed as following:

1) PS-b-PMMA with 180 nm thickness
2) PS-b-PMMA/10% Au NP with 180 nm thickness
3) PS-b-PMMA/10% Au NP with 120 nm thickness

3.1.2. PS-PMMA, As-cast/Annealed

The second block copolymer is PS-PMMA which contains no gold nanoparticles and it is a pure block copolymer. Lamellar BCP film with the molecular weight of \( 260 \text{kg/mol} \) and \( 289 \text{kg/mol} \) Ps-b-PMMA were flow-casted. From this block copolymer the following sample was fabricated.

1) PS-PMMA 183nm, As-cast

The thickness of the cast film is 183nm. Then the sample was vacuum oven annealed for 3 hours at 180° C.
AFM measurement was done on the oven annealed sample with the purpose of the phase separation. AFM measurements of the As-cast show that the film is basically smooth without phase separation structures. AFM measurement of the annealed sample is provided in Figure 3.1. Sample surface is very smooth. The lack of distinguishable features indicates parallel orientation of lamellae.

Figure 3.1 AFM measurement of the PS-PMMA 183nm/3 hour oven annealed

3.1.3. PS-P2VP/AuNP

The third block copolymer studied in this thesis is the poly (styrene-\textit{b}-2-vinylpyridine) PS-\textit{b}-P2VP diblock copolymer. Figure 3.2 shows the chemical structure. The PS-\textit{b}-P2VP diblock copolymer used in this study has the molecular weight of PS 40 kg / mol \textsuperscript{-1}, P2VP 18 kg / mol \textsuperscript{-1} (Total Thiol- terminated polystyrene (PS-SH) Au NPs
with average core diameter \( <d> \approx 6.8\text{nm} \) were synthesized by phase transfer reduction of \([\text{AuCl}_4]^{-}\) in the presence of the thiol ligands PS (red section).

The concentration of Au NP with respect to PS-\(b\)-P2VP is 6%. The samples made from this block co polymer with different thickness are listed as the following:

1) PS-P2VP/Au NPs 105 nm
2) PS-P2VP/ Au NPs 40 nm

Note that 105nm and 40nm are the thicknesses of the samples. After the initial experiments on as-cast samples they were vacuum oven annealed for 1hour at 180°C. Optical experiments were repeated for annealed samples. AFM measurements were done for PS-P2VP/ Au NPs 40 nm annealed sample and PS-P2VP/Au NPs 105 nm annealed sample are provided in Figures Figure.3.3 and Figure.3.4. Figure.3.5 represents the schematic of the PS coated AuNP.
Figure 3.3 AFM measurement of the PS-P2VP annealed sample contains 6% Au NP with 40nm thickness

Figure 3.4 AFM measurement of the PS-P2VP annealed sample contains 6% Au NP with 105nm thickness
3.2. System Components and Calibration of Optical Devices

Previously, optical experiments were done mostly manually and they require a long period of time to record the data. For the purpose of saving time in performing experiments of this study, liquid crystal (LC) devices are considered and considerable performing time of the experiments was reduced. LC devices have electronic control hence they are automated. LC retarder and rotators used in the experiments of this study require electronic control to change the polarization states of the beam. This is yield by applying voltage to LC devices. With no voltage applied maximum retardance will achieve because the molecules lie parallel to the surface. When the voltage is applied to the liquid layer the molecules will change their position toward the direction of applied electric field which introduces retardance for different polarization states. A controller is needed for liquid crystal devices in order to produce a square wave with changing amplitude that controls the retardation. The controller consists of a driver and a VI’s to connect the devices to the LabVIEW. Before starting the optical experiments, the optical
devices need to be calibrated and the acquired calibrated data should be tested using the known Muller matrix components. System calibration setup is illustrated in Figure.3.6

![System calibration setup.](image.png)

Figure.3.6 System calibration setup.

3.2.2. System components

The optical system is composed of the following component and the complete list of the components and detailed information of each component are provided in appendix B of this thesis.

a. Laser: Pilas Model #PiL 106 which is 1065 nm laser with modulation frequency of 200Hz.

b. Detector: THORLABS Femtowatt Photoreceiver PDF10C

c. Oscilloscope: The manual measurements and alignment are made using LeCroy 7300A.

