Chapter 1

NONLINEAR OPTICAL PROPERTIES OF ORGANIC AND POLYMER SYSTEMS

Abstract

The review deals with recent and important developments in the field of organic polymers for second-order nonlinear optics. Second order nonlinear optical (NLO) properties of polymeric materials have attracted a lot of attention, especially for potential applications such as fast wave guides, electrooptic (EO) modulation and frequency-doubling devices. The review provides a survey of NLO active polymeric materials with a brief introduction which comprises the principles and the origin of nonlinear optics, chirality, donor-acceptor chromophores and the various kinds of polymeric materials for nonlinear optics, including guest-host systems, side chain polymers, main chain polymers, crosslinked polymers and chiral polymers.

1.1. Introduction

Nonlinear electromagnetic phenomena occur when the response of a medium (including the electric polarization and its time derivative, the current density or the magnetisation) is a nonlinear function of the applied electric and magnetic field amplitudes. Earlier, nonlinear responses were observed with the application of dc or low frequency electric and magnetic fields. Pockels and Kerr effects, Raman Scattering etc. were some of the earlier nonlinear optical effects.

Nonlinear optics refers to any light-induced change in the optical properties of a material. Its domain encompasses those phenomena for which electric and magnetic intensities of higher powers than the first play a dominant role. Nonlinear optics is the basis of all the fledging photonic technologies, where light works with or even replaces electrons in applications traditionally carried out by microelectronics. Nonlinear optics has applications in the domain of optoelectronics and photonics, and materials with high nonlinear optical properties are used in high performance electro optic switching elements for telecommunication and optical information processing. Inorganic materials,
organometallic compounds, liquid crystals, organic molecules and polymers have been investigated for their nonlinear optical properties.

The nonlinear optical phenomena were demonstrated after the invention of laser in 1960. By 1961, optical harmonics were already being generated and other nonlinear phenomena such as sum and difference frequency mixing, the optical Kerr effect, four-wave mixing, stimulated scattering (Raman and Brillouin) and self-induced transparency, soon followed. Franken et al were the first to demonstrate SHG of light in 1961. They used pulses of a ruby laser, first realised by Maiman in 1960 and on the passage of the ruby laser pulse (3-kw pulse of red light, 694.3 nm) through a quartz crystal, some ultraviolet photons at twice the frequency (347.15 nm) were generated.

![Figure 1.1: Schematic illustration of optical frequency doubling using KDP crystal. IM is the index matched direction at an angle of θ to the optic axis.](image)

This led to the development of inorganic materials such as lithium niobate (LNB), potassium titanyl phosphate (KTP), potassium dihydrogen phosphate etc. Maker et al and Giordmaine soon showed how the second harmonic generation would be enhanced by many orders of magnitude by phase matching of the fundamental and harmonic wave with the compensation of colour dispersion by birefringence in an anisotropic KDP crystal (Figure 1.1).

1.1.1 Polymers for optical devices

Organic polymers have a number of desirable properties, which make them materials of choice for optical devices. Organic materials are intrinsically fast (electronic response, femto second response) due to the virtual process of polarizing electrons, and have low dielectric constants, which permit low capacitance leading to high-speed devices. They could have exceptionally high nonlinear activity resulting in improved device performance and can be tailored by conventional synthetic methods to meet specific requirements (e.g.: transparency at particular wavelength and stability at particular temperature).
They offer many processing options towards desired device formats, which should reduce the cost of active devices and are found to be more adept at manipulating light than their inorganic counter parts. They are also easy to prepare, process and fabricate into devices. Also they can be readily integrated with semiconductor electronics and fiber-optic transmission lines. As a result, polymeric materials promise to make optoelectronic technologies more practical and wide spread. They could make major impacts on telecommunication, optical signal processing, computing and data storage. As polymer based electro optic modulators and switches begin to enter the market, other applications are waiting in the wings.

1.2 Theory of nonlinear optics

Before the invention of laser, under the ordinary experience of every day life, the optical properties and parameters of a medium were independent of the intensity of light that permitted observation of the optical phenomena such as reflection, refraction, diffraction, absorption, and scattering. This is the realm of what is called linear optics. The invention of laser gave rise to the study of optics at high intensities, leading to new phenomena not seen with ordinary light such as the generation of new colors from monochromatic light in a transparent crystal, or self-focusing of an optical beam in a homogeneous liquid. At the intensities used to generate these types of effects, the usual optical parameters of materials cannot be considered constant but become functions of light intensity. The science of optics in this regime is called nonlinear optics. This is because of the reason that the field strength of the conventional light source used before the advent of lasers, were much smaller than the field strength of atomic and inter-atomic fields. The electric charges in matter are held in equilibrium by atomic fields of the order $10^8-10^9$ V/cm, and anharmonicity in their motion can only be observed by using perturbing fields that are not negligible compared to these values. Due to coherence, the laser beam can be focused to an area $A \approx \lambda^2$. If the laser wavelength is assumed to be $1\mu$, then $A = 10^{12}$ m$^2$ and hence $j_E \approx 10^{18}$ MW/m$^2$ giving $E \approx 3 \times 10^{10}$ V/m which is with in the range of atomic field. At such high fields, the relationship between the electric polarization $P$ and the field strength $E$ ceases to be linear and some interesting nonlinear effects come to the fore.
When a ray of light of frequency $\nu$ strikes a material system, the elementary particles of which it is made of are influenced in their relative motion and begin to oscillate with the frequency $\nu$. By this induced polarization, the material system is transformed into a secondary emitter like an antenna. The simple assumption concerning such a scattering process is that electric field component of the electromagnetic radiation induces an oscillating dipole in the molecule, the magnitude of which is proportional to the electric field. If an elastic or linear scattering occurs, no net energy is transferred from the radiation to the molecule, i.e., the molecule will be in the same energy state before and after the scattering. However, during the time of scattering, the molecule is not in a pure stationary state. But it is in a time dependent, non-stationary state, which may be described as a superposition of many stationary states. The duration of such a scattering process may be estimated from the angular frequency of the interacting radiation. If it is $\omega$, the time for such an interaction lasts is $\tau=1/\omega$. In spite of this very short time, the molecule can interact several times with the radiation. As a direct consequence, the radiation-induced polarization consists of a major part, which depends on the first power of field strength, but may also contain nonlinear contributions, which are proportional to the radiation field to second, third or even higher order. Thus the induced polarization consists of a variety of contributions giving rise to very fast secondary re-emission, i.e., scattering at different frequencies $^{11,17-20}$.

![Virtual state](image.png)

Figure 1.2: Schematic representation of second harmonic generation

Nonlinear interaction between electromagnetic radiation and matter can be described in quantum mechanical terms as multi photon process. In multi photon process an interaction between radiation and matter accompanied by absorption or emission or both, of not less than two photons per elementary act is observed. Second harmonic generation is a three-photon process as shown in Figure 1.2. Two photons, each with energy $\hbar\omega$, are absorbed and one photon
with energy $2h\omega$ is emitted. The state of the quantum system remains unaltered. This gives an impression that two colliding photons merge "directly" into a single one. The levels shown in the figure by dotted lines are the "virtual levels".

1.3. Electromagnetic basis of nonlinear optics

Ordinary matter consists of a collection of positively charged cores (of atoms or molecules) and surrounded by negatively charged electrons. Light interacts primarily with matter via the valence electrons in the outer shells of electron orbital. The fundamental parameter in this light-matter interaction theory is the electronic polarization of the material induced by light. When an electric field is applied to a dielectric medium (of neutral electric charge), a separation of bound charges is induced. Within the electric-dipole approximation, this separation of charge results in a collection of induced dipole moments $\mu$, which, as designated, may be rapidly oscillating if induced by a rapidly varying applied field.

$$\mu = -er$$

where $e$ the electric charge, $r$ the displacement induced by the electric field.

The electric polarization $P$ is defined as the net average dipole moment per unit volume and is given by

$$P = N \langle \mu \rangle$$

where $N$ is the number of microscopic dipoles per unit volume, and the angular bracket indicates an ensemble average over all the dipoles in the medium. In what follows, any permanent dipole with in the medium will be ignored since they will not be oscillating at optical frequencies and hence will not radiate electromagnetic waves.

By the principle of causality (the relationship between causes and effects), $P$ must be a function of the applied field $E$. To an excellent approximation, at the low intensity levels of natural light sources, the relation of the applied field is linear i.e. proportional to the applied field. This is the regime of linear optics. The most general form of the electric polarization for a homogeneous medium is given by

$$P_l(r,t) = \int\int \chi^{(1)}(r-r',t-t'),E(r',t')dr'dt'$$

where $e$ the electric charge, $r$ the displacement induced by the electric field.
Chapter 1

The equation is in cgs system. In SI system the equation should be multiplied with \( \varepsilon_0 = 8.85 \times 10^{-12} \text{ farad/meter} \), the electric permittivity of free space, where the subscript L signifies a linear polarization. \( \chi^{(1)}(r-r', t-t') \) is the linear dielectric response tensor. The functional form of \( \chi^{(1)} \) reflects the principles of space and time invariance. In other words, the polarization response of the medium does not depend on whether (in an absolute sense) the driving field is applied, or not, but only on the time, since it was applied. Consequently, \( \chi^{(1)}(r-r', t-t') \) must be defined in such a way that it vanishes when \( t-t' < 0 \) to preserve causality. Similarly, the polarization response in a homogeneous medium does not depend on the absolute position in space of the applied field, but only on the distance away from this position. A non zero value of \( \chi^{(1)}(r-r', t-t') \) for \( r \neq r' \) is called a non local response. If there is no response except within a small neighborhood where \( r = r' \), then the response is called local. This is equivalent to saying that the linear dielectric response tensor has a \( \delta \)-function dependence. For the vast majority of problems in nonlinear optics, the media of interest produces approximately a local response. Consequently we shall ignore the spatial dependence of \( \chi^{(1)} \).

