Chapter 1 - Literature Review

1.1 Introduction to Optics, optical devices and the use of polymers in Optical applications

This research concerns the use of ionically self-assembled monolayer films for producing second order nonlinear optical materials that can be used in optical devices such as electro-optic modulators as well as biosensors. First, nonlinear optical phenomena are briefly reviewed followed by a discussion of nonlinear optical materials and the specific applications of second-order nonlinear optical materials. Among the nonlinear optical materials covered are some of the organic materials currently used and how they compare with new polymeric nanostructures. Due to the versatility of polymeric materials, better devices with higher efficiencies and easier processability can be made with the use of polymers at lower costs. Secondly, the different ways in which polymers can be processed for their use in optical devices is discussed, especially thin films. This section will cover the various deposition techniques for thin films such as Langmuir Blodgett films, poled polymer films and ionically self-assembled monolayer (ISAM) films along with the distinct advantages of ISAM films, which is the primary focus of this thesis. There are certain difficulties associated with these films that compromise their usability for nonlinear optical applications. One of these is specific orientation of the NLO-active material in the film films, caused potentially by the interpenetration of the different monolayers deposited. To counter this problem we have used a synthetic hectorite, Laponite RD, which deposits as thin platelets and thus reduces the interpenetration of the different monolayers. There are several other advantages with using these platelets, which are discussed in more detail in the subsequent chapters.

1.1.1 Introduction to nonlinear optics and its applications

“Your network can’t be too cheap or have too much capacity”. This is the equivalent of the famous phrase of the Duchess of Windsor “You can’t be too rich or too thin”, in the fiber-optics communications industry. Bandwidth at a bargain is the primary driver of the fiber-optics industry and drives it to feverishly strive for the cutting-edge technology to meet this goal [1]. Telecommunications technologies have created the need
for high performance optical devices such as lasers, electro-optical modulators, image processors and optical memories. In this research, we concentrate on one of these specific areas, which is the use of materials exhibiting second harmonic generation or frequency doubling that are used in electro-optic (EO) modulators. This has been a subject of much interest and study since Franken et al. [2] first observed frequency doubling in quartz. Frequency changing occurs due to the materials ability to change its refractive index and thus altering the frequency of the light passing through it [3]. This phenomenon of frequency altering by a medium when an electric field is applied is called the Pockels effect [4]. An example of this is the conversion of the commercial infrared laser (wavelength of 1064 nm), to green light (wavelength of 532 nm), when passed through one of these second-order nonlinear media. This transformation is useful because it quadruples the amount of information the laser can write on an optical disc [5]. Materials that exhibit this frequency doubling undergo a polarization when subjected to an electric field, which is given by

\[ P = \chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \ldots \ldots \]  

(1.1)

Where,

E is the applied electric field

\( \chi^{(1)} \) is the linear dielectric susceptibility

\( \chi^{(2)}, \chi^{(3)} \) are the higher order nonlinear susceptibilities.

When the higher order terms are zero, the material is said to be linear. A nonlinear material has non-zero higher order susceptibilities. The specific classes of nonlinear materials that are discussed in this study are the second-order nonlinear materials or the ones that have a non-zero \( \chi^{(2)} \). This can only be obtained from nonlinear noncentrosymmetric materials. Figure 1.1 shows the different polarization responses to the applied field. Nonlinear noncentrosymmetric media have a finite time-averaged polarization (Figure 1.1d). These materials have vast applications in the field of electro-optics and various electro-optic devices. An example of an electro-optic device is a Mach Zehnder interferometer shown in Figure 1.2.
Figure 1.1: Electric field and corresponding polarization fields in various media. (a) Incident electric field. (b) Polarization field of (a) in linear, centrosymmetric medium. (c) Polarization field of (a) in centrosymmetric, nonlinear medium. (d) Polarization field of (a) in noncentrosymmetric, nonlinear medium. Only (d) has non-zero time-averaged polarization field (and non-zero $\chi^{(2)}$)
1.1.1a Mach Zehnder Interferometer

The Mach Zehnder interferometer is an electro-optic device used to modulate wave amplitude [6]. As seen in fig 1.2, an incident electric wave with intensity $I_0$ enters through one end and the beam is split into the two arms of the interferometer. The second order nonlinear material is placed in one of the arms where a DC bias voltage is applied. This alters the refractive index of the material and the wave exits the arm at a different wavelength and combines with the beam exiting from the second arm. The optical beam passing through the NLO material under an electric field experiences a phase shift, and the voltage required for a $180\,^\circ$ phase shift, $V_{\pi}$, is given by:

$$V_{\pi} = \frac{d\lambda}{\ln n_0^3} r_{33}$$

Where,

$d$ is the gap between the electrodes

$\lambda$ is the optical wavelength

$n_0$ is the ordinary refractive index of the material

$l$ is the length of the two arms of the interferometer and

$r_{33}$ is the EO coefficient of the waveguide material

By changing the DC voltage, the waves can interfere constructively (phase-shift of $180\,^\circ$) or destructively and thus can be used as a modulator. The interest in the materials used in these devices derives from the need for high-speed (wide bandwidth), low drive–voltage
(low $V_\pi$) EO modulators. The drive-voltage has remained persistently high ($V_\pi \sim 5V$), and the current efforts [7] are concentrated on getting it below 1V.