Other optical components such as retarder, rotator and polarizer have their own Muller matrix which is essential for calibrated voltages verification.
d. LC retarder

Equation 3.1 represents the Muller matrix for a liquid crystal retarder [1]. The retarder is composed of two axes: (F) which is the fast axis and (S) which is the slow axis. In this Equation, fast axis is defined by $\theta$ and phase deference is represented by $\phi$. Fast axis is the axis which is parallel to surface of the plate of retarder and the slow axis is the axis which is perpendicular to the surface of the plate of retarder. Light propagates at different speed along the fast axis comparing to slow axis, and the outcome is a phase difference.

$$M_{\text{RET}} = \begin{bmatrix}
1 & 0 & 0 & 0 \\
0 & \cos(2\theta) + \cos(\phi)\sin(2\theta)^2 & (1 - \cos(\phi)\sin(2\theta)\cos(2\theta)) & -\sin(\phi)\sin(2\theta) \\
0 & (1 - \cos(\phi)\sin(2\theta)\cos(2\theta)) & \sin(2\theta) + \cos(\phi)\cos(2\theta)^2 & \sin(\phi)\sin(2\theta) \\
0 & \sin(\phi)\sin(2\theta) & -\sin(\phi)\cos(2\theta) & \cos(\phi)
\end{bmatrix}$$

In the current experimental setup, the fast axis is fixed at 45°, so

$$M_{\text{RET}} = \begin{bmatrix}
1 & 0 & 0 & 0 \\
0 & \cos(\phi) & 0 & -\sin(\phi) \\
0 & 0 & 1 & 0 \\
0 & \sin(\phi) & 0 & \cos(\phi)
\end{bmatrix} \quad (3.2)$$

e. LC Rotator

The liquid crystal retarder is made of two internal retarders. The first is a LC variable retarder and the second one is fixed quarter wave retarder. Muller Matrix of the LC rotator is the production of the Muller matrixes of two internal retarders as described in Equation 3.3

$$M_{\text{ROT}} = M_{\text{RET(\text{fixed})}} \ast M_{\text{RET(\text{variable})}} \quad (3.3)$$

Thus the Muller matrix of the rotator is

46
In the experimental setup, $\theta_1$ and $\phi_1$ are fixed at $135^\circ$ and $45^\circ$ for the fixed retarder, respectively. The variable retarder's fast axis or $\theta_2$ is fixed at $0^\circ$ (which is $45^\circ$ from fixed retarder fast axis) while the $\phi_2$ remains variable. By substituting these values in the Equation (3.4) we will have Equation (3.5).

$$M_{ROT} = \begin{bmatrix}
1 & 0 & 0 & 0 \\
0 & \cos(2\theta_1) + \cos(\phi) \sin(2\theta_1)^2 & (1 - \cos(\phi) \sin(2\theta_1) \cos(2\theta_1)) & -\sin(\phi) \sin(2\theta_1) \\
0 & 1 - \cos(\phi_1) \sin(2\theta_1) \cos(2\theta_1)) & \sin(2\theta_1) + \cos(\phi_1) \cos(2\theta_1)^2 & \sin(\phi_1) \sin(2\theta_1) \\
0 & \sin(\phi_1) \sin(2\theta_1) & -\sin(\phi_1) \sin(2\theta_1) & \cos(\phi_1) \\
\end{bmatrix}$$

$$M_{ROT} = \begin{bmatrix}
1 & 0 & 0 & 0 \\
0 & \cos(\phi) & 0 & \cos(\phi) \\
0 & 0 & 1 & 0 \\
0 & -\cos(\phi) & 0 & \sin(\phi) \\
\end{bmatrix}$$

f. Polarizer

Equation 3.6 is the Muller matrix of polarizer where maximum transmission axis is defined by $\theta$.

$$M_{POL} = \frac{1}{2} \begin{bmatrix}
1 & \cos(2\theta) & \sin(2\theta) & 0 \\
\cos(2\theta) & \cos(2\theta)^2 & \sin(2\theta) \cos(2\theta) & 0 \\
\sin(2\theta) & \sin(2\theta) \cos(2\theta) & \sin(2\theta)^2 & 0 \\
0 & 0 & 0 & 0 \\
\end{bmatrix}$$

3.2.3. Calibration of the Optical System

A three-step calibration procedure took place consisting of following steps:
i. Optical system alignment:

The first step is calibration of optical system. The optical system need to be aligned and optimized to minimize errors in the estimation of polarimetric quantities.

ii. Calibration of the liquid crystal retarder and rotator:

To find the calibrated voltage of crystal devices first the generator arm was calibrated and then analyzer arm is calibrated. The calibration is done by adding each component at a time. Different polarization states are named: Horizontal (H), Vertical (V), +450 linear (P), -450 linear (M), Left circular (LCP), and Right circular (RCP). To find the appropriate retardation or rotation for all the states, different voltages were applied to devices.

The calibration was performed using a technique named Null-intensity. In this method the polarizer at the analyzer arm is always kept cross polarized to the polarizer at the generator arm and the voltage is applied to each of the liquid crystal devices to obtain the null intensity. Due to some system noise in the experiment, it is hard to achieve the null using this technique of alignment. Therefore, a different method is used for calibration of the optical system. In this method, polarizer of the analyzer arm is rotated by tiny angle $\Delta \theta$ to measure the intensities at $90^0 + \Delta \theta$ and $90^0 - \Delta \theta$. When these two measurements are getting equal, the null is exactly between these two angles. To find the two equal measurements we need to repeat the measurements. This method is called the method of Swing [3].