The form of the linear dielectric response tensor allows a simpler relation to be made between the Fourier transforms of the polarization and the applied field,

\[
P_i(\omega) = \chi^{(1)}(\omega)E(\omega)
\]

where \( \chi^{(1)}(\omega) \), the linear susceptibility tensor, is the Fourier transform of the linear dielectric response tensor. The tensor relation in equation (4) can also be written as

\[
P_{IJ}(\omega) = \sum_{I} \chi^{(1)}_{IJ}(\omega)E_{I}(\omega)
\]

where the subscript \( I \) signifies the \( I \)th Cartesian coordinate (\( I = x, y, z \)) and the sum is over \( J=x, y, z \). The tensor \( \chi^{(1)}(\omega) \) thus has nine components. In an isotropic medium, there is only one independent, non-zero component, and the susceptibility is written as a scalar quantity, \( \chi^{(1)}(\omega) \). This can be represented in the molecular (microscopic) level as

\[
\langle \mu(\omega) \rangle = \alpha^{(1)}(\omega)E_{\text{local}}(\omega),
\]

where \( \alpha^{(1)} \) is the molecular polarizability, \( E_{\text{local}} \) is the local electric field (at the molecule), which is a superposition of the applied field \( E \) and the net field due to the surrounding dipoles. An analytical expression for the local field can be
Chapter 1

obtained for isotropic and cubic medium. The relationship between the susceptibility and the polarizability for this media is given by

\[ \chi^{(1)} = \left( \frac{n^2 + 2}{3} \right) N \alpha^{(1)} \]  

(7)

The quantity \( f(\omega) = \left[ n^2(\omega) + 2 \right] / 3 \) is called the local field factor.

The nonlinear optical phenomena arise from the break down of equation 4 at sufficiently intense fields. As the applied field strength increases, the polarization of the medium is no longer linear. Only after the advent of the laser could optical fields of sufficient intensity be produced to observe this effect. To account for the “nonlinearity” of the medium response, the induced polarization is given as a power series expansion in the applied electric field.

It is assumed that the nonlinear polarization can be written as

\[ P = P_L + P_{NL} \]  

(8)

\[ P_{NL} = P^{(2)} + P^{(3)} \]  

(9)

\[ P^{(2)}(r,t) = \int \int \chi^{(2)}(t-t',t-t'') : E(r,t')E(r,t'')dt'dt'' \]  

(10)

\[ P^{(3)}(r,t) = \int \int \int \chi^{(3)}(t-t',t-t'',t-t') : E(r,t')E(r,t'')E(r,t'')dt'dt''dt''' \]  

(11)

It is important that the field in the equations above is the total applied field, which can be a superposition of many fields of different frequencies. \( \chi^{(n)} \) is called nth order dielectric response, and is a tensor of rank \( n+1 \). As for the linear dielectric response, it is assumed that the response is local and hence the spatial dependence of \( \chi^{(n)} \) is suppressed.

If the applied field is a superposition of monochromatic or quasi monochromatic waves, then it is possible to write expressions analogous to equations (10) and (11) in terms of Fourier transforms of the nonlinear polarization, fields, and the dielectric response tensor, provided the frequency dependence of the Fourier transform of \( \chi^{(n)} \) is slowly varying in the region of each Fourier components (e.g., its various laser frequencies), then, the nonlinear polarization will consist of several terms oscillating at various combination frequencies. For example, if the total field consists of two waves oscillating at frequencies \( \omega_1 \) and \( \omega_2 \), the second-order nonlinear polarization will have components oscillating at \( 2\omega_1, 2\omega_2, \omega_1+\omega_2, \) and \( \omega_1-\omega_2 \) and dc terms at zero
frequency. Similarly, with three fields oscillating at frequencies $\omega_1$, $\omega_2$, $\omega_3$, the third-order polarization will oscillate at $3\omega_1$, $3\omega_2$, $3\omega_3$, $\omega_1+\omega_2+\omega_3$, $\omega_1+\omega_2-\omega_3$, etc.

Thus, applying Fourier transform, the equation (10) can be written as follows. Consider a second-order polarization oscillating at $\omega_3$ due to the presence of fields oscillating at frequencies $\omega_1$ and $\omega_2$ with $\omega_3 = \omega_1 + \omega_2$. Then the $i$th Cartesian component of the complex polarization amplitude is expressed as

$$P_i^{(2)}(\omega_i) = D^{(2)} \sum_{jk} \chi_{ijk}^{(2)}(-\omega_i; \omega_j, \omega_k) E_j(\omega_j) E_k(\omega_k)$$

(12)

$$D^{(2)} = \begin{cases} 1 & \text{for indistinguishable fields} \\ 2 & \text{for distinguishable fields.} \end{cases}$$

where $\chi^{(2)}(-\omega_3; \omega_1, \omega_2)$ is the second order susceptibility and Fourier transform of $\chi^{(2)}(t)$. The form of equation (12) allows for the possibility that the frequencies $\omega_1$ and $\omega_2$ are equal or equal in magnitude and opposite in sign. In this case, there may actually be only one field present, and the degeneracy factor $D^{(2)}$ takes this into account. This notation is easily extended to higher orders. When three frequencies $\omega_1$, $\omega_2$, $\omega_3$ are present, the third-order polarization at $\omega_4 = \omega_1 + \omega_2 + \omega_3$ is given by

$$P_i^{(3)}(\omega_i) = D^{(3)} \sum_{jkl} \chi_{ijkl}^{(3)}(-\omega_i; \omega_j, \omega_k, \omega_l) E_j(\omega_j) E_k(\omega_k) E_l(\omega_l)$$

(13)

where degeneracy factors, in this case, becomes

$$D^{(3)} = \begin{cases} 1 & \text{all fields indistinguishable} \\ 3 & \text{two fields indistinguishable} \\ 6 & \text{all fields distinguishable} \end{cases}$$

This form of third-order polarization allows for various combination frequencies, even when only two fields are present, such as $\omega_1 + 2\omega_2$, or $2\omega_1 - \omega_2$, etc. the degeneracy factor is just due to the number of different ways in which the products of the Fourier components appear in the expansion of the total field to some power.

Hence the total polarization can be represented as

$$P_i(\omega_i) = \sum_j \chi_{ij}^{(1)}(-\omega_i; \omega_j) E_j(\omega_j) + \frac{1}{2} \sum_{jk} \chi_{ijk}^{(2)}(-\omega_i; \omega_j, \omega_k) E_j(\omega_j) E_k(\omega_k) +$$

$$\frac{1}{6} \sum_{jkl} \chi_{ijkl}^{(3)}(-\omega_i; \omega_j, \omega_k, \omega_l) E_j(\omega_j) E_k(\omega_k) E_l(\omega_l) + \ldots$$

(14)
Chapter 1

The macroscopic susceptibilities are related to the corresponding molecular susceptibilities by local field corrections \( f \) \(^2\) \(^3\) and the molecular number density \((N)\) \(^2\) \(^6\):

\[
\chi^{(1)}_{ii} = N \sum f_i \langle \cos \theta_i \rangle f_j \langle \cos \theta_j \rangle \alpha_{ij} \quad (15)
\
\chi^{(2)}_{ik} = N \sum f_i \langle \cos \theta_i \rangle f_j \langle \cos \theta_j \rangle f_k \langle \cos \theta_{ik} \rangle \beta_{ijk} \quad (16)
\
\chi^{(3)}_{ijk} = N \sum f_i \langle \cos \theta_i \rangle f_j \langle \cos \theta_j \rangle f_k \langle \cos \theta_{ik} \rangle f_l \langle \cos \theta_{il} \rangle \gamma_{ijkl} \quad (17)
\]

where the variables, \( i, j, k \) and \( l \) now span the molecular axes, and the angle between the macroscopic axis \( I \) and microscopic \( i \) is denoted as \( \theta_{ii} \). The local field factors are essentially correct for the difference between an applied field that would be felt by the molecule in free space and the local field detected in a material. These factors usually take the form of the well known Onsagar\(^2\)\(^4\) or Lorentz\(^2\)\(^5\) correction fields. The microscopic polarization \((p_i)\) can then be expressed as

\[
p_i(\omega) = \sum_f \alpha_{ij} (-\omega_1, \omega_2) E_f(\omega_2) + \frac{1}{2} \sum_{jk} \beta_{ijk} (-\omega_1, \omega_2, \omega_3) E_j(\omega_2) E_k(\omega_3) + \ldots \quad (18)
\]

The manifestation of nonlinear optical behavior can be clearly seen by substituting a sinusoidal field \( E = E_0 + E_1 \cos \omega t \) in to the polarization. Substituting this in equation (14) gives:

\[
P = (E_0 + E \cos \omega t) \chi^{(1)} + (E_0 + E \cos \omega t)^2 \chi^{(2)} + (E_0 + E \cos \omega t)^3 \chi^{(3)} + \ldots \quad (19)
\]

Rearranging the equation,

\[
P = (\chi^{(1)} E_0 + \chi^{(2)} E_0^2 + \chi^{(3)} E_0^3) + (\chi^{(1)} E_1 + 2\chi^{(2)} E_0 E_1 + 3\chi^{(3)} E_0^2 E_1) \cos \omega t
\]

\[
+ (\chi^{(2)} E_1^2 + 3\chi^{(3)} E_0 E_1^2) \cos^2 \omega t + (\chi^{(3)} E_1^3) \cos^3 \omega t + \ldots \quad (20)
\]

Using Trigonometric relations, \( \cos^2 \omega t = (1 + \cos 2\omega t)/2 \), \( \cos^3 \omega t = (\cos 3\omega t + 3 \cos \omega t)/4 \), equation (20) becomes

\[
P = (\chi^{(1)}[E_0 + E_1 \cos \omega t] + \chi^{(2)}[E_0^2 + (1/2)E_1^2 + 2E_0 E_1 \cos \omega t] + (1/2)E_0^2 \cos 2\omega t]
\]

\[
+ \chi^{(3)}[E_0^3 + (3/2)E_0 E_1^2 + 3E_0^2 E_1 \cos \omega t] + (3/4)E_1^3 \cos 3\omega t]
\]

\[
+ 3/2E_0 E_1^2 \cos 2\omega t] + (3/4)E_1^3 \cos 3\omega t] + \ldots \quad (21)
\]

The 1st term in the brackets for all \( \chi^{(n)} \) are constant factors. They give rise to a dc field across the medium.
1.4. Second order nonlinear optical processes

This section explains the processes associated with the $\chi^{(2)}$ in detail. From equation (21),

$$P^{(2)} = \chi^{(2)}[E_0^2 + (1/2)E_1^2 + 2E_0E_1\cos \omega t] + (1/2)E_1^2 \cos 2\omega t] \quad (22)$$

The coefficients $E_0$, $E_1$ corresponds to the linear electro-optic effect and is represented as $\chi^{(2)} (-\omega; \omega, 0)$. The sign attached to a frequency is negative if the photon is emitted and positive, if it is absorbed. The last term, which is square in the ac electric field and has a frequency of $2\omega$ is known as second harmonic generation (SHG) process.