1.1.2 Materials used currently in electro-optic devices

Most of the materials that are used currently in these electro-optic devices are inorganic single crystals such as lithium niobate, potassium dihydrogen phosphate and $\beta$-barium borate [6]. The $\chi^{(2)}$ exhibited by these materials range from 1-100 x $10^{-9}$ esu, which is comparable to the one obtained from quartz (1.53 x $10^{-9}$ esu). But fabrication of these single crystals is a complicated process requiring conditions of high pressures and temperatures [8]. Incorporation of these crystals into commercial devices is also a difficult procedure [5]. Some other disadvantages of these crystals are that they have a large mass, high cost, poor environmental stability, and also exhibit weakness to atmospheric humidity. All these limitations associated with the organic crystals has led to the quest for better electro-optic materials, among which organic polymers show the most promise.

1.1.3 Use of polymers in second-order nonlinear optical devices

To overcome the difficulties posed by inorganic single crystals, much research has been done on new materials that can potentially replace them. For EO applications, organic NLO optical materials have three distinct advantages over their inorganic counterparts [9]. One is the low dielectric constants characteristic of organic (polymeric) materials. A low dielectric constant reduces the resistor-capacitor (RC) delay time constant and therefore increases the speed of the device. The second is the relatively constant refractive index of organic EO polymers for wavelengths from infrared to microwave region and thus ensures proper modulator operation over that range. Thirdly, polymeric materials offer the advantage of ease of integration with semiconductor electronics [10].

Progress in this direction of finding new polymeric materials requires these materials to possess large nonlinear coefficients, good thermal, temporal and mechanical stability as well as ease of processing. These materials should be easily integrated into optical devices that are compatible with fiber optics, have low power consumption and
operate at higher frequencies [11]. Some of the advantages offered by polymeric materials are due to the fact that they can be prepared in fiber and thin-film forms, they offer low optical loss, and are significantly cheaper than their inorganic counterparts.

Selection of the organic materials for the EO modulator films is the key issue. Since the drive-voltage $V_\pi$ should be as low as possible, the coefficient $r_{33}$ should be as high as possible (from equation 1.2). This EO coefficient $r_{33}$, is linearly proportional to the second-order nonlinear susceptibility $\chi^{(2)}$, of the medium [4]. Thus, for optimum device performance, it is important for the film in the device to exhibit high values of $\chi^{(2)}$. $\chi^{(2)}$ depends on a number of variables and can be written as

$$\chi^{(2)} = NF\beta \langle \cos^3 \theta \rangle$$

(1.3)

where,
N is the number of NLO active molecules,
F is the local field correction factor,
$\beta$ is the hyperpolarizability of the polymer used and
$\langle \cos^3 \theta \rangle$ is the average cosine $^3\theta$, where
$\theta$ is the angle of molecular orientation of the chromophore as shown in Figure 1.3.

![Figure 1.3: Molecular orientation angle – It is the angle that the chromophore makes with the axis normal to the substrate.](image)

As mentioned earlier, in the electro-optic effect, the refractive index of the material is controlled through the application of an electrical field. This electric field induces a nonlinear polarization of individual chromophores, which slows down the light passing through the material, if the chromophores are acentrically ordered. This effect in
the chromophores is additive [9], and thus the number density of the chromophore is an important factor in achieving a $\chi^{(2)}$, as is shown in equation 1.3. The molecular polarizability $\beta$ depends on the molecular structure of the polymer molecule and should be as high as possible. This can be achieved by coupling strong donor and acceptor groups through a conjugated electron system, e.g. an aromatic ring [12]. The effect of the increase in the conjugation length between the donor/acceptor groups is shown in Figure 1.4. Both the nonlinear optical materials (called chromophores) that are covered in this study have at least two aromatic rings. Another aspect that contributes to a higher $\beta$ is a large charge separation (large dipole moment), which can be achieved by increasing the conjugation length between the donor and acceptor groups. However, these requirements for better optical coefficients are often accompanied with non-transparency, which interferes with good device-making, since for device applications polymers used must possess excellent linear optical properties such as transparency at the desired wavelengths. Thus these two aspects – strong polarizability and good linear optical properties – have to be traded off carefully, against each other [12-13]. The hyperpolarizability $\beta$, can be measured experimentally with the electric field induced SHG (EFISH) method for chromophores with no ionic groups and with the Hyper Rayleigh Scattering (HRS) for the chromophores with ionic groups attached [15].
<table>
<thead>
<tr>
<th>Chromophore</th>
<th>Structure</th>
<th>$b_0 \left(10^{-3} \text{cm}^5/\text{esu}\right)$</th>
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<tbody>
<tr>
<td>DMNA</td>
<td>$\text{H}_3\text{C} - \text{N} - \text{NO}_2$</td>
<td>12</td>
</tr>
<tr>
<td>Disperse Red 1</td>
<td>$\text{H}_3\text{C}_2\text{H}_2\text{C} - \text{N} - \text{N} - \text{NO}_2$</td>
<td>47</td>
</tr>
<tr>
<td>DMADCVS</td>
<td>$\text{H}_3\text{C} - \text{N} - \text{NC} - \text{C}$</td>
<td>133</td>
</tr>
</tbody>
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Figure 1.4: Hyperpolarizability of selected chromophores. From DMNA to DMA-DCVS, the hyperpolarizability increases as the strength of the donor/acceptor groups increases and the conjugation length between these groups increases.
Polymers with high $\beta$ can be synthesized by incorporating the desired functionalities into the molecule. This is one of the biggest advantages that the use of polymers has over other materials. Most of polymers used for the optics applications are used in the form of films. This is because films offer great ease of fabrication and can be easily incorporated into devices. There are several film fabrication techniques that are used for making nonlinear optical films such as guest-host systems that are spin casted on a substrate, Langmuir Blodgett films, covalent self-assembly films and ionically self-assembled films. For this study we have used ionically self-assembled films.