iii. Accuracy test

The developed system was used to calculate the Muller matrix of different nanostructure samples and to analyze their optical properties. After the calibration of
liquid crystal devices such as retarders and rotators, obtained calibrated voltages need to be tested and verifies using some components with known Muller matrix value. The components used for this verification were air, Linear Horizontal Polarizer (LHP) or a polarizer which its transmission axis is in the horizontal direction and Linear Vertical Polarizer (LVP) or a polarizer which its transmission axis is in the vertical direction. To run these experiments the setup was placed in the transmission mode, which means the analyzer and generator arms were placed in the face to face direction. The object which needs to be tested is placed between the two arms. For the air experiment no object is used. The polarizers used in these experiments (LHP or LVP) are appropriate for use in the wavelength range of 700 nm to 1100 nm, which is in the range of the laser wavelength being used in the experiments. Figure 3.7 depicts the setup of devices for verifying the obtained calibrated data.

Figure 3.7 Experimental Setup for the Test of the Calibration Voltages

Table 3.1 the comparison of the experimental and ideal Muller matrix intensities. Plots of the obtained Muller matrix intensities of a calibration targets, air, left horizontal polarizer
and right horizontal polarizer are depicted in Figure.3.8 and Figure.3.9 and Figure.3.10.

As we can see in this table the standard deviation values for the Muller matrix of air, LHP and LVP are 0.114, 0.0478 and 0.0364 respectively. We can conclude from these values that the measurements have high degree of accuracy.

As we can see in this table the standard deviation values for the Muller matrix of air, LHP and LVP are 0.114, 0.0478 and 0.0364 respectively. We can conclude from these values that the measurements have high degree of accuracy.

3.3. NI LabVIEW interface/ System automation

The high level of automation is required to minimize the time of data measurement and data acquisition. The system was utilized in this study was automated to calculate Muller matrix of the sample. Automation of the system was achieved using Labview and Matlab. The system inputs are controlled by a graphical user interface (GUI) which is developed in Labview.

In this GUI the calibration voltages of the LC devices could be applied to the system and the measured voltages from the detector could be write into an excel file. Before starting the experiments some input data should be assigned to the Labview GUI. Following is the list of inputs for the system:

a) Calibration voltages of the LC retarders and rotators

b) Delay time of liquid crystal

c) Sampling rate for DAQ.

d) Measurement time: this time should be greater that the delay time plus the time required acquiring all the sample measurements.
<table>
<thead>
<tr>
<th>Element</th>
<th>Measured Muller Matrix</th>
<th>Ideal Muller Matrix</th>
<th>Element Variance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Air</td>
<td>LHP</td>
<td>LVP</td>
</tr>
<tr>
<td>m11</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>m12</td>
<td>0.014</td>
<td>0.974</td>
<td>-0.992</td>
</tr>
<tr>
<td>m13</td>
<td>-0.005</td>
<td>0.023</td>
<td>-0.066</td>
</tr>
<tr>
<td>m14</td>
<td>0.028</td>
<td>-0.058</td>
<td>0.043</td>
</tr>
<tr>
<td>m21</td>
<td>0.030</td>
<td>0.947</td>
<td>-0.974</td>
</tr>
<tr>
<td>m22</td>
<td>0.940</td>
<td>0.923</td>
<td>0.968</td>
</tr>
<tr>
<td>m23</td>
<td>0.257</td>
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<td>0.060</td>
</tr>
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</tr>
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<td>m31</td>
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<td>m32</td>
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<td>-0.038</td>
<td>0.020</td>
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<tr>
<td>m33</td>
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<td>m34</td>
<td>-0.335</td>
<td>0.001</td>
<td>0.000</td>
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<td>m41</td>
<td>0.001</td>
<td>-0.094</td>
<td>0.058</td>
</tr>
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<td>m42</td>
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<td>-0.089</td>
<td>-0.059</td>
</tr>
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<td>m43</td>
<td>0.067</td>
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<td>-0.003</td>
</tr>
<tr>
<td>m44</td>
<td>0.972</td>
<td>0.007</td>
<td>0.003</td>
</tr>
</tbody>
</table>

Standard Deviation

<table>
<thead>
<tr>
<th></th>
<th>Air</th>
<th>LHP</th>
<th>LVP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.14E-01</td>
<td>4.78E-02</td>
<td>3.64E-02</td>
</tr>
</tbody>
</table>
e) Measurement time: this time should be greater that the delay time plus the time required acquiring all the sample measurements.

f) Voltage threshold level: The voltages above this level are recorded and other voltages are discarded.

g) Waveform data: Which is the number data points obtained in order to display the waveform in Matlab or Excel.

h) Number of the times the experiment is repeated.

i) Laser modulation frequency.

j) Minimum number of the samples Analog to Digital will collect. This number is the minimum number of datapoints, which their value are above the threshold level and is defined by Equation 3.7

\[ D_{\text{min}} = (10\% \text{of } \frac{1}{F_{\text{mod}}}) \times \frac{1}{T_s} \]  

(3.7)

Where in this Equation \( F_{\text{mod}} \) is the modulation frequency of the laser and \( T_s \) is the sampling time.