Consider that two coherent light waves of unequal frequencies $\omega_1$ and $\omega_2$ are traveling in the material, then the $2^{nd}$ and $4^{th}$ terms in the previous equation (22) becomes

$$\chi^{(2)}(1/2)E_1^2 \left[ \cos(\omega_1 - \omega_2) + \cos(\omega_1 + \omega_2) \right] \quad (23)$$

Thus it contains two frequencies, $(\omega_1 + \omega_2)$ and $(\omega_1 - \omega_2)$. This phenomenon is known as optical mixing. While $(\omega_1 + \omega_2)$ is called sum frequency generation (SFG), $(\omega_1 - \omega_2)$ is called the difference-frequency generation (DFG). The second harmonic generation (SHG) process, actually, is a special case of SFG, where the frequencies of the photons from the incident beams are equal $(\omega_1 = \omega_2)$. Similarly, optical rectification (OR) is a special case of DFG for $(\omega_1 = 0)$). Thus OR susceptibility, is represented as $\chi^{(2)}(0; \omega, -\omega)$.

Three-wave mixing (two inputs and one output) is known as a parametric process, if the initial state and the final state of the system remain unchanged after interaction with light. This is because, in an emission process, the system comes back to the same state after emission. The same is not true for an absorption process where the initial and final states differ. The most prominent example of a non-parametric process is two-photon absorption. Various processes in nonlinear optical spectroscopy are listed in Table 1.1. Parametric processes can be used to make various devices. For example, Optical Generators can produce a wave of higher (up-conversion) or lower frequency (down-conversion) than the initial frequency. In Parametric Amplifiers three waves interact at frequency $\omega_1$, $\omega_2$ and $\omega_3$, so that one wave at frequency $\omega$ grows at the expense of the input frequency called the pump frequency. A very important device using parametric amplification is the Optical Parametric Oscillator. In this
Chapter 1

device, one uses a single pump source as an input and the output intensity can be controlled by changing the positions of the two mirrors surrounding the material.

Table 1.1: Some important processes involving Nonlinear Optical Spectroscopy

<table>
<thead>
<tr>
<th>Process</th>
<th>Order</th>
<th>Frequency relation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear Response</td>
<td>1</td>
<td>$-\omega; \omega$</td>
</tr>
<tr>
<td>Pockels Effect (EO effect)</td>
<td>2</td>
<td>$-\omega; \omega, 0$</td>
</tr>
<tr>
<td>Sum Mixing</td>
<td>2</td>
<td>$-\omega_1; \omega_1, \omega_2$</td>
</tr>
<tr>
<td>Second Harmonic Generation (SHG)</td>
<td>2</td>
<td>$2\omega; \omega, \omega$</td>
</tr>
<tr>
<td>Optical Rectification (OR)</td>
<td>2</td>
<td>$0; \omega; -\omega$</td>
</tr>
<tr>
<td>Intensity-dependent refractive index</td>
<td>3</td>
<td>$-\omega; \omega, -\omega, \omega$</td>
</tr>
<tr>
<td>Optical Kerr Effect</td>
<td>3</td>
<td>$-\omega; \omega_2, -\omega_2, \omega_1$</td>
</tr>
<tr>
<td>Dc Kerr Effect</td>
<td>3</td>
<td>$-\omega; 0, 0, \omega$</td>
</tr>
<tr>
<td>Two-photon Absorption (TPA)</td>
<td>3</td>
<td>$-\omega_1; \omega_2, -\omega_2, \omega_1$</td>
</tr>
<tr>
<td>Third Harmonic Generation (THG)</td>
<td>3</td>
<td>$3\omega; \omega_1, \omega_2, \omega_3$</td>
</tr>
<tr>
<td>Coherent anti-stokes Raman scattering</td>
<td>3</td>
<td>$(2\omega_1, -\omega_2); \omega_1, \omega_1, -\omega_2$</td>
</tr>
<tr>
<td>General four Wave mixing (FWM)</td>
<td>3</td>
<td>$-\omega_1; \omega_1, \omega_2, \omega_3$</td>
</tr>
<tr>
<td>Three-Photon Absorption (TPA)</td>
<td>5</td>
<td>$-\omega_1; \omega_2, -\omega_3, \omega_3 \omega_2, \omega_1$</td>
</tr>
<tr>
<td>$n^{th}$ Harmonic Generation</td>
<td>$n$</td>
<td>$n\omega; \omega_1, \omega_2, \ldots, \omega$</td>
</tr>
<tr>
<td>Multi-photon Absorption</td>
<td>$2n-1$</td>
<td>$-\omega; \ldots, -\omega, \omega; \ldots, \omega$</td>
</tr>
</tbody>
</table>

Owing to the spherical nature of nearly all molecular structures, and the differing atomic charges, $\delta^+$ and $\delta^-$, that each element possesses relative to each other in a given molecule, the overall polarization inevitably has a net direction, i.e., it is anisotropic. The relative orientation of a molecule with respect to others with in the repeating (unit cell) crystal-lattice motif is also important, since the SHG effect is a supramolecular rather than a molecular one. This polarization anisotropy is therefore three dimensional and thus (beyond the molecule) dependent upon supramolecular symmetry. The associated mathematics of the symmetry considerations is therefore very much involved, since the SHG effect is a third rank tensor. But it is only the results that are important here: in total
the symmetry conditions dictate that SHG active compounds can only occur in 18 out of the 32 crystallographic point groups.\(^{19}\)

\[
\begin{align*}
\text{a) Linear, b) Centrosymmetric nonlinear,} \\
c) Non-centrosymmetric nonlinear
\end{align*}
\]

Figure 1. 3: Symmetry requirements for second-order process showing the dissipation of the optical polarization. a. Linear, b. Centrosymmetric nonlinear, c. Non-centrosymmetric nonlinear

In 1962 Kleinman found that in many nonlinear processes where all the interacting frequencies are far away from resonance, energy is simply exchanged between the fields and not dissipated in the medium.\(^{26,27}\) Thus, the dispersion of the \(\chi^{(n)}\) is negligible and therefore the susceptibility tensors are invariant under any permutation of their Cartesian indices. For instance, in the \(\chi^{(2)}\), the symmetry relations give rise to

\[
\chi^{(2)}_{ik} = \chi^{(2)}_{ji} = \chi^{(2)}_{ki} = \chi^{(2)}_{ji} = \chi^{(2)}_{ij} = \chi^{(2)}_{ji}
\]

Thus due to Kleinman symmetry relations, the number of independent components of \(\chi^{(2)}\) reduces from 27 to 10 and that of \(\chi^{(3)}\) from 81 to 15.

Thus for a medium to exhibit frequency conversion process mediated by \(\chi^{(2)}\), the medium must have \(\chi^{(2)} \neq 0\). This condition requires that at a molecular level the nonlinear coefficient \(\beta\) must be nonzero. Furthermore, the orientationally averaged sum of \(\beta\) gives rise to the macroscopic \(\chi^{(2)}\) should not be zero. These two conditions lead to the following symmetry requirements for the realization of \(\chi^{(2)} \neq 0\). The molecules are non-centrosymmetric (do not possess an inversion symmetry), \(\beta\)-being an odd rank (3\(^{rd}\) rank) tensor-is not zero.

A molecular design often used to make molecules with large \(\beta\) values is D-\(\pi\)-conjugation-A. This is the one in which the molecular unit involving \(\pi\)-conjugation is connected to an electron donor, D, at one end and to an electron acceptor group, A, at the other end. The donor-acceptor systems show charge transfer between electron donating and electron withdrawing groups. Effective NLO polymers were obtained by the incorporation of highly active
chromophore molecules which have a large molecular hyperpolarizability $\beta$. Factors such as increased length, increased planarity and overall increased conjugation and the strength of donors and acceptors (i.e., the Hammett substituent-constant parameters) all play significant roles in nonlinear optics and are amenable to design.

1.5. NLO chromophores

NLO chromophores are molecules with electron donor and acceptor conjugated $\pi$-systems\textsuperscript{28}. The $\pi$ conjugated system could be azobenzene, stilbene, biphenyl, heterocycles, polyenes etc. The electron acceptors and donors that can be attached to a $\pi$-conjugated system are as follows: Acceptor Groups: NO$_2$, COOH, CN, CHO, CONH$_2$, CONHR, CONR, CONR$_2$, SO$_2$R, CF$_3$, COCH$_3$, CH=\text{C(CN)$_2$} etc and donor Groups: NH$_2$, NHR, NR$_2$, F, Cl, Br, OR, OH, C(CH$_3$)$_3$, COOR etc.

Ouder and Chemla suggested a two-state model to guide the design of second-order NLO chromophores\textsuperscript{29}

\[ \beta = \frac{(\mu_{ee} - \mu_{eg})(\mu_{ge})^2}{(E_{ge})^2} \]

where $\mu$ and $E$ are the dipole matrix element and transition energy, respectively, between the ground state (g) and the excited state (e). In fact, molecules for second order NLO applications were based simply upon aromatic $\pi$-electron systems asymmetrically end capped with electron donating and accepting groups which impart the directional bias. By the development of the EFISHG technique and by two level model, several one dimensional charge transfer systems with good NLO properties were developed during the 1980s. Typical examples of such systems are p-nitroaniline (PNA) and dimethyl- amino nitrostilbene (DANS). In DANS, the two benzene rings and the double bond provide the conjugated $\pi$-system and the polarizable electrons, the dimethylamino group acts as the donor and the nitro group acts as the acceptor which is shown in Figure 1.4. DANS was considered to be quite nonlinear at that time and is still being used as a typical benchmark to evaluate NLO properties of other molecules\textsuperscript{30}. Attempts carried out to increase the nonlinearity were usually aimed at increasing the donor-acceptor strength or increasing the
length of the conjugation bridge\textsuperscript{31}. In addition, chromophores with other types of conjugation bridges have been investigated. Many of these systems fall into the category of substituted benzenes, biphenyls, stilbenes, azostilbenes and tolanes\textsuperscript{32-34}.