1.2 Different types of techniques for fabricating polymer films for second-order nonlinear optical applications

1.2.1 Introduction:

Ultrathin films and multilayered film structures are important for many applications, including x-ray optics [16], nonlinear optics [17], microelectronics [18] and are under investigation for various biosensors. There are several techniques employed for the fabrication of polymer thin films and ultrathin films, some of which are discussed in this section. We have focused on the techniques that are used for fabricating noncentrosymmetric films that exhibit SHG. One of these is the deposition of preformed monolayers from a gas-liquid interface to a solid planar substrate called the Langmuir-Blodgett (LB) deposition [19-20]. Covalent self-assembly of molecular adsorbates onto solid substrates involves covalent bonds between the monolayers and is used to overcome the instability problems associated with the LB films [21]. Another technique used for applications of polymer films in nonlinear optical applications is the guest-host technique (poled polymers), in which the polymer films are deposited by mechanical methods such as spin-casting on a substrate. Here an NLO-active chromophore is doped into an optically inactive polymer and then aligned with an electric field. Lastly we talk about ionic self-assembly [22], in which polymers are adsorbed onto charged substrates in a self-limiting manner and the monolayers are stably held together by ionic interactions and possibly hydrogen bonding interactions. Films fabricated by these methods are easier to incorporate in devices and have enhanced optical properties. A variety of characterization
techniques can be used for these films [23] such as ellipsometry, UV/Vis spectroscopy, infrared spectroscopy and quartz crystal microbalance (QCM). In this study we have used ellipsometry, atomic force microscopy (AFM) and UV/Vis spectroscopy as the primary tools for characterizing the films.

1.2.2 Langmuir Blodgett Films

Langmuir-Blodgett (LB) films are usually formed by transferring monomolecular films of lipids layer-by-layer from a water surface onto a solid substrate. The monolayers may be designed to possess desired molecular architectures and functions and may be stacked into complex multilayered systems. This monolayer and multilayer arrangement was first discussed by Langmuir [24] and was pioneered by Kathreen Blodgett [25] and may be used to introduce different functionality to different layers. Both polymeric and monomeric systems can be deposited with this method [26].

Molecules that are best for this method are linear amphiphiles that are hydrophobic at one end and hydrophilic at the other [26]. These are then spread over a water surface and compressed for better alignment. A substrate is then dipped into this system and the film deposits as shown in Figure 2a. Depending on whether the substrate is hydrophobic or hydrophilic and whether films are deposited while the substrate is immersed or removed, or both, different types of films can be formed which are shown in Figure 2b. Y-type films are formed while depositing during insertion and removal, while the X and Z types are formed with just insertion or removal. For both, the X and Z type films, molecules in adjacent layers possess a net orientation and thus exhibit high nonlinear susceptibilities. Ashwell et al., have shown that for Z-type films $\chi^{(2)}$ values of about 10 times that of $\beta$- barium borate have been obtained [27-28]. By contrast, the Y-type film is inherently centrosymmetric and thus, although it is the most thermodynamically stable configuration, it is not used for nonlinear optical applications without some modifications. A Y-type film can be designed with interleaving monolayers with NLO units only in one of the monolayers. This generates a thermodynamically stable structure with a bulk second-order NLO response. Eva et al., have reported that such films have $\chi^{(2)}$ values of about $16 \times 10^{-7}$, which are about 20 times that of $\beta$- barium borate [29].
Figure 2: Langmuir-Blodgett and covalent self-assembly processes. (a) Deposition of Langmuir-Blodgett molecules (hydrophilic ends represented as arrowheads) on a hydrophobic substrate. Deposition occurs both on substrate insertion and removal (Y-Type). (b) X, Y, and Z type L-B films.
There are several disadvantages involved with this method. One of them is that it can only be used for molecules that water-insoluble and have surfactant-like properties. Another aspect that has to be controlled accurately for this type of deposition is the surface pressure, which has to be held constant. Any change in the pressure could change the packing of the molecules and hence alter the orientation of the chromophores. Excess pressure could also break the monolayer. The resultant films formed are held together by Van der Waals forces and hence have poor thermal and mechanical stability [19-20]. These films also experience time decay of chromophore orientation. In some cases, X and Z type films can re-orient and form the thermodynamically stable Y-films [30].