The outputs of the automated systems are listed as following:

1) Average peak-to-peak voltage for each of the 16 states. They are saved in an excel sheet. For the number of repeated times these average values are recorded in excel sheet.

2) Raw peak-to-peak amplitude is recorded for each of 16 states in excel sheet. (Totally 2500 data points)
Figure 3.8 Ideal Vs Experimental Mueller matrix plot for Air

Figure 3.9 Ideal Vs Experimental Mueller matrix plot for LHP
3) Waveform samples are recorded for each state.

For the experiments which were done manually the 16 states value were recorded and saved in an excel sheet. The output excel sheet will be the input of Matlab code for process and obtaining the Muller matrix of the object, decomposition Muller matrix which are the depolarization matrix, diattenuation matrix and the retardance matrix as discussed in chapter 2. Depolarization coefficient, diattenuation coefficient, total retardance and linear retardance are the other outputs of the Matlab routine which will be saved in an excel sheet. The excel sheet are capable of saving 30 repetitions of the experiment.
3.4. Experimental Arrangement

The experiments for the polymer nanostructure samples were performed under back scattered geometry. The geometry is shown in Figure 3.11. The complete list of the components used in these experiments is listed in APPENDIX B. We used the laser 1065 nm to excite the polymer samples. The generator arm consists of a polarizer, LC rotator and retarder. The analyzer arm composed of the same components placed in backscattered geometry. The polymer samples were placed after the generator arm and before the analyzer arm so the laser beam interacts with them. The backscattered signal was collected by a detector and it was observed by a LeCroy Wavepro 3GHz bandwidth oscilloscope.

In order to make the angular measurements the samples were mounted on a sample holder which controls by a motor capable of rotating. The rotation accuracy of the motor is 0.01°. To make sure that the alignment is completed successfully the sample was rotated until the highest amplitude of the signal was achieved. This angle was considered as the 0° degree.

The signal from the detector could be saved by the oscilloscope or by a subroutine which was developed in Labview. Sixteen polarization intensities are needed in order to find the Muller matrix of the object. These 16 polarimetric intensities are derived by combining 4 polarization states in generator arm and analyzer arm, respectively. As stated previously, 6 calibration voltages were calculated but four of these voltages were applied to the GUI namely: Linear horizontal (H), Linear vertical (V), Linear +450 (P) and Right Circular (RCP).
The combination of these 4 states in each arm results in the 16 states intensities. Following values were applied to the graphical user interface of Labview subroutine. The
combination polarization states of the generator and analyzer arm are provided in Table 3.2.

Table 3.2 combination polarization states of the generator and analyzer arm

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sampling rate</td>
<td>100 KHz</td>
</tr>
<tr>
<td>Liquid crystal delay time</td>
<td>1 sec</td>
</tr>
<tr>
<td>Measurement time</td>
<td>2500 ms</td>
</tr>
<tr>
<td>Voltage threshold level</td>
<td>0.011 V</td>
</tr>
<tr>
<td>Waveform data</td>
<td>2500</td>
</tr>
<tr>
<td>State data</td>
<td>75000</td>
</tr>
<tr>
<td>Repetitions</td>
<td>6</td>
</tr>
<tr>
<td>Laser modulation frequency</td>
<td>50 Hz</td>
</tr>
</tbody>
</table>

After calculating 16 polarimetric intensities, the Muller matrix calculation and Muller matrix decomposition were estimated using a MATLAB code. The Lu-Chipman algorithm was used and the resulting decomposed matrices namely: diattenuation, depolarization and retardance were obtained. In addition to these matrices their corresponding coefficients were calculated. For the automated system the experiments were repeated 6 times, for increased statistical accuracy.

Two sets of the experiments for both PS-PMMA samples were performed manually and the 16 states intensities were achieved using the oscilloscope. For this purpose the mean value of the obtained signal for each angle was recorded after the number of the recorded samples were exceed 200. The remaining calculation of the Muller matrix, decomposition matrices, diattenuation, decomposition and depolarization
coefficients and further parameters analysis such as Stokes parameters calculation, and polarizance calculation following the same procedure as what we did in the automated part. For the output data achieved by automated system (6 set data for each rotation angle for each sample) first, second and third order of the statistics like standard deviation, skewness and kurtosis could be obtained.
CHAPTER IV
RESULTS AND DISCUSSION

This chapter provides the experimental results of the polymer matrices and functionalized nanopolymers. The Muller matrix of polymers were obtained after recording the backscattered intensity signals for all 16 states, at different aspect angles, after applying the “Data Reduction Method” as discussed in chapter 2. The depolarization coefficient and diattenuation coefficient of the Mueller matrices of the different samples were estimated through Mueller Matrix decomposition. The Stokes parameters, Degree of polarization (DOP), degree of linear polarization (DOLP), and degree of circular polarization (DOCP), polarizance coefficient and several other optical parameters are presented.