\textbf{Figure 1. 4:} Dimethylamino nitrostilbene (DANS)

Schmidt et al. reported 2-dicyanomethylidene-4, 5, 5- trimethyl-2, 5-dihydrofuran group as a strong acceptor in second-order NLO chromophores which possess high $\beta$, excellent thermal stability and when incorporated in a PMMA film results in a high value of electro-optic coefficient $r_{33}\textsuperscript{35}$. Rutkis et al. studied the NLO efficiency of the poled host-guest films of eight different dimethylamino benzylidene 1, 3- indandione (DMABI) (\textbf{Figure 1. 5}) derivative chromophores which resulted in high NLO efficiency\textsuperscript{36}.

\textbf{Figure 1. 5:} Structure of DMABI

Azo dyes are widely used as chromophores for organic nonlinear optics (NLO) in modern technology. Rezaeifard et al.\textsuperscript{37} reported the synthesis of several varieties of azo chromophores and their characteristics. Sreekumar et al. developed biphenolic azo diol chromophores, bis (4-hydroxy phenylazo)-2, 2'-dinitro diphenylmethane and bis (4- hydroxy phenylazo)-2, 2'-dinitrodi phenylsulfone\textsuperscript{38-40}, the structure are shown in (\textbf{Figure 1. 6}).
Disperse Red 1 (Figure 1.7) and its derivatives are widely exploited as a side chain chromophore in the field of nonlinear optics.

Odobel et al.\textsuperscript{41} used DR1 chromophore as the active NLO unit for the successful preparation of new EO materials based on hyperbranched dendritic polymers. Although hyperbranched polymers have been known since 1950\textsuperscript{42}, their use for EO application has been reported only recently\textsuperscript{43-44}. They proposed three types of organization for the chromophores for a branched material like main chain, side chain and peripheral form.

1.6. Polymers as second-order nonlinear optical materials

The nonlinear optical response of a material can be used to make a variety of all-optical devices and the material criteria depend on the need for each specific device. Optical quality, transparency, tailorable refractive index, the ability to make specialized structures with the materials (such as thin films and fibers) and nonlinear susceptibility are some important properties that make an ideal NLO material.

Polymers are now considered as the most important specialty materials, as they combine the nonlinear optical properties of conjugated π-electron systems with the feasibility of creating new materials with appropriate optical and structural properties. Polymers that contain NLO active chromophores are promising candidates due to several advantages that are linked with polymers\textsuperscript{45}.
Chapter 1

They provide tremendous architectural flexibility to tailor the desired photonics functions and material performance. Polymers provide ease of processing and they are compatible to metal, glasses, ceramics and other substrates. They can be chemically modified to generate new materials. Also, polymers are environmentally stable and robust materials and are also tough and lightweight\(^\text{17}\). As a result of all these, nonlinear optical polymers have received considerable attention in the development of photonic, and optoelectronic based technologies for high speed data processing, transmission and storage in the past two decades\(^\text{46-48}\).

Nonlinear optical chromophores can be incorporated into the macroscopic environment by several ways. The most important and most widely used is the incorporation of dipolar chromophores into a polymer host by simply dissolving the chromophore into a polymeric material (guest-host systems), by covalently attaching the chromophores to a polymeric backbone (side-chain polymers) or by incorporating the chromophores into the backbone of the polymer (main-chain polymers).

1.7. Guest-host systems

Guest-host (GH) systems were the first organic materials investigated, in which SHG was induced by noncentrosymmetric ordering of NLO chromophores under electrical poling. The main problem of guest host systems is the decrease of the glass transition temperature of the host (polymer) dramatically due to plasticization by the guest (chromophore)\(^\text{49}\). GH systems are also undesirable because the chromophores are labile; at elevated temperatures they diffuse to the surface of the film and evaporate or sublime. However, GH systems offer several advantages: they can use a wide variety of noncentrosymmetric NLO chromophores for SHG activity, ease of processing into thin film by coating, dipping, and lithography, ease of fabrication onto a large area of substrate of any dimensions, inexpensive production of NLO materials, wide range of operating frequencies and low dielectric constant\(^\text{50, 51}\). A guest-host system is generally prepared by mixing a NLO dye, possessing large molecular hyperpolarisability \(\beta\), into an amorphous polymer matrix of high optical transparency. NLO dye is dissolved in the polymer host using a
common solvent; spin coated as a film to the substrate and the films are dried under vacuum. It is then poled at elevated temperatures.

Meredith et al. in 1982 reported SHG active guest-host system by doping a side chain liquid crystal polymer with 4-(dimethylamino)-4'-nitrostilbene. The poled-polymer approach in an amorphous system was first demonstrated by dissolving (N-ethyl-N-(2-hydroxyethyl) amino-4'-nitroazobenzene) (DRI) in poly (methyl methacrylate) (PMMA) (Figure 1.8).

**Figure 1.8:** Polymer backbone and azo chromophore

Wu et al. developed guest-host system with good temporal stability and high $T_g$ polyimide at a high temperature. Guest chromophores were typically introduced into solutions of polyamic acids which was processible into thin films. Thermal and chemical imidisation under a poling field at temperatures up to 360°C have resulted in impressive temporal stability at 200-300°C. Petsalakis et al. developed crosslinked host polymers to improve the temporal stability of a guest-host system and in a composite of 4-N, N-dimethyl-4'-nitrostilbene (DANS) with a highly crosslinked epoxy network, good temporal stability at room temperature was achieved (Figure 1.9).

**Figure 1.9:** 4- N, N-dimethyl-4'-nitrostilbene (DANS)

Physical aging of guest host systems was demonstrated by Lee et al. Physical aging can reduce the free volume of the polymer or change the
distribution of free volume and size and therefore, physical aging seems to be a good technique for improving the stability of polymers. Boyd et al.58 suggested that large dopant molecules were effective in preventing the decay of SHG activity and large dopant molecules with high thermal stability59, 60 were reported. Although high temporal stability can be achieved with high Tg host polymers, problems such as low solubility, thermal degradation, sublimation and the plasticizing effect of the guest molecules have prevented the attainment of both high stability and nonlinearity61. So in guest-host nonlinear optical polymers, the primary factor influencing the relaxation state is the Tg of the doped system. Because of this observation, high Tg thermoplastic polyimides were used as hosts62.

Recent investigations have confirmed the suitability of disposable recycled polystyrene63 as a host polymer to accommodate NLO active chromophores (guest molecules) that can lead to cheap NLO active device materials. Nonlinear optical properties of a guest host system consisting of the chromophore (Lemke's dye) embedded in poly (bisphenol A carbonate) matrix were studied and the polymer system formed a good optical quality, regular and slightly birefringent thin films.64

The phase stability and photorefractive properties of the guest-host system of poly (N-vinyl carbazole) (PVK)-based photorefractive polymer composite was achieved by modifying the structure of a nonlinear optical chromophore, 4-butoxy-3-propyl-1-(4'-nitrophenyazo) benzene. The shelf life of a sample with a modified NLO chromophore, 4-(2-ethylhexyloxy)3-propyl-1-(4'-nitrophenyazo) benzene was extended by more than five months even though it had a low glass transition temperature (Tg) of -19°C. This material also had a short photorefractive response time constant of 33 ms and a high diffraction efficiency of 49% at an electric field of 100V/μm and a total writing intensity of 942mW/cm². These desirable characteristics are due to the plasticizer nature of chromophore, which enhanced the orientation of the NLO chromaphore and secondly, the solubility of the chromophore in the polymer matrix was increased, inhibiting crystallization and providing high optical quality56.

Zang et al. used some conjugated polymers to functionalize single walled carbon nanotubes and the experimental results showed that different polymer backbones had considerable influence on the nonlinear optical properties of
carbon nanotubes. It is one of the recent works based on guest-host systems as nanotubes.

1.8. Side-chain polymer systems

An NLO chromophore may be covalently bonded as a pendant group to the polymer backbone directly or through a spacer group. Functionalized polyalkylacrylates are the most studied polymer systems for nonlinear optics. The good optical and dielectric properties of PMMA and the synthetic accessibility of its derivatives have contributed to the great demand for the acrylates. Works on co- and homopolymers of functionalized polyacrylates demonstrated that large nonlinearity was possible due to the much higher number density compared with guest-host systems (Figure 1.10).

![Figure 1.10: DRI functionalized methacrylate copolymer](image)

Poled polymers with polystyrene type backbones were obtained which showed good optical and dielectric properties, relatively high $T_g$ and ease of functionalization. Functionalized polystyrenes have been obtained via polymer reaction and polymerization of functionalized vinyl monomers (Figure 1.11).

![Figure 1.11: Poly-4-[N-methyl-N-(4'-nitrophenyl) aminomethyl] styrene](image)

Yin et al. have reported a second order nonlinear optical poly (ester amide) possessing good organo solubility, excellent film-forming property, high glass transition temperature and high thermal stability. Side chain polyimides
are now widely used, as they have high glass transition temperatures leading to high thermal and temporal stabilities and make them good choices for applications in photonic devices. Peng et al., Yang et al., and Yu et al. have designed side chain polyimides with dialkylamino nitrostilbene and dialkylaminomethyl sulfonyl stilbene (Figure 1.12).