1.2.3 Covalent Self-Assembly

With this technique it is possible to construct highly organized multilayer structures that exhibit exceptional mechanical and chemical stabilities that are not obtained with LB films. Crosslinking of these films can also be done to further improve its properties [31], which include mechanical, chemical, thermal, and electrical stability. In this method, a treated surface is brought in contact with a material that can covalently bind to the surface. This deposited monolayer is then chemically treated to enable the deposition of the next layer. Cao and co-workers fabricated thin films composed of diazoepoline and poly (4-vinylphenol) that were assembled electrostatically, but were then exposed to UV radiation, as a result of which H-bonds were formed [32]. This significantly increased the chemical stability of the resultant films. Xu et al., have shown that this method can produce films of (dialkylamino)stilbazole chromophore on benzyl chloride-prefunctionalized surfaces that have $\chi^{(2)}$ values of about 60 times that of $\beta$-barium borate [6, 33]. Marks and co-workers have done considerable work with various systems on the enhancement of second harmonic generation of covalently assembled films [34-37]. Several studies have been done on the examination of SHG of covalently assembled hybrid films containing organic and inorganic components. Coradin et al demonstrate that covalently assembled films containing certain NLO inactive inorganic compounds (transparent layered MPS$_3$ compounds, where M = Mn, Cd or Zn) and NLO active organic materials (cationic chromophores derived from the stilbazolium skeleton) exhibit enhanced SHG signals, caused due to dye aggregation [38]. In other studies done
by Katz and co-workers, there was considerable increase in the SHG signal of hybrid films of various dyes such as 4-\{4-[N,N-bis(2-hydroxyethyl)amino]phenylazo\}phenylphosphonic acid, 1-(4-bromophenol)-4-phenylpiperazine, and others that had interlayers of zirconium phosphate-phosphonate, assembled covalently [17,39].

Covalent self-assembly can be a tedious, time consuming process and requires suitable control of reaction conditions. It is also limited in the choice of reactants. This is because certain reactions may require deposition conditions of high temperatures and pressures and thus can be expensive. Yang et al., have reported that the immersion times could vary from 4 hours to several days for films with a calyx(4)arene-based NLO chromophore[40]. This method is also limited by the extent of reaction for each of the assembly processes. Thus, although this method boasts of high optical constants, its limitations have so far prevented from becoming commercially feasible.

1.2.4 Poled polymers and Guest-Host systems

In this method, NLO polymers are poled by applying an electric field [41]. Typically a polymer containing NLO chromophores is first spincoated on a conducting substrate forming films that are about a micron thick [42]. The film is then heated to its glass transition temperature, where in its rubbery state, it is exposed to a strong static electric field, so that the chromophores are aligned to achieve the necessary noncentrosymmetry. The polymer is then cooled to room temperature in the presence of the field to freeze the alignment. The electric field is then removed, and the restricted mobility below the glass transition temperature of the polymers preserves the chromophore orientation even in the absence of the electric field. Two common methods of electric field poling are corona-poling or contact electrode poling [41]. As seen by the processing, it is obvious that materials that can be used for this technique must have a high glass transition temperature. This is because, to be useful for device applications, the nonlinear response should be stable during device processing and fabrication, which may involve elevated temperatures exceeding 100-150 °C, even for a period of minutes. Materials that have a low glass transition may lose orientation during the fabrication processes involving elevated temperatures.
An alternative to covalently attaching the chromophore to the polymer is to dope the chromophore into an optically inactive polymer and then the mixture is deposited on the surface. This is called a guest-host system. The alignment process is the same as the one used for optically active polymers. Although the nonlinear susceptibilities obtained with this process are comparable to the ones currently seen in the organic crystals used, there are several disadvantages involved.

The poled system is a thermodynamically unstable system and the poled polymers tend to relax back to their centrosymmetric state as a function of time and temperature [43]. One way to improve this, apart from increasing the glass transition, is crosslinking, which can limit the mobility of the poled chromophore in the matrix. For example, in guest-host systems, the use of polyimides has achieved considerable reduction in chromophore mobility [44-45]. However, in a study done by Dalton and co-workers [46] on the effect of crosslinking in NLO-active polyurethane films, they have shown that excessive crosslinking deteriorates electric poling of long chromophores. Therefore crosslinking by itself may not be a good approach to enhance the stability of these films. In another study, Dalton et al. demonstrated that increasing the number of crosslinking points increased the thermal stability of the films by about 33 °C, but a simple guest-host system (without crosslinking) increased the EO coefficients by about 150 % [47]. In general though, the guest-host systems can have problems of low chromophore solubility, which could limit the NLO response. Another problem arises if the chromophore acts as a plasticizer and reduces the glass transition temperature, the stability of these films could further deteriorate. Thus, all these limitations have limited the utility of this method for commercial applications.