4.1. Results of PS-PMMA/Au NPs (PS, PMMA 82kg/mol)

As described in chapter 3, the polymers for this study were purchased from the Polymer Source Inc. with the following properties and used as obtained. The first block copolymer is PS-b-PMMA or Poly (styrene-block-methyl methacrylate) with molecular weight of PS 57kg/mol, PMMA 25kg/mol (total molecular weight 82kg/mol). Thiol- terminated polystyrene (PS-SH) Au NPs with average core diameter \( <d> \approx 3.61\pm1.29 \text{ nm} \) and degree of polymerization of surface-grafted chains \( N = 9 \) were
synthesized by phase transfer reduction of \([AuCl_4]^{-}\) in the presence of the thiol ligands. Appropriate amount of AuNPs were mixed with the PS-PMMA solutions. The concentration of PS-b-PMMA in toluene is 3wt%. The concentration of Au NP with respect to PS-b-PMMA is 10%. Thin films (120nm and 180nm) were flow-coated on ultraviolet-zone-cleaned silicon substrates.

Three samples were fabricated as following,

1) PS-b-PMMA with 180 nm thickness
2) PS-b-PMMA/ 10% Au NP with 180 nm thickness
3) PS-b-PMMA/ 10% Au NP with 120 nm thickness

4.1.1. Muller Matrices and Stokes Parameters Analysis

The Mueller matrix plot of different polymer shows that discrimination between the samples can be obtained from the Mueller matrix diagonal elements. The diagonal elements of the Mueller matrix represent the isotropic absorption of light after it interacts with the sample. It is thus clear from the results that PS-b-PMMA/Au NP 120 nm exhibits reduced isotropic backscattered light than other samples. Thus, depolarization of light obtained from PS-b-PMMA/Au NP 120 nm is higher than the other samples.

The Depolarization coefficients of Figure.4.2 indicates that PS-PMMA 120 nm with 10% gold nanoparticles depolarizes polarized light more than the other samples, within a narrow angle of observation. This claim is supported by the previous analysis of Figure.4.1.
Figure 4.1 Muller matrix plots Comparison for the PS-PMMA 180nm (pure block copolymer), PS-PMMA 180 nm contains 10% Au NPs and PS-PMMA 120 nm contains 10% Au NPs.
Figure 4.2 Comparison of depolarization coefficient for the PS-PMMA 180 nm (pure block copolymer), PS-PMMA 180 nm contains 10% Au NPs and PS-PMMA 120 nm contains 10% Au NPs.

The diattenuation coefficients plot of Figure 4.3 clearly indicates that the polymer matrix PS-b-PMMA 180 nm exhibits increased diattenuation within a narrow angle of observation, while, PS-b-PMMA/10% Au NP 180 nm exhibits the least one.

Figure 4.3 Comparison of diattenuation coefficient for the PS-PMMA 180 nm (pure block copolymer), PS-PMMA 180 nm contains 10% Au NPs and PS-PMMA 120 nm contains 10% Au NPs.
Similarly, both the Degree of Polarization plots and Degree of Linear Depolarization of Figure 4.4 and Figure 4.5, respectively, indicate that the functionalized nanopolymer PS-b-PMMA/10% Au NP 180 nm maintain the highest degree of linear polarization, while the sample PS-b PMMA/10% Au NP 120 nm the least one, acclaim that is supported by the results of Figure 4.1 and Figure 4.2.

**Figure 4.4** Comparison of the degree of polarization for the PS-PMMA 180 nm (pure block copolymer), PS-PMMA 180 nm contains 10% Au NPs and PS-PMMA 120 nm contains 10% Au NPs.

**Figure 4.5** Comparison of the degree of linear polarization for the PS-PMMA 180 nm (pure block copolymer), PS-PMMA 180 nm contains 10% Au NPs and PS-PMMA 120 nm contains 10% Au NPs.
The results of Figure 4.6 indicate that the functionalized nanopolymer PS-b-PMMA/10%Au NP 120 nm exhibits higher degree of degree of circular polarization with respect to the other samples.

To further differentiate the samples, one of the properties of Mueller matrix, known as polarizance is plotted for all the different samples which can be seen in Figure 4.7. It can be clearly seen that the polarizance of functionalized nanopolymer PS-b-PMMA/10%Au NP 180 nm is less than the other samples.

The Stokes parameters plots are depicted in Figures 4.8-4.11. The plot of Figure 4.11. indicates that the functionalized nanopolymer PS-PMMA 120 nm /10% Au NPs exhibits higher S3 Stokes parameter with respect to the other samples, in agreement with Figure 4.6. Similarly, the functionalized nanopolymer PS-PMMA 180 nm /10% Au NPs, exhibits higher S1 Stokes parameters than the other samples, in agreement with Figures 4.4-4.5.
Figure 4.7 Comparison of the Polarizance coefficient for the PS-PMMA 180nm (pure block copolymer), PS-PMMA 180 nm contains 10% Au NPs and PS-PMMA 120 nm contains 10% Au NPs.