![Figure 1.12: Styrene/p-[4-nitro-4’-(N-ethyl-N-2-oxyethyl)azobenzene] methyl styrene copolymer](image)


Azobenzene-containing side-chain photorefractive polyphosphazene P3-P8 were obtained via a post-azo coupling reaction. The photorefractive polymers obtained showed high glass transition temperature and good optical transparency. The polyphosphazenes possessed relatively large magnitude of photoinduced birefringence. The polymers with structurally isomeric and free-radically polymerizable methacrylates bearing azo-naphthol group in the side chain spaced away from the backbone by a hexamethylene spacer and substituted at 4-position with electron-withdrawing and donating substituents were reported for NLO applications and their photo-isomerization properties were studied. The results revealed that these polymers possessed potential applications in nonlinear optics.
Ju et al. synthesized a polyimide with two aromatic hydroxyls in the repeat unit by condensation polymerization between 2, 2-bis (3-amino-4-hydroxyphenyl) hexafluoropropane and oxydiphthalic anhydride followed by imidization reaction. Mitsunobu coupling was carried out to incorporate the NLO chromophore into the polyimide backbone, resulted a side-chain polymer with $T_g$ at 168°C and thermal stability up to 370°C. The polymer solution was spin coated on the ITO glass to produce an optical quality film. The electro-optic coefficient of the film was obtained using 1.55 μm laser source, giving 31 pm/V with an electrical poling field of 1 MV/cm.

Chen et al. reported a side chain polymer by using the bis fluoro NLO chromophore monomer, 4-[(4-cyanophenyl) diazenyl] phenyl-2, 6-difluorobenzoate, azobenzene-functionalized poly (aryl ether) (azo-PAE) was prepared via a nucleophilic aromatic substitution polycondensation. The results showed that azo-PAE had high glass transition temperature, good thermal stability and large nonlinear susceptibility (Figure 1.13).

Zhao et al. reported NLO side-chain polymers, obtained by attaching the NLO chromophore to a hydroxyl containing polymer BPAN resulted in a good performance of BPAN, such as good film formation property and crosslinkability. Crosslinked poled polymer with even higher content of NLO chromophore was obtained by taking the same kind of NCO-containing chromophore as crosslinking agent.

Golemme et al. developed the homopolymers and copolymers which are multifunctional side chain polymers exhibiting chiral, semiconducting, photochromic and nonlinear optical (azo aromatic moieties) properties. The high $T_g$, non-poled photorefractive polymers were advised for a variety of
applications ranging from holography to image processing. Li et al.\textsuperscript{85} proposed the synthesis of azobenzene containing side chain homopolymers and copolymers with controllable molecular weight by means of atom transfer radical polymerization. The influence of push pull electronic effect of chromophores to the macroscopic NLO properties of homopolymers and copolymers were explained in detail.

A broad variety of side chain NLO polymers have been demonstrated through post functionalization of commercially available polymers using the Mitsunobu reaction, azo coupling, tricyanovinylation, Knoevenagel condensation and acid and base catalyzed esterification. More recently, the click chemistry based Diels Alder reaction has emerged as a powerful strategy to construct NLO polymers. Jen et al. conducted a systematic study for constructing high-performance NLO polymers via Diels Alder based click chemistry. By using the DA reaction, highly nonlinear and chemically sensitive phenyltetraene based NLO chromophores were incorporated into side chain polymers to achieve good processibility, large NLO coefficients and excellent thermal stability\textsuperscript{36}.

1. 9. Main chain polymer systems

In main chain polymers, a high concentration of NLO chromophores can be introduced by covalently functionalised polymers. The polymers containing covalently attached NLO chromophore show increased stability towards relaxation after poling. A main chain polymer may show improved tensile and mechanical properties, relative to a side chain polymer\textsuperscript{87}. Main chain polymers, which contain chromophores in a head-to-tail arrangement within the polymer backbone, were used as nonlinear optical materials and the potential advantages include high temporal stability and a poling enhancement resulting from the backbone correlated dipole orientation. Low $T_g$, low solubility and high crystallinity of the main chain polymers were the major difficulties encountered\textsuperscript{88-91}. The ‘accordion’ polymer approach, in which the polymer backbone is folded like an accordion with the chromophoric segments in head-to-tail arrangement, showed encouraging results\textsuperscript{92}. Despite rather low nonlinearity, a $T_g$ of 143°C and room temperature temporal stability of the polar order were reported\textsuperscript{93}. A random main chain polymer in which the
chromophoric backbone consisted of a statistical mixture of head-to-head, tail-to-tail and head-to-tail arrangements, showed better results\textsuperscript{94,95}. When the results from the random main-chain polymer systems are compared to those obtained from an acrylate side-chain copolymer with similar $T_g$ and chromophoric content, similar poling efficiency (within 80\%) was shown\textsuperscript{96}. The temporal stability of the polar order is also similar in both polymers. This suggests that the degree of coupling between the polymer backbone motion and the chromophoric orientation are similar for both side-chain and main-chain polymers, despite their considerable structural differences\textsuperscript{61}.

Kim et al. reported a novel T-type polyester containing dioxynitrostilbenyl groups as the NLO chromophores obtained by the polycondensation of 2, 5-di-(2’-hydroxy ethoxy)-4’-nitrostilbene with terephthaloyl chloride, adipoyl chloride, and sebacoyl chloride, which possessed high thermal stability up to 260°C with a glass-transition temperature in the range 90-95°C and a high second harmonic generation (SHG) coefficient ($d_{33}$) of poled polymer films, hence was found to be acceptable for NLO device applications\textsuperscript{97}.

Angiolini et al. reported corona poling behaviour of optically active photochromic copolymers derived from methyl methacrylate (MMA) and the methacrylic ester of (S)-3-hydroxy pyrrolidine linked through the nitrogen atom to the highly conjugated photochromic 4’-(β-cyano-β-(methylsulfonyl) vinyl)-4-azobenzene moiety with the aim to evaluate the effect on the nonlinear optical properties originated by the presence of inactive side-chain MMA groups along the main chain. The corona poled polymeric films have $d_{33}$ values in the range 10-86 pm/V. The temporal and thermal stability of the optimal SHG signals obtained after corona poling process of all the macromolecular materials has been investigated and compared. The results indicated that the maximum of these properties could be obtained at a molar percentage of photochromic units around 20-40\%\textsuperscript{98}.

Lee et al. reported the synthesis of polyamides by using 2, 3-dioxynitrostilbenyl groups as NLO-chromophores and 2, 3-Bis-(3, 4-dicarboxy phenyl carboxy ethoxy)-4’-nitrostilbene dianhydride, which was obtained by the reaction with 4, 4’-oxydianiline and 4, 4’-diaminobenzenanilide. Polymers showed thermal stability up to 300°C with $T_g$ values in the range of 135-141°C. The material possessed high SHG coefficients ($d_{33}$) of poled polymer films ($6.14 \times 10^{-9}$
The dipole alignment of poled polymer films exhibited exceptionally high thermal stability even at 30°C higher than $T_g$ and there was no SHG decay below 170-190°C due to the partial main chain character of polymer structure, which was acceptable for NLO device applications.

Yoon et al. had done a comparative study in between side chain and main chain polymers. They designed carbazole-based push-pull type nonlinear optical (NLO) polymers, $P_{(Cz-CN)}$, $P_{(Cz-DR 19)}$, and $P_{(Cz-TCN)}$. The structure of $P_{(Cz-CN)}$ was designed to contain di-acceptor-chromophores in the main chain and to have a two-dimensional (2D) charge transfer (CT) configuration. $P_{(Cz-DR 19)}$ and $P_{(Cz-TCN)}$ were designed to have NLO chromophores in the side chain. All the polymers synthesized were thermally stable approximately up to 250 °C. The glass transition temperatures ($T_g$) of $P_{(Cz-DR 19)}$ and $P_{(Cz-TCN)}$ appeared at 117 °C and 104 °C, respectively. The ratio of the second harmonic coefficients ($d_{33}/d_{31}$) was 1.5 in $P_{(Cz-CN)}$ and 3.3 in $P_{(Cz-DR 19)}$ and $P_{(Cz-TCN)}$. $P_{(Cz-CN)}$ showed enhanced off-diagonal tensor components due to 2D CT effects. The $d_{33}$ values of $P_{(Cz-DR 19)}$ and $P_{(Cz-TCN)}$ were 61.6 pm/V and 41.7 pm/V, respectively. The electro-optic coefficients ($r_{33}$) of $P_{(Cz-DR 19)}$ and $P_{(Cz-TCN)}$ were 40.5 pm/V and 17.8 pm/V at 632.8 nm, respectively. $P_{(Cz-DR 19)}$ showed higher second-order optical nonlinearity than that of $P_{(Cz-TCN)}$ due to higher $\beta$-values of DR 19 moiety in the side chain. $P_{(Cz-DR 19)}$ and $P_{(Cz-TCN)}$ showed stable NLO coefficient up to 98 °C and 75 °C, respectively. The intensity of SHG of $P_{(Cz-DR 19)}$ was stable up to 20 days at room temperature.

Lee et al. developed novel Y-type polyurethanes containing 2,3-dioxy benzylidene malononitrile group as a nonlinear optical (NLO)-chromophore, which was obtained by the condensation of 2, 3-di-(2'-hydroxyethoxy) benzylidene malononitrile with 2, 4-toluene diisocyanate and 3, 3'-dimethoxy-4, 4'-biphenylene diisocyanate. The polyurethanes showed a thermal stability up to 270°C and the glass-transition temperatures ($T_g$) obtained were around 116-135°C. The second harmonic generation coefficients ($d_{33}$) of poled polymer films at 1064nm fundamental wavelength were around $2.72 \times 10^{-9}$esu. The dipole alignment exhibited high thermal stability up to 10°C higher than $T_g$, and there was no SHG signal decay below 145°C due to the partial main-chain character of
the polymer structure, which was acceptable for nonlinear optical device applications\textsuperscript{101}.

Polymers containing azo group in the main chain showed that the presence of azo group in the main chain increased the second order NLO efficiency. This can be explained as the electron donating effect of azo group. The presence of azo group in the main chain increases the donor acceptor strength, polar order and efficiency to form higher molecular weight polyester, which increases the second order NLO response. Sreekumar et al. developed main chain chiral polymers by using the biphenolic azo diol chromophores, bis (4-hydroxy phenylazo)-2, 2'-dinitro diphenylmethane and bis (4-hydroxy phenylazo)-2, 2'-dinitrodiphenyl sulfone\textsuperscript{38-40} (Figure 1.14).