1.2.5 Ionically Self-Assembled monolayer (ISAM) thin films

This is a relatively new method for the fabrication of thin films. Although the possibility of creating monolayer and multilayer thin films in an organized manner was suggested by Langmuir [48] as early as 1917, the first description of multilayer assemblies by spontaneous adsorption of alternating layers of positively and negatively charged colloids on a charged substrates was suggested by Iler [49]. In this method a charged substrate is alternately dipped into oppositely charged polyelectrolytes to formed
controlled multilayers. This pioneering work of Iler was further developed by Decher et al. in recent years, which mainly deals with fabrication of organized thin films by layer-by-layer adsorption of linear polyions [22, 50-52]. The method has distinct advantages over the other thin film fabrication processes [53]. Firstly the preparative procedure is simple and elaborate apparatus is not required. Secondly, since this process is based on the adsorption of dissolved components onto solid substrates without having any restrictions on the hydrophilic or hydrophobic nature of the components, there are a variety of polyions that can be used. A large number of the available polyions are water soluble and thus their use can be extremely cost-effective. Finally, the simplicity of this process makes it suitable to use any kind of charged substrate, thus expanding the scope of the possible applications. The monolayers formed are physically strong even on rough surfaces [54]. Further a variety of polymeric materials from biopolymers in the form of proteins [55-60] to inorganic materials such as clays [61-62] can also be used with this technique. We will discuss ISAM films and their applications in more detail in the next chapter.

1.3 ISAM films and their applications

As discussed earlier, ISAM films are made by the alternate immersion of charged substrates into polyelectrolyte solutions. Figure 3.1 depicts the manner in which the ISAM films are fabricated. As seen in Figure 3.1(b), the surface charge is reversed when the negatively charged substrate is immersed into the positively charged solution as the positively charged monolayer is deposited. Charge reversal occurs again when the now positively charged surface is dipped into a polyanion solution as seen in Figure 3.1(c). Section 3.1 deals with the details of the mechanism of this deposition including the Debye-Huckel theory, charge overcompensation and counterion release.
Figure 3.1: ISAM Deposition – (a) negatively charged substrate  (b) charge reversal due to deposition of positively charged electrolyte  (c) charge reversal due to negatively charged electrolyte.

In the subsequent sections we will discuss in more detail the applications of these films, which then lead to the main objectives that this thesis addresses, as well as the different methods used for the characterization of these films. We will also discuss the effect of different deposition conditions such as solution concentration, pH, and ionic strength for controlled deposition.

1.3.1 Mechanism of ISAM growth

As shown in Figure 3.1, the subsequent layers are deposited as the surface charge is reversed every cycle. For most charged surfaces, the actual charge is determined by an equilibrium process involving exchange of charged species between the bulk solution and the interface [63]. The final equilibrium state is determined by an interplay between three free energy contributions: the short range chemical interactions such as hydrogen bonds and dipole-dipole interactions at the surface that promote adsorption; the long-range electrostatic interactions that act to prevent the formation of highly charged surfaces (to maintain overall electroneutrality); and the entropy of the absorbing ion, which typically favors desorption and the formation of the charged surface. For those substrates where the short range interactions are substantial, the surface charge is first neutralized by the ions in the solution, and then reversed, as these forces (short-range, long-range and entropic) are balanced. By short-range interactions being substantial, we mean that the substrate is sufficiently charged, and for that chemical modifications are usually made [64]. The charge reversal then depends on the concentration of the ions in solution. If the solution contains more than the stoichiometric number of charges (relative to the substrate), the surface charge is reversed [65-67]. This charge of the solution can be
estimated by measuring the zeta (ζ) potential. This can be estimated experimentally and it further determines whether the solution is charged and the extent of the charge of the ions present in solution. These ions in the solution form a diffuse layer near the surface as shown in Figure 3.2.

![Figure 3.2: Formation of diffuse layer at a charged substrate immersed in an oppositely charged solution.](image)

The thickness of this diffuse layer depends on the concentration of the electrolyte in solution. The characteristic length of the diffuse layer is known as the Debye screening length, κ⁻¹, and is defined as the distance from the charged surface over which the electrostatic potential decays by a factor e⁻¹. It is also known as the charge penetration length as it represents the charge overcompensation level [68]. The Debye length for a 1:1 electrolyte in an aqueous medium at 25 °C is given by

\[
\frac{1}{\kappa} = 3.04 \times 10^{-10}/I_{\text{eff}}^{0.5} \text{ (m)}
\]  

(3.1)

where \(I_{\text{eff}}\) is the effective molar concentration of the polyelectrolyte in solution.

Equation 3.1 comes from the solution to the Poisson-Boltzmann equation which governs the electrostatic potential around a charged object in a solution of electrolyte [69-]
The Debye length is an important factor in the deposition mechanism since it affects whether deposition would indeed occur as well as thickness of the monolayer deposited in the cycle.