Figure 4.8 Comparison of the S0 for the PS-PMMA 180nm (pure block copolymer), PS-PMMA 180 nm contains 10% Au NPs and PS-PMMA 120 nm contains 10% Au NPs.
Figure 4.9 Comparison of S1 for the PS-PMMA 180nm (pure block copolymer), PS-PMMA 180 nm contains 10% Au NPs and PS-PMMA 120 nm contains 10% Au NPs.

Figure 4.10 Comparison of S2 for the PS-PMMA 180nm (pure block copolymer), PS-PMMA 180 nm contains 10% Au NPs and PS-PMMA 120 nm contains 10% Au NPs.
Figure 4.11 Comparison of S3 for the PS-PMMA 180 nm (pure block copolymer), PS-PMMA 180 nm contains 10% Au NPs and PS-PMMA 120 nm contains 10% Au NPs.

The second sample was considered for the experiment is lamellar BCP thin film with the molecular weight of 260 kg/mol and 289 kg/mol Ps-b-PMMA. The experiments highlighted the optical characteristic of the as-cast and annealed samples.

The sample is PS-PMMA pure block copolymer fabricated with 183 nm thickness. The experiment was performed on the as-cast sample and repeated for the oven annealed sample defined as annealed in the reported plots.

The Mueller matrix plot of as-cast and annealed polymer samples shows that discrimination between the samples can be obtained from the Mueller matrix diagonal elements. The diagonal elements of the Mueller matrix represent the isotropic absorption of light after it interacts with the sample. It is thus clear from the results that PS-b-PMMA/183 nm as-cast exhibits reduced isotropic backscattered light than other samples.
Thus, depolarization of light obtained from PS-b-PMMA/183 nm as-cast is higher than the other sample.

Figure 4.12 Muller matrix plots Comparison for the PS-PMMA 183nm (pure block copolymer) as-cast and annealed sample.
The depolarization coefficients of Figure 4.13 indicates that PS-PMMA 183 nm as-cast depolarizes polarized light more than the other samples, within a narrow angle of observation. This claim is supported by the previous analysis of Figure 4.12.

Figure 4.13 Comparison of the depolarization coefficient of the as-cast and annealed PS-PMMA 183 nm (no Au NPs) sample for different rotation angles of the object.

The diattenuation coefficients plot of Figure 4.14 clearly indicates that the polymer matrix PS-b-PMMA 183 nm as-cast exhibits increased diattenuation within a narrow angle of observation, while, PS-b-PMMA 183 nm annealed exhibits the least one.

Figure 4.14 Comparison of the diattenuation coefficient of the as-cast and annealed PS-PMMA 183 nm (no Au NPs) sample for different rotation angles of the object.
Similarly, both the Degree of Polarization plots and Degree of Linear Depolarizations of Figure.4.15 and Figure.4.16, respectively, indicate that the functionalized nanopolymer PS-b-PMMA 183nm annealed maintain the highest degree of linear polarization, while the sample PS-b-PMMA 183nm as-cast maintains the least one, acclaim that is supported by the results of Figure.4.12 and Figure.4.13.

![Comparison of Degree of Polarization for PS-PMMA/ as-cast and annealed](image_url)

Figure.4.15 Comparison of the DOP of the as-cast and annealed PS-PMMA 183nm (no Au NPs) sample for different rotation angles of the object.
Figure 4.16 Comparison of the DOLP of the as-cast and annealed PS-PMMA 183nm (no Au NPs) sample for different rotation angles of the object.

The results of Figure 4.17 indicate that the functionalized nanopolymer PS-b-PMMA/183nm as-cast exhibits higher degree of circular polarization with respect to the other samples.

Figure 4.17 Comparison of the DOCP of the as-cast and annealed PS-PMMA 183nm (no Au NPs) sample for different rotation angles of the object.
To further differentiate the samples, one of the properties of Mueller matrix, known as polarizance is plotted for all the different samples which can be seen in Figure 4.18. It can be clearly seen that the polarizance of functionalized nanopolymer PS-b-PMMA 183 nm annealed is less than the other sample.