Figure 1.14: Main chain polyester unit

1.10. Crosslinked polymeric systems

Crosslinking is a natural strategy aimed at stabilizing the order of parameter relaxation in poled polymers\textsuperscript{61}. The NLO chromophore is incorporated in a polymer backbone with high glass transition temperature. With high glass transition temperature with the exception of polyimides, crosslinked networks have provided the highest temporal stability. Thermally activated crosslinking and photochemically activated crosslinking were the methods used to prepare such systems\textsuperscript{61}.

For thermal crosslinking, methods used were epoxy-amino coupling, radical-initiated thermal polymerization of multi-functional methacrylate monomers, epoxy-alcohol coupling, isocyanate-hydroxyl coupling, isocyanate-amino coupling, alcohol condensation of alkoxysilane and ethynyl thermal intramolecular reaction\textsuperscript{61}. The most widely used are the epoxy and isocyanate
coupling chemistry and the diepoxide (bisphenol-A) was used for the early works on crosslinked materials for nonlinear optics (Figure 1.15).

![Crosslinked epoxy polymer from 4-nitro-1, 2-phenylene diamine and bisphenol-A diglycidyl ether](image)

Figure 1.15: Crosslinked epoxy polymer from 4-nitro-1, 2-phenylene diamine and bisphenol-A diglycidyl ether.

The reactive sites in side-chain polymer backbone may be crosslinked to improve temporal stability. An example was provided by the epoxy crosslinking of a polyhydroxy styrene copolymer. Photocrosslinking was explored as an alternative route for crosslinked networks, which have advantages over thermal crosslinking. If a highly crosslinked network can be obtained under an electric field at low temperature, poling efficiency may be improved through both the Boltzmann factor and the possibility of a higher poling field. Also, under a poling electric field, the illuminated region of the polymer can be finely patterned, as in photolithography, creating not only a pattern in the refractive index, but also a pattern in the nonlinear optical susceptibility through the subsequent dipolar relaxation in the uncrosslinked regions.

Mandal et al. have reported the doping of a bis cinnamoyloxy functionalized chromophore into a photo-crosslinkable polymer matrix, which is shown in Figure 1.16. Photo-crosslinking with a few minutes of UV exposure under a poling field at its glass transition temperature resulted in both high nonlinearity and good temporal stability.

Polyimides possessing both high $T_g$ and crosslinked networks seem to be a rational approach to enhance the NLO stability. Addition-type polyimides may be used to circumvent the need for thermal imidisation. Improved processability can be achieved without sacrificing properties such as excellent thermal stability and mechanical properties. Jeng et al. have prepared a
series of maleimide based crosslinked organic and organic-inorganic materials, which showed large second order optical nonlinearity after poling and curing.

![Diagram of crosslinked polymer of polyvinylcinnamate doped with 3-cinnamoyloxy-4-[4-(N, N-diethylamino)-2-cinnamoyloxyphenyl azo] nitrobenzene](image)

**Figure 1.16:** Crosslinked polymer of polyvinylcinnamate doped with 3-cinnamoyloxy-4-[4-(N, N-diethylamino)-2-cinnamoyloxyphenyl azo] nitrobenzene

1.11. Poling

To exhibit second-order nonlinear optical effects, the isotropic symmetry in amorphous polymers must be broken. The noncentrosymmetric nonlinear optical molecules must be arranged in the materials in such a manner that the bulk material also does not have an effective centre of symmetry, for the polymer materials to exhibit bulk second order optical nonlinearities. To achieve the necessary noncentrosymmetry, the chromophores in the polymer matrix are poled. Poling is the procedure in which the chromophores are aligned electrically, thermally or by radiation. For a poled polymer, acentricity is imparted with a poling electric filed. If a polar alignment of the dipolar species in the polymer occurs during poling, this acentricity can be maintained, upon the removal of the poling field, for a time period determined by the orientation-relaxation time of the dipoles.

Poling is carried out near the polymer glass-transition temperature where the dipolar orientation time is short, for attaining maximum alignment. The polar alignment is then dynamically “frozen” into the polymer by cooling under the poling field. At reduced temperatures, the relaxation of the polar order...
slows down considerably. If this relaxation can be reduced to an acceptable minimum, an amorphous material with quasi-permanent second order nonlinearity is obtained. The poled polymer approach offers more rational controls in the organization of molecular nonlinearity. On incorporation of chromophores into a polymer matrix, optically nonlinear thin films and fibers can be obtained easily, allowing for large area coverage as well as long interaction length. By linking the chromophores covalently into a polymer network, high number density and thus, high nonlinearity is possible. The optical quality of the polymer can also be optimized through compositional designs. Electric field poling can be achieved in several ways and two common methods are corona-poling or (sandwich) contact electrode poling. Each method has its own advantages and disadvantages, contact electrode poling requires high quality polymer films and a careful electrode design. On the other hand, electrode poling is compatible with electro-optic and second harmonic device processing requirements. The most commonly used method in poling experiments is corona poling. Extremely high electric fields can be obtained and the quality of thin films is not so critical. As alternatives to thermally activated corona or contact poling, other techniques have been reported including the use of a plasticizing gas, or photo induced cis-trans isomerization to assist orientational mobility.

1.12. Chiral polymers in second order nonlinear optics

Frequency conversion of lasers is a significant application of second order nonlinear optics. For this, the nonlinear optical material should be noncentrosymmetric or otherwise it will not have a second-order nonlinear response. In most of the materials, macroscopic centrosymmetry has to be broken artificially by employing physical methods such as electric field poling of molecules embedded in polymers and Langmuir-Blodgett film fabrication. These techniques result in polar order, the net alignment of molecular dipoles along an axis, the polar axis of the materials. However, a major drawback is the decay of their nonlinear response with time. Host-guest complexation and intercalation, salt formation, uses of molecules with negligible dipole moment or octupolar molecules are some other approaches used. Introduction of special functionalities such as H-bonding groups, optimally
long alkyl chains\textsuperscript{123} and sterically bulky groups\textsuperscript{124} have also proved useful in many cases. However, none of these approaches guarantee a noncentrosymmetric lattice\textsuperscript{125}. When the fundamental frequency of the light source becomes sufficiently intense, two or three photon processes such as hyper-Rayleigh Scattering\textsuperscript{126}, Sum-frequency generation\textsuperscript{127}; second and third harmonic generation, the electro-optic effects etc. were observed\textsuperscript{128}. Only noncentrosymmetric systems will give a second harmonic response on the macroscopic level and so the polar order must be introduced.

Chiral materials provide a new approach to second order nonlinear optics. Chiral materials are inherently noncentrosymmetric and therefore possess an electric-dipole allowed\textsuperscript{127,129,130} second order and higher even-order nonlinearity\textsuperscript{131}. Such nonlinear responses due to chirality do not require polar ordering and permits even in macroscopic samples with high symmetry. Chiral molecules may possess strong magnetic-dipole transitions, which allow second order nonlinearity in macroscopically centrosymmetric materials\textsuperscript{132,133}. Amino acid family single crystals are gaining importance as highly feasible second order nonlinear optical materials. Efforts have been made to combine amino acids with interesting organic and inorganic matrices to produce materials\textsuperscript{134} which are gaining prominence in view of their high laser damage threshold, wide transparency window, low UV cut-off and high NLO coefficients.

There are mainly two theories proposed to explain the large SHG efficiency of chiral films and materials.

\textit{Electric-dipole approximation}: By this method, there are different number of chiral and achiral tensors of $\beta$ and $\chi^\text{2}$. Chiral tensor components arise due to the chirality of the medium and the contribution of these components will be higher in chiral media while it is negligible in achiral media.

\textit{Magnetic-dipole approximation}: Chiral molecule may possess strong magnetic-dipole transitions, in addition to the electric-dipole transitions, which allow second-order nonlinearities in macroscopically centrosymmetric materials.

The strongest experimental evidence supporting the significance of magnetic–dipole contributions to chiro-optical effects in SHG was presented by Persoons et al.\textsuperscript{135,136}. Despite the wide spread use of magnetic-dipole contributions in interpreting chiral SHG measurements, there is a significant
body of evidence suggesting that magnetic dipole contributions may be of only minor importance in oriented systems.\textsuperscript{137}

\section*{1.13. Chiral Polymers}

The recent focus of the molecular material research has been on fabricating materials fine tuned for enhanced attributes such as electrical, magnetic, optical and nonlinear optical characteristics\textsuperscript{125}. Organic polymers, with combined functions of electric, magnetic and chiral properties are expected to be target molecules of current material chemistry\textsuperscript{138}. The important advantage of organic polymers is the manipulation of the molecular structure or molecular designing and the ease of processability. Helical and \(n\)-conjugated polymers would be potential candidates for such functional materials based on well defined chiral structures\textsuperscript{138}.

The simplest method of synthesizing optically active polymers involves the polymerization of optically active monomers. However, this is often less attractive from the view point of the polymerization reaction. Asymmetric polymerization which produces configurationally or conformationally specific optically active polymers starting from optically inactive monomers is much more attractive and challenging, and remarkable advances, particularly on helical polymers, have been made over the past two decades. Optically active polymers may be obtained in several ways including (a) polymerization with a chiral catalyst or initiator,\textsuperscript{139, 140} (b) chiral doping of achiral (racemic) polymers with enantiopure chiral ions,\textsuperscript{141} (c) separation of racemic mixture of enantiomeric helices using chiral stationary phase (CSP) chromatography (for nondynamic systems,\textsuperscript{142} (d) chiral complexation of achiral or racemic polymers with enantiopure chiral ligands/guests,\textsuperscript{143} (e) post- polymerization functionalization with chiral moieties,\textsuperscript{144} (f) polymerization of enantiopure chiral monomers,\textsuperscript{145} (g) incorporation of enantiopure chiral end groups\textsuperscript{146} and (h) copolymerization of enantiopure chiral monomers with achiral monomers or with an enantiomeric excess (ee) of one enantiomer over the other\textsuperscript{147}. In the last two cases, it is the presence of enantiopure chiral “seeds” which results in the adoption of a preferential helical screw sense; in even non-enantiopure-substituted backbone regions by the preferential stereo relationship between enantiopure chiral side chains and their nearest neighbours.
The chiro-optical properties exhibited by optically active polymers are very useful for understanding their configurational and conformational characteristics. Optical activity is a physical spectral property of a chiral material caused by asymmetric configurations and conformations, which have no plane or centre of symmetry. Chirality (optical activity) can be introduced in a macromolecule by attaching chiral centers in the lateral chains or in the main chain\textsuperscript{149, 150}. The attachment of chiral groups in the polymer chain is observed to twist the main chain in predominantly one screw sense to generate helical structures\textsuperscript{149, 150}. Polymers with chirality in the main chain were also reported to have twisted helical crystal shape\textsuperscript{151}. Polymers without any asymmetric center (carbon or hetero atom) can have chiral conformation links or steric hindrance, which direct such molecules into helical conformation and their mirror planes pass through bonds and not through atoms\textsuperscript{148}.