It is important to note that ISAM deposition can be achieved even for monomeric species as long as they have multiple charges. The advantage that polyelectrolytes offer in comparison with monomeric systems is that due to the size of the chains, polymers can bridge over underlying defects and thus the newly created surface is mostly dependent on the chosen polyelectrolyte and the adsorption conditions rather than the chosen substrate [72]. This was demonstrated in preliminary film deposition experiments with a polymeric chromophore PCBS and the monomeric chromophore Mordant Orange 10 (MO 10). Figure 3.3 shows the structure of the two different chromophores. Films formed with MO 10 were typically very inhomogeneous compared to those formed with PCBS. Thus polymeric systems tend to be self-healing, can smoothen underlying surface defects and hence are less dependent on the substrate or the substrate charge density [73] as compared with monomeric systems. In the next section we can consider the effects of these deposition conditions.

(a)

(b)

Figure 3.3: Structure of the chromophores (a) PCBS (b) Mordant Orange 10.
1.3.2 Effect of deposition conditions on film formation

When considering these ISAM films for second-order non-linear optical applications, we need more than just the deposition of these films. As suggested by equation 1.2, for a high $\chi^{(2)}$, not only do we need high chromophore deposition (high N), but also a good orientation of the chromophore in the film (low $\theta$). This orientation of the chromophore in the film can be controlled by selecting suitable deposition conditions. These conditions will also determine the thickness of the resulting films, which also contributes to the changes in orientation of the chromophore.

Depending on the pH and the ionic strength of the solution, the polymer chains can be either coiled or stretched due to the mutual forces of attraction and repulsion in the chains. The deposition on the substrate reflects these solution conditions and hence the polymer deposition can occur either as flat trains or as coiled loops as shown in Figure 3.4. This would then affect the thickness of the deposited monolayer and thus the overall film thickness.

![Figure 3.4: Deposition of polymer film as (a) flat trains (b) coiled loops](image)

The conditions to be adjusted for deposition also depend on the polyelectrolytes that are used in the process. When dealing with polyelectrolytes such as poly-(styrene sulfonate) and poly(diallyl dimethylammonium chloride) or PDDA, which are fully charged, strong polyelectrolytes, molecular organization is controlled by adjusting the ionic strength of the dipping solutions [74]. This approach is limited as it provides a narrower window of opportunity regarding the control over bilayer thickness and composition. To fine-tune the thickness further and widen this window, it is suggested that weak polyelectrolytes such as poly(allylamine hydrochloride) (PAH) be used. Since the linear charge density of these polymers is sensitive to the solution pH around the pKa of the polymer, it further increases the scope for fine-tuning the bilayer thickness control. Changing the pH thus controls the functional group ionization. Further, Yoo et al have shown that the thickness of the adsorbed layer only depends on the pH of the solution from which it was adsorbed.
and not on the thickness of the previously adsorbed layer [74]. For the experiments conducted in this study, the cationic polyelectrolytes used were PDDA and PAH. The structures of these polycations are given in Figure 3.5.

![Chemical structures of PDDA and PAH](image)

(a) PDDA  (b) PAH

Figure 3.5: Structures of the polycations used – (a) PDDA  (b) PAH

The orientation of the chromophore in the film or the tilt angle of the chromophore can be measured experimentally. As seen from equation 1.2, making this angle closer to 0° results in increasing \( \chi^{(2)} \). One of the reasons that good control over the tilt angles is limited for ISAM films is that the polymers in two-component multilayers are not stratified into well-defined layers but are dispersed and interpenetrating. This interpenetration is minimized in the layers closest to the solid substrate.

The potentially beneficial effect of a solid interface on improving chromophore orientation led to the investigation of incorporating clay particles in ISAM films. Laponite, a clay that forms platelets in aqueous suspensions, deposits well with polycations that bear quaternary amines and hence most of the work done so far with Laponite ISAM films has been done using PDDA as the polycation. Glinel et al [75] have studied the deposition of Laponite with other polycations of varying structures, and the best (organized, flat, layer-by-layer) deposition results were obtained with PDDA as the polycation. They also show that the presence of Laponite in the multilayers formed with each of the polycations prevents the interpenetration of the different polymer layers.
1.3.3 Applications of ISAM films

ISAM films can be used for a variety of thin film applications since they are easy to fabricate, inexpensive in comparison with some of the alternative methods, and can be controlled easily by simple changes in solution pH and ionic strength. Another extremely important advantage these films have is that they deposit within just a few minutes as compared to the time-consuming and high temperature conditions associated with some of the alternative methods. McAloney et al [76] have shown that the initial polymer adsorption occurs in less than 10 seconds. In our own study for all polymeric systems, the maximum deposition time has been not more that 5 minutes. Thus within a matter of hours, a multilayer film can be prepared with relative ease. For similar number of layers, other techniques can take as much as a few days. The primary focus of this thesis is the use of ISAM films in nonlinear optical applications, such as electro-optic modulators.