![Polarizance](image)

Figure 4.18 Comparison of the Polarizance coefficient of the as-cast and annealed PS-PMMA 183nm (no Au NPs) sample for different rotation angles of the object

The Stokes parameters plots are depicted in Figures 4.19 -4.22. The plot of Figure 4.22 indicates that the functionalized nanopolymer PS-PMMA 183nm as-cast exhibits higher S3 Stokes parameter with respect to the other samples, in agreement with Figure 4.17. Similarly, the functionalized nanopolymer PS-PMMA 183nm annealed, exhibits higher S1 Stokes parameters than the other samples, in agreement with Figure 4.15 and Figure 4.16
Figure 4.19 Comparison of S0 for the PS-PMMA 183nm (pure block copolymer) as-cast and annealed

Figure 4.20 Comparison of S1 for the PS-PMMA 183nm (pure block copolymer) as-cast and annealed
Figure 4.21 Comparison of S2 for the PS-PMMA 183nm (pure block copolymer) as-cast and annealed

Figure 4.22 Comparison of S3 for the PS-PMMA 183nm (pure block copolymer) as-cast and annealed
The third and final experiment was performed on the PS-b-P2VP diblock copolymer with molecular weight of PS 40kg/mol, P2VP 18kg/mol (total 58kg/mol). The samples made from this diblock copolymer are:

1) PS-P2VP/6% Au NPs with 105 nm thickness 
2) PS-P2VP/6% Au NPs with 40 nm thickness 

The experiments were performed on the annealed samples to characterize different thickness of the annealed sample.

Figure 4.23 Comparison of the Muller matrix elements for the annealed PS-P2VP 105nm/6% Au NPs and PS-P2VP 40nm/6% Au NPs samples.
The Mueller matrix plot of different polymer shows that discrimination between the samples can be obtained from the Mueller matrix diagonal elements. The diagonal elements of the Mueller matrix represent the isotropic absorption of light after it interacts with the sample. It is thus clear from the results that PS-b-P2VP/6% Au NP 105 nm annealed exhibits reduced isotropic backscattered light than other sample. Thus, depolarization of light obtained from PS-b-P2VP/6% Au NP 105 nm is higher than the other sample.

The Depolarization coefficients of Figure.4.24 indicates that PS-b-P2VP/6% Au NP 105 nm depolarizes polarized light more than the other samples, within a narrow angle of observation. This claim is supported by the previous analysis of Figure.4.12.

Figure.4.24 Comparison of depolarization coefficient for the PS-P2VP 105 nm contains 6% Au NPs nm/ Annealed and PS-P2VP 40nm contains 6% Au NPs/ Annealed
The diattenuation coefficients plot of Figure 4.25 clearly indicates that the polymer matrix PS-b-P2VP/6% Au NP 40nm exhibits increased diattenuation within a narrow angle of observation, while, PS-b-P2VP/6% Au NP 105nm exhibits the least one.

Figure 4.25 Comparison of diattenuation coefficient for annealed PS-P2VP/ Au NPs

Similarly, both the Degree of Polarization plots and Degree of Linear Depolarizations of Figure 4.26 and Figure 4.27, respectively, indicate that the functionalized nanopolymer PS-b-P2VP/6% Au NP 40 nm maintain the highest degree of linear polarization, while the sample PS-b-P2VP/6% Au NP 105 nm maintains the least one, acclaim that is supported by the results of Figures Figure 4.23 and Figure 4.24.
Figure 4.26 Comparison of DOP for the PS-P2VP 105 nm contains 6% Au NPs mm/ Annealed and PS-P2VP 40nm contains 6% Au NPs/ Annealed

Figure 4.27 Comparison of degree of linear polarization for the PS-P2VP 105 nm contains 6% Au NPs mm/ Annealed and PS-P2VP 40nm contains 6% Au NPs/ Annealed
The results of Figure.4.28 indicate that the functionalized nanopolymer PS-b-PS-b-P2VP/6% Au NP 105nm annealed exhibits higher degree of degree of circular polarization with respect the other samples.

Figure.4.28 Comparison of degree of circular polarization for the PS-P2VP 105 nm contains 6% Au NPs/Annealed and PS-P2VP 40nm contains 6% Au NPs/Annealed

To further differentiate the samples, one of the properties of Mueller matrix, known as polarizance is plotted for all the different samples which can be seen in Figure.4.29 It can be clearly seen that the polarizance of functionalized nanopolymer PS-b-PS-b-P2VP/6% Au NP 40nm annealed is less than the other sample.
Figure 4.29 Comparison of Polarizance coefficient for the PS-P2VP 105 nm contains 6% Au NPs nm/ Annealed and PS-P2VP 40nm contains 6% Au NPs/ Annealed

The Stokes parameters plots are depicted in Figure 4.30 to Figure 4.33. The plot of Figure 4.33 indicates that the functionalized nanopolymer PS-b-PS-b-P2VP/6% Au NP 105 nm annealed exhibits higher S3 Stokes parameter with respect to the other samples, in agreement with Figure 4.28. Similarly, the functionalized nanopolymer PS-b-PS-b-P2VP/6% Au NP 40 nm annealed, exhibits higher S1 Stokes parameters than the other samples, in agreement with Figures Figure 4.27 and Figure 4.28.
Figure 4.30 Comparison of S0 for the annealed PS-P2VP 105 nm / 6% Au NPs and annealed PS-P2VP 40 nm / 6% Au NPs

Figure 4.31 Comparison of S1 for the annealed PS-P2VP 105 nm / 6% Au NPs and annealed PS-P2VP 40 nm / 6% Au NPs
Figure 4.32 Comparison of $S_2$ for the annealed PS-P2VP 105 nm / 6% Au NPs and annealed PS-P2VP 40nm / 6% Au NPs