Helical polymers are representative chiral macromolecules and have precisely ordered structure. The chirality of helical polymers has attracted the interest of synthetic polymer scientists because their chirality leads to stereo regularity in the polymers and also provided much information about the polymer structures\textsuperscript{152}. The chiro-optical activity of the helical polymers is based on the structural (or conformational) chirality of the helical polymers and whether or not the polymer involves a chiral unit in the monomeric moiety.

Self assembly based on chiral molecules is one approach in material development, which shows, how molecular engineering strategies can be used to develop new features in nonlinear optical systems\textsuperscript{153}. Helicenes, which are aromatic helical molecules composed of fused benzene and/or thiophene rings, have been synthesized because of their helical structure and very good nonlinear optical properties\textsuperscript{154}.

Verbiest\textsuperscript{155} et al. have investigated the self-assembly of chiral molecules, in which chirality and supramolecular organisation play key roles. In the Langmuir-Blodgett films of a chiral helicenebisquinone\textsuperscript{156, 157} the molecules form supramolecular arrays that enhance the second-order nonlinear optical susceptibility about 30 times larger for the nonracemic material than for the racemic material with the same chemical structure. The susceptibility components that are allowed only by chirality dominate the second-order NLO response. The second harmonic generation for the highly symmetric thin films of
Helicene and thiaheterohelicene have also been extensively studied\textsuperscript{158-160} and are shown in Figure 1.17. The films were prepared by spin-coating, and no external force, such as electric filed poling, was used to induce the noncentrosymmetry. The SHG susceptibility values were significantly high, which indicated the formation of highly symmetric thin films with considerable second-order nonlinearity.

![Figure 1.17: Structure of chiral helicenebisquinone, helicene and thiaheterohelicene](image)

Helicene structures have also been incorporated into metal phthalocyanines. The molecules are constructed by fusing copper and nickel octaazaaphthalocyanines to four non racemic helices\textsuperscript{156, 157, 161}. These compounds tend to aggregate strongly in thin films and in appropriate solvents. Even though the molecules are symmetrical, their Langumir-Blodgett films gave very large second order nonlinear responses, dominated by the components of the susceptibility tensors that are allowed, only because the materials are chiral\textsuperscript{162}.

Cooperative responses to chiral information and magnification effects can be extremely large in helical polymers\textsuperscript{148, 163}. Green et al.\textsuperscript{164, 165} demonstrated that helical reversals along the chain are highly sensitive to chiral effects. Incorporation of a small number of units with pendant chiral groups in copolymers with hexylisocyanate, results in the control of helical reverses that force large number of polymer chain units to cooperate in directing the chirality of the polymer (Figure 1.18). Green et al. formulated a majority rule and the so called "sergeants and soldiers" principle. A tiny majority of R over S monomers or a small amount of chiral units (sergeants) is incorporated within the achiral units (soldiers), can dictate the helical sense.
Several interesting NLO phenomena in chiral media have been theoretically predicted\textsuperscript{166-168} and some of them have been verified experimentally in chiral, helical polymeric media\textsuperscript{169-174}. Many reports have demonstrated the presence of chiral effects in second harmonic generation from monolayer of the chiral polymers and the chirality gave rise to a new electric-dipole-allowed component of the second order susceptibility tensor and to significant contributions to the nonlinearity. The results of the study also show that the overall nonlinear optical properties of chiral molecules can be significantly enhanced by optimizing the magnetic contributions to the nonlinearity and this is important in the field of electro-optics for the development of a material with high nonlinear optical response\textsuperscript{174}.

The occurrence of chirality at different levels of the polyisocyanide structure suggests that chiral and nonlinear optical properties of new materials can be optimized independently without losing the coupling between the properties\textsuperscript{175}. Persoons et al.\textsuperscript{176, 177} observed strong chiral effects in the second-order nonlinearity of poly (isocyanide)s (Figure 1.19).

They showed that nonlinear optical chromophores could be organized in a fixed noncentrosymmetric arrangement as side groups of polymers with a rigid backbone. They investigated the second order response of chiral polyisocyanides\textsuperscript{177} that contained nonlinear chromophore as side groups. The
Chapter I

Chirality of the material was associated with the helical supramolecular configuration of the backbone. This resulted in a strong orientational correlation of side groups.

Evidence of high magnetic-dipole contributions to the nonlinearity was observed in Langmuir-Blodgett (L.B) films of a chiral poly (thiophene) (Figure 1.20). The sample studied was a ten layer L.B film of the regioregular chiral poly (thiophene), poly [3-[2-((S)-2-methylbutoxy)-ethyl] thiophene]178,179 and the magnetic dipole contributions observed in these L.B films were of the same order of magnitude as the electric-dipole nonlinearities. The nonlinear response arises from properties of the \( \pi \rightarrow \pi^* \) transition, which corresponds to displacement of electrons along the helical conjugate backbone. Spin coated thin films of a chiral poly (3-alkylthiophene) were investigated by Verbiest et al.180. They found that the films showed a significant SHG and exhibited magnetic-dipole nonlinearities, in addition to the usual electric dipole contribution.

![Figure 1.20: Structure of chiral polythiophenes](image)

Chen et al. reported the synthesis of novel optically active polyurethanes based on chiral 1, 1'-binaphthol via direct hydrogen transfer addition polymerization (Figure 1.21). They found that the polymers showed better thermal stability and exceptionally good optical activity171.

![Figure 1.21: Structure of 1, 1'-binaphthol](image)

The incorporation of chiral binaphthyl units into polymer chains by Pu et al. led to a class of conjugated polymers with inherently chiral main chains
which are shown in Figure 1.22. These polymers possessed a highly stable main chain chiral helical configuration, which made them potentially useful for nonlinear optics. The NLO chromophores can be organized in chiral binaphthyl polymer chains to construct non-centrosymmetric and multipolar materials\(^{181,182}\).

Pu et al. prepared a dipole oriented chiral binaphthyl based polymers containing different electron acceptors and conjugated dipole units which have large dipole moments since the dipole units are tilted in one direction along the polymer axis\(^{181}\). Polymers of such organized geometry are very interesting since, orientation correlated NLO chromophore on a helical polymer have been observed to generate an enhanced second order NLO response\(^{181-182}\).

Sreekumar et al. developed several varieties of chiral polymers containing donor acceptor n-conjugated polar segments and chiral building block in the main chain (Scheme 1.1). Chiral doping is made in a sense to attain noncentrosymmetric ordering of dipoles in macroscopic dimensions by chemical synthesis. Several polyesters containing push-pull electronic azobenzene mesogenic groups in the main chain were developed. The multifunctional polyesters were prepared by the polycondensation of terephthaloyl chloride, chiral diols (isosorbide, isomannide, camphane diol and diethyl (2R, 3R) tartrate) and Bis (4-hydroxyphenylazo)-2,2’ dinitro-3, 5, 3’, 5’-tetramethyl diphenyl methane as NLO chromophores, showed liquid crystalline behaviour with high glass transition temperatures, stable liquid crystalline mesophases and high second harmonic generation efficiency. The second order nonlinear optical
susceptibility values were also studied as a function of the percentages of the
chiral building units. A novel synthetic approach has been developed to incorporate donor-
acceptor substituted \( \pi \)-conjugated segments and chiral centres in main chain
polymeric systems. The polycondensation products obtained by using \((2R, 3R)\)–
\((-\)-diethyl tarteatarate, terephthaloyl chloride and the biphenolic chromophores
bis(4-hydroxy phenylazo)-2, 2'-dinitrodiphenylmethane and bis(4-hydroxy
phenylazo)-2, 2'-dinitrodiphenylsulfone were used for NLO measurement. The
optical activity of the polymers showed that the introduction of a substantial
amount of chiral groups in the polymer chain led to the formation of non-centric
configurations. The polyesters showed glass transition temperatures in the range
100-190\(^\circ\)C and were thermally stable (350\(^\circ\)C). By the condensation of
azobenzene-4, 4'-dicarboxylic chloride with 1, 4: 3, 6- dianhydro-D-sorbitol and
biphenolic chromophores, bis(4-hydroxy phenylazo)-2, 2'-dinitrodiphenyl-
methane and bis(4-hydroxy phenylazo)-2, 2'-dinitrodiphenylsulfone, the
products which exhibited glass transition temperature in between 100 and 160\(^\circ\)C
were having high thermal stability (upto 400\(^\circ\)C).

NLO active polyesters by varying the composition of the chiral diols were
also developed (Scheme 1.1). The polycondensation products of acid chloride of
azobenzene-4, 4'-dicarboxylic acid with the chromophore, bis (4-hydroxyphenyl
azo)-2, 2'-dinitro diphenylmethane and chiral diols, isosorbide, isomannide,
diethyl -L-tartarate and exo, exo-camphene diol were studied and concluded that the polymeric system which was having isomannide chiral moiety possessed more SHG efficiency. The polymer with isomannide chiral diol has more polar order and has shown higher Tg value which induced high SHG efficiency.

The second harmonic generation of the chiral polyesters synthesized was studied in thin films. The thin films of achiral polyesters were SHG inactive and chiral polyesters can provide an excellent noncentrosymmetric media and showed good second harmonic efficiency even in the absence of poling. The SHG in the thin films of chiral polymers also possessed temporal stability and indicated the thermal stability of the dipole orientation in the polymer. The hydrogen bonded liquid crystalline poly (ester-amides) (PEA)s were synthesized from 1, 4- terephthaloyl [bis- (3-nitro- N- anthranilic acid)] and 1, 4-terephthaloyl [bis- (N-anthranilic acid)] with and without nitro groups respectively through the separate condensation of each with hydroquinone or dihydroxy naphthalene. It was found that, the polymers were NLO active liquid crystalline polymers in which PEAs containing nitro groups exhibited polymorphism (smectic and nematic) where as those without nitro groups exhibited only one phase transition (nematic threaded texture). This group reported the development of highly efficient NLO active side chain and main chain polyesters, poly (ester-amides), polyurethanes etc.