As mentioned earlier, ISAM films in electro-optic modulators need to have a large SHG signal, or a high $\chi^{(2)}$. This requires good orientation of the chromophore in the film. And one of the problems for achieving better control on the orientation and also increasing the tilt angle of the chromophore is the interpenetration of the monolayers in the film and the loss of the effect of the solid substrate. In fact several studies have confirmed that two-component multilayers are not stratified into well-defined layers but are dispersed and interpenetrating [72,77-78]. Our hypothesis was that if we introduce a layer in these films that mimics the effect of a solid substrate, we could optimize the orientation. For this purpose we chose to use a synthetic hectorite called Laponite RD. This is a water-dispersible clay that deposits as negatively charged platelets of about 35 nm on charged surfaces. The introduction of platelets of this size would then duplicate the effect of the charged glass substrate that we use in our ISAM films.

1.4 Introduction to the use of Clays in ISAM Films

Fabrication of organic/inorganic nanostructured materials is an important target of modern materials research. These systems have been assembled using a variety of techniques, including Langmuir monolayers which consist of ordered multilayers
composed of CdS, ZnS, PbSe and silver nanoparticles sandwiched between amphiphile bilayers [79]. Kotov et al [80] have also done some work with hectorite plates included in Langmuir monolayers. The recent interest in the intercalation of organic polymers into layered ceramics has been based on the access it can give to these novel polymer-ceramic nanocomposites, which exhibit unique physical and mechanical properties attributed to the synergism of the individual components [81]. Even more elaborate nanocomposite structures would be available if these similar structures could be built layer-by-layer rather than the all-in-once manner. This has led to further investigations in these studies with various multilayer-assembling techniques such as some of the work done by Kotov et al. The first work with clays and ISAM films was done by Kleinfeld and Ferguson [82] where they use the electrostatic layer-by-layer adsorption of oppositely charged components to produce ultrathin ceramic/polycation multilayers. A variety of clays have been studied for this, but the majority of the work with ISAM films has been done with montmorillonite [62] and Laponite. In the next section we will discuss our choice of the inorganic clay for our study.

1.4.1 Selection of Laponite RD

Our study of introducing clay particles in ISAM films is based on a couple of ideas. Firstly we would like to get ordered and extremely controllable nanostructures. Secondly we want to investigate the hypothesis that these clay platelets mimic the effect of silica-glass substrates that we use in our work and indeed give us better control of the orientation of the NLO-active chromophores by limiting the degree of interpenetration of the adjacent polymer layers. Figure 4.1a shows the proposed deposition sequence for testing controlled deposition and Figure 4.1b shows how we tested the effect of varying the placement of the platelets so as to introduce a solid impenetrable surface when the effect of the original glass substrate is lost.
For this sequence, negatively charged platelets are needed that can form a solid, mostly impenetrable surface. For optimal deposition for NLO films, the platelets should have a narrow size distribution and be chemically stable at the operating conditions of ionic strength and pH. For the platelets to be deposited as negatively charged particles, they need to have cations balancing the negative charges, which are released when in solution. Another important aspect is the pH-dependence of the charges on the platelets. In aqueous systems, particle surfaces develop electrical charges in two principal ways [83]: either permanently, from isomorphic substitution of ions in the crystal lattice or conditionally, from the reactions of surface functional groups with dissolved ions in the aqueous phase (e.g. Al-OH or Fe-OH groups). Clay lamellae constituted from silica tetrahedral and alumina octahedral sheets have negatively charged sites on the basal planes. However, situated at the broken edges of clay lamellae are conditionally charged amphoteric groups (Al-OH) that could be positive or negative depending on the pH. The point-of-zero-charge (PZC) is the pH at which the net charge on the particle is zero. The PZC, also referred to as the iso-electric point, along with the suspension pH determines the net charge on particles and thus pH control is critical for controlled deposition of particles in ISAM films.

Even if the overall charge on a particle is negative, the presence of amphoteric groups can lead to the aggregate formation of these platelets in solution since the positive charges from one part of the platelet would tend to attract the negatively charged parts of the other platelet. Thus, in making the choice for a clay that is suitable for ISAM films, it
is important to select one that has a preponderance of one type of charged groups on its surface so as to inhibit the formation of aggregates and thus facilitate flat deposition.

Another factor in choosing the type of clay for film deposition is whether the clay is naturally derived or is synthetic. Suspensions of natural colloidal clay platelets exhibit a wide variety of structural and mechanical properties and are frequently used as thickeners, fillers and antisettling agents. Montmorillonite is one such natural clay which deposits as single sheets or thin platelets composed of 2-3 sheets in which the negative charge is balanced by inter and intra-lamellar sodium cations [84]. These platelets are about 200 nm in size. The disadvantage that natural clays have when compared with their synthetic counterparts is that they are usually very polydisperse in both shape and size. Synthetic clays comparatively have a much higher degree of monodispersity when in solution. Van duffel et al [85], in a study where they compare the synthetic clay Laponite and a natural hectorite have shown that the films formed by natural clays are much rougher than synthetic clays. The origin of this was ascribed to a higher extent of overlap and/or lower surface coverage by the natural clay particles. Hence for better control of film growth, we chose a synthetic clay.