Figure 4.33 Comparison of $S_3$ for the annealed PS-P2VP 105 nm / 6% Au NPs and annealed PS-P2VP 40nm / 6% Au NPs
CHAPTER V

FUTURE WORKS

As part of future study, is proposed the interrogation of the samples with additional wavelengths from the visible and NIR spectrum. This will provide additional information regarding the optical properties of the polymer nanostructures.
REFERENCES


[12] photonic , principles and practices adbul al-azzavi , crc press


[34] Ingrosso, C.; Panniello, A.; Comparelli, R.; Curri, M. L.; Striccoli, M. Materials 2010, 3, 1316.


APPENDICES
APPENDIX A

ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFRL</td>
<td>Air Force Research Laboratory</td>
</tr>
<tr>
<td>LC</td>
<td>Liquid Crystal</td>
</tr>
<tr>
<td>LHP</td>
<td>Linear Horizontal Polarizer</td>
</tr>
<tr>
<td>LVP</td>
<td>Linear Vertical Polarizer</td>
</tr>
<tr>
<td>MM</td>
<td>Mueller Matrix</td>
</tr>
<tr>
<td>DOP</td>
<td>Degree of Polarization</td>
</tr>
<tr>
<td>DOLP</td>
<td>Degree of Linear Polarization</td>
</tr>
<tr>
<td>DOCP</td>
<td>Degree of Linear Polarization</td>
</tr>
<tr>
<td>HH</td>
<td>Horizontal-Horizontal Measurement State</td>
</tr>
<tr>
<td>HV</td>
<td>Horizontal - Vertical Measurement State</td>
</tr>
<tr>
<td>PP</td>
<td>+45° +45° Linear Measurement State</td>
</tr>
<tr>
<td>RR</td>
<td>Right Circular - Right Circular Measurement State</td>
</tr>
<tr>
<td>NP</td>
<td>Nanoparticle</td>
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</table>
# APPENDIX B

## LIST OF COMPONENTS USED FOR THE EXPERIMENT

<table>
<thead>
<tr>
<th>Components</th>
<th>Manufacturer</th>
<th>Model Number</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>PiLas 1065nm Pulsed Laser</td>
<td>Advanced Laser Diode Systems</td>
<td>PiL106</td>
<td>The laser is modulated at 200Hz with tune value of 100%. Maximum power output of this laser is 2500mW.</td>
</tr>
<tr>
<td>Liquid Crystal Retarders And Rotators</td>
<td>Meadowlark Optics</td>
<td>LRC-100(Retarder) and LPR-100(Rotator)</td>
<td>The purpose of using rotator is to convert the linear polarized light to different states and The purpose of using retarder is to convert the linear polarized light to circular polarized light and vice versa.</td>
</tr>
<tr>
<td>Linear Polarizers</td>
<td>Meadowlark Optics</td>
<td>UPM-100-VIS</td>
<td>The linear polarizer allows transmitting the light parallel to its transmission axis and other light components are rejected.</td>
</tr>
<tr>
<td>Oscilloscope</td>
<td>LeCroy</td>
<td>WavePro 7300A</td>
<td>The purpose of using oscilloscope is to display the back scattered signals collected by the photoreceiver.</td>
</tr>
<tr>
<td>InGaAs Amplified Detector</td>
<td>Thorlabs</td>
<td>PDF10C</td>
<td>The detector has a 0.5 mm diameter and is a InGaAs Amplified Detector which can detect light in the range of 800-1700nm.</td>
</tr>
<tr>
<td>Component</td>
<td>Supplier</td>
<td>Model/Part Number</td>
<td>Description</td>
</tr>
<tr>
<td>----------------------------</td>
<td>-------------------</td>
<td>-------------------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Optics Mounts</td>
<td>Thorlabs</td>
<td></td>
<td>These components are utilized in order to hold the polarizers, retarders,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>rotators, photoreceiver and sample.</td>
</tr>
<tr>
<td>Optics Table Posts</td>
<td>New Focus</td>
<td>9912</td>
<td>These posts are the posts that attaches the optics mounts to the optics</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>table.</td>
</tr>
<tr>
<td>Optics Experimental Table</td>
<td>Melles Griot</td>
<td></td>
<td>The table is utilized to hold the optical components, photoreceiver,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>rotating motor, sample holder.</td>
</tr>
<tr>
<td>Motor Controller</td>
<td>Velmex Inc.</td>
<td>VP9000; Stepping</td>
<td>The motor controller is used to rotate the object and to align it with the</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Motor-PK01AA.</td>
<td>laser. The accuracy of motor is 0.01.</td>
</tr>
<tr>
<td>Object Mount</td>
<td>Edmund Optics</td>
<td>NT54-997</td>
<td>This mount is used to hold the object (Polymer thin films) [2].</td>
</tr>
</tbody>
</table>