Yashima et al. reported some chirality-responsive π-conjugated polymers. The electrochemically polymerized emrealdine base form of polyaniline is known to show an induced circular dichroism (ICD) in the long absorption region in solution or in the film when doped with optically active strong acids, such as (R)-or (S)-camphorsulfonic acid (CSA). The (R)-CSA-dedoped polyaniline thin films retained their optical activity which responded to the chirality of a pair of phenylalanine enantiomers and exhibited a different color change by responding to the chirality of the enantiomers. A partially hydrolyzed polythiophene (PT) derived from an optically active PT is sensitive to the chirality of the (R)- and (S)-2-amino-1-butanol and exhibited ICDs of almost mirror images to each other. Optically inactive π-conjugated copolymers with the C2-symmetric carboxy biphenol units as the main chain component also exhibited an ICD in the copolymer backbone regions in the
presence of chiral amines. The chiral information of the amines is first transferred to the carboxybiphenol moieties with a dynamic axial chirality through noncovalent acid-base interactions, and subsequently the induced axial chirality with an excess single handed twist sense may be further amplified in the n-conjugated copolymer backbones as an excess of a single-handed helix.

Akagi et al. developed chiral dopants with nonbridged and bridged type axially chiral biphenyl derivatives to prepare chiral nematic liquid crystals available for an asymmetric reaction field producing helical conjugated polymers (Figure 1.23). The nonbridged binaphthyl derivatives exhibited transoid and cisoid conformations in isotropic and in liquid crystal solvents and bridged binaphthyl derivative formed cisoid conformation irrespective of solvents. The liquid crystals thus prepared were used as the asymmetric solvents for the synthesis of helical polyacetylene. The usage of the nonbridged and bridged binaphthyl derivatives, as chiral inducers having the same configuration but opposite helical sense, afforded a convenient way to construct the helicity controlled liquid crystal reaction field.

Koeckelberghs et al. reported the synthesis of a series of chiral 3, 6 substituted polythienothiophenes (PTTs) and the influence of the substituent on the chiroptical properties. 3, 6-dialkoxy substituted PTTs, 3, 6-dialkyl thio substituted PTTs and alternating copolymers of 3, 6-dialkoxythienothiophenes and 3, 6-dialkythieno thiophenes were used for the investigation, which are shown in Figure 1.24. It is found that the substituent appeared to play a decisive role in the polymer’s macromolecular structure and supramolecular organization. They also studied the chirooptical properties of
cyclopentadithiophene based conjugated polymers. They proved rigid and highly conjugated strands for the chiral substituted conjugated polymers containing the cyclopentadithiophene. Polycyclopentadithiophenes, polythienothiophene-alt-cyclopentadithiophenes and polythiophene-alt-cyclopenta dithiophenes were the systems studied. (Figure 1.24)

Figure 1.24: Chiral 3,6 substituted polythienothiophenes and conjugated polymers containing the cyclopentadithiophene

Tuuttila et al. developed chiral donor π-acceptor azo benzene dyes in which the chiral moieties namely (S)-(+)2-(6-methoxy-2-naphthyl) propionic acid (naproxen) and (S)-2-aminopropionic acid (L-alanine), were attached to either the donor end or the acceptor site of the azo compound using ester or amide bonds respectively. They reported that the developed chiral donor-acceptor azobenzene molecules are potential NLO materials because the donor-acceptor functionality of the azobenzene part supplemented with the chiral unit controlling the intermolecular interaction. Koeckelberghs reported the synthesis of a chiral 9,10-dialkoxy functionalized poly (3,6-phenanthrene) by using the Suzuki cross-coupling reaction. They demonstrated that 3,6-polyphenanthrene systems adopted a random coil in a good solvent and a helical conformation in a nonsolvent rather than stacking in a supramolecular way.

In past decades, the NLO polymers were reported to be of various shapes such as A-shape, X-shape, Y-shape, U-shape, otupolar, dentron etc. The H-shape and AB-type second order nonlinear optical (NLO) polymers were
prepared for the first time by Zhong'an et al. The linkage positions of chromophores in the H-shape polymers were shoulder-to-shoulder, in which the chromophore moieties were part of the polymeric backbone. The subtle structure could be easily modified by the introduction of different isolation groups, to adjust the property of the resultant polymers. All the polymers exhibited good film-forming ability, thermal stability, large SHG coefficients of $d_{33}$ values, and relatively good long-term temporal stability.

No et al. recently reported the synthesis and nonlinear optical properties of novel Y-type polyurethane containing tricyanovinyl thiazole with enhanced thermal stability and second harmonic generation. The Y-type polyurethane is shown in Figure 1.25.

Figure 1.25: Y-type polyurethane containing tricyanovinyl thiazole

Brasselet et al. developed two new classes of octupolar nonlinear optical chromophores, derived from 1, 3, 5-triazines and oligothienylic crystal violet analogues which have been synthesized and their nonlinear optical properties investigated using the harmonic light scattering experiment. The easy preparation of these molecules made them attractive candidates for optical applications. Off-resonant measurements show high nonlinearities together with an excellent transparency, which made these compounds of promising interest for the emerging schemes of nonlinear optical applications whereby the multipolar character of the chromophores is of particular importance.
1.14. spacer effects in second harmonic generation of polymers

The molecular second order NLO efficiency depends, on the strength of the donor and acceptor groups, on the extent of the \( \pi \)-conjugated path, on conjugating spacers based on aromatic systems and on the resonance stabilization energy of the aromatic system. Intensive studies regarding the NLO efficiencies of molecules containing \( \pi \)-conjugated spacers are seen in the literature\(^0\). Sreekumar et al. have studied the effect of alkyl spacers on the nonlinear optical properties. The polymer was designed as a condensation product of PNA derivatives with varying number of spacers and an azomesogen chromophore, azobenzene-4, 4'-dicarbonyl chloride. A series of polymers with varying number of CH\(_2\) groups from 1-7 in the polymer chain were designed (Figure 1.26).

From measurements of SHG efficiency of polymers, it is found that the systems have shown increase in SHG efficiency with respect to increase in the number of alkyl spacer groups rather than showing an odd-even oscillation\(^2\). Sreekumar et al. recently reported the synthesis of nonconjugated amidodiol based chiral polyurethanes and its nonlinear optical activity.\(^3\)-\(^9\)

1.15. conclusion

The chapter has overviewed the recent and important developments in the field of organic chromophores and chiral polymers with nonlinear optical properties. The review gives a survey of NLO active polymeric materials with a brief introduction which comprises of principles and the origin of nonlinear optics and the various kinds of polymeric materials for nonlinear optics, including guest-host systems, side chain polymers, main chain polymers, crosslinked polymers and chiral polymers etc. It discusses the influence of
donor-acceptor chromophores and the influence of chirality for designing second order nonlinear optical materials.

One of the challenges in this century being faced by scientists is the commercialization of nonlinear optical devices, which are gaining greater interest in the field of communication technology and data storage. The introduction of the devices, however, is hampered by the limitations in achieving certain material properties. The materials should meet the requirements such as excellent thermal stability, processability, ease of fabrication, excellent mechanical and physical properties, high optical nonlinearity and at the same time should be commercially viable. In this respect, polymeric materials, which have the combination of all these properties, become important. Poled polymeric materials are potential candidates for nonlinear optics. They show greater promise due to their controlled nonlinearity, tailoring properties, ease of processing and fabrication to devices, fast response times, excellent mechanical and physical properties, low cost etc. However, problems such as the relaxation of poled order, thermal instability at operating temperatures etc faced by polymers are serious impediments to their development. Present study in nonlinear optics is therefore mostly concerned with improving the performance of NLO polymers for better thermal stability, orientational stability and processability. In this chapter many approaches have been discussed to achieve a long-term temporal stability of NLO properties and electro optic effects.

1.16. Instrumentation used in this work

The UV-Visible spectra were recorded using Spectro UV-Visible Double beam UVD- 3500 instrument. FT-IR spectra of the powdered samples were recorded on JASCO 4100 FTIR spectrometer using KBr discs. The MALDI-MS analysis was carried out using Shimadzu Biotech Axima instrument. Optical rotations were measured using Atago AP100 automatic digital polarimeter. The fluorescence spectra were recorded using FluroMax-3 instrument. The refractive index measurements were carried out using ABBE Refractometer (ATAGO) using the wavelength of 589nm. NMR spectra were recorded using Bruker 300MHz instrument. The XRD analysis was carried out using Rigaku X-ray Photometer. The XRD pattern was taken 10°-90° angles with an increment of
0.05° angle and with the rotation speed 5 degree per minute. TG/DTA measurements were performed using Perkin Elmer Pyrex diamond 6 instrument. The weight of the sample was plotted against temperature to get a thermogram. The analysis was done under nitrogen atmosphere using a heating rate of 10°C /min from room temperature to 800°C using platinum crucible. The second harmonic generation test for polymers was performed by Kurtz and Perry powder technique using Nd: YAG laser (1064 nm). The conductivity measurements were carried out using Keithley 2400 sourcemeter by 2 probe method. FTIR measurements were done at SAIF CUSAT Cochin, MALDI-MS analysis at NIIST Trivandrum and the NMR analysis at SAIF, IIT Chennai, NRC, IISc Bangalore. NLO measurements were done at IPC, IISc Bangalore.

1.17. References

Chapter 1

Chapter 1

41 Scarpaci A, Blart E, Montembault V, Fontaine L, Rodriguez V, Odobel F, Appl Mater Interfaces, 2009, 1, 1799
Chapter 1


Chapter 1

Chapter 1

Chapter 1


Davis D, Ph. D thesis, Department of Applied Chemistry, Cochin University of science And Technology, 2005.