There are several synthetic clays from which to choose. Synthetic Takovite is one of the clays that can be carefully modified to suit various applications due to its interesting sol-gel transition properties [83]. Although platelets of high monodispersities can be manufactured and the anionic groups can be altered for different applications, these have certain amphoteric groups, which make it susceptible to variable charging and aggregation in suspension. For all these reasons, Laponite seemed to be best suited for our applications since it is a negatively charged synthetic hectorite that has a high degree of monodispersity and also has a large surface area (900 m²/g) [86].

In a study of the second harmonic generation of clay/polymer films by van Duffel et.al., they demonstrated that the second harmonic intensity (I₂ω, which is the intensity of the light wave with double the frequency of the incoming wave) of Laponite films was higher than that of smecton and hectorite [87]. This is another important reason for the selection of Laponite since the goal for using Laponite is to increase this SHG signal by exercising better control over chromophore orientation. The Laponite used in this study was obtained from Southern Clay Products, Inc, Texas, which is a part of Laporte
Industries Ltd., UK. There are several grades of Laponite that are available depending on the applications. These applications can be divided into two broad categories - as a rheology modifier that can be used in surface coatings, household cleaners and personal care products and as a film former that is used for producing electrically conductive, antistatic and barrier coatings. Among these there are gel-forming grades and sol-forming grades. The sol grades have a polyphosphate dispersing agent and thus can be used in applications that require high Laponite concentrations. Since our applications do not require high concentrations, we chose to use the gel-forming grade that is used for general lab and industrial purpose: Laponite RD. Among the general-purpose grades there is Laponite RDS as well, which is a sol-forming grade and hence is suitable for higher concentration applications. Some examples of the other grades are: Laponite D, DS, DF that are used in personal care products such as toothpastes and Laponite S and SJS are high sol stability grades that are used for electrically conductive, antistatic and barrier films. Laponite RD can hydrate rapidly at concentrations below 2 % in tap water and below 3 % in deionized water. For our study we have used 0.2 % in deionized water. The reason for this low concentration selection was that we wanted well-dispersed solutions that deposit as flat single sheets in films.

1.4.2 Use of Laponite in ISAM Films

Laponite is a purely synthetic hectorite-type clay with density 2570 Kg/m$^3$ and a mean chemical composition: SiO$_2$ 66.2 %, MgO 30.2 %, Na$_2$O 2.9 %, and Li$_2$O 0.7 % \cite{88}. The idealized chemical formula for Laponite RD is given by \[(Si_8(Mg_{5.34}Li_{0.66})O_{20}(OH)_4)Na_{0.66}.\] The cation exchange capacity (CEC) of Laponite platelets is 0.95 meq/g. The deposited platelets are nanometer size with a thickness of about one nanometer.

An important property of Laponite is its ability to hydrate well. As mentioned earlier, Laponite hydrates very rapidly without aggregating when the concentrations are reasonably low. Full dispersion is a very essential condition for organized flat deposition. For this proper pH control is required and it is found that best results in terms of dispersion are obtained at neutral to slightly basic conditions. This is because the charge on the oxide edge of the Laponite platelets is variable due to the amphoteric groups, and
depends on the solution pH. These neutral to slightly basic conditions can be achieved by using NaOH or LiOH, since Na\textsuperscript{+} or Li\textsuperscript{+} induce maximum swelling due to the hydration power of the cations. The slightly basic conditions give negatively charged edges thus causing the elementary clay sheets to repel each other and hence prevent aggregation. Thompson et al have done a pH study on Laponite that indicate that it is best for the pH of Laponite to be around 10 to avoid degradation or dissolution of the Laponite particles [89]. Even a high pH (>11.0) is not favorable, since at this pH some chemical breakdown could occur and also the ionic strength at this pH is too high for full dispersion.

The next section outlines the main objectives of this thesis which are based on fabricating ISAM films in such a way as to optimize chromophore orientation and, hence, second harmonic generation.

1.5 Thesis Objectives

1) The first objective is to determine if it is possible to obtain flat, tile-like deposition of Laponite platelets at every layer, even when a large number of layers are deposited, for ISAM films that contain a polyanionic NLO-active chromophore. This has not been demonstrated in any previous work. Film characterization will be done by ellipsometry for film thickness monitoring, by absorbance measurements to check the amount of chromophore adsorbed every cycle, and by AFM imaging to check film roughness.

2) The second objective of this work is to find study the effect of an impenetrable interface on the orientation of the NLO-active chromophores in ISAM films. Specifically, we investigate whether the placement of Laponite platelets in ISAM films results in improved chromophore orientation and hence increased second harmonic generation. Part of this work involves trying to find the optimum location of Laponite platelet layers in an ISAM film. Ultimately we wanted to test the hypothesis that Laponite can mimic the effect of the underlying glass substrate and hence result in better films for applications in electro-optic modulators.

The following chapters detail the experimental work that concerns these objectives.
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