Nonlinear Optical Organic Colorants


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Abstract

Non linear optics (NLO) is a dynamic research field vigorously investigated by numerous chemists, physicists and electrical engineers. Non linear optical processes in pi-electron organic and polymeric systems have attracted considerable interest because their understanding has led not only to compelling technological promise but also to new phenomenon, new theoretical insights, and new materials and devices. In this article along with **new developments** in this field, **organic colorants** which can be used in non linear optics are studied in relation to their **non linear optical properties** and **application** in various fields.

Keywords: Non linear optics (NLO), Organic colorants, Non linear optical properties, New developments, Application.

1. Introduction

Nonlinear optics is concerned with the interaction of electromagnetic radiation with various media to produce new radiations which is altered in phase, frequency, amplitude, etc; from the incident radiation. The rapid growth of laser technology coupled with telecommunications, industry's need for sophisticated optical switching devices required for data transmission in this computer age has prompted an enormous interest in non linear optical materials. Organic colorants are best understood as pi-electron organic molecules with conjugated donor and functional groups. Non linear optical processes in pi-electron organic and polymeric systems have attracted considerable interest because their understanding has led not only to compelling technological promise but also to new phenomenon, new theoretical insights, and new materials and devices. The pi-electron systems are invariably excited by electromagnetic reactions and this is so with organic colorants which invariably interact with the visible portions of the electromagnetic radiations. Such pi electron excitations occurring on the individual molecules or polymer chain, units are the basic origin of the observed non-resonant nonlinear optical coefficients which are often usually large. The coefficients are often broad band and ultra fast. The frequency dependence of these coefficients are determined by many body electron correlations effects. **New challenges** in non linear optics (NLO) materials are being presented, resulting in new methods of ultra structure synthesis and the discovery of entirely new materials and high performance compositions exhibiting high thermal, mechanical, and chemical stability. NLO materials are of widespread interest for opto-electronic applications such as electro-optic waveguiding, frequency modulation or optical information processing. We synthesize and study **organic dyes, oligomers and polymers** with NLO properties.

NLO properties are characterized by molecular hyperpolarizabilities, the second order terms of which can be measured by EFISH (electric field induced second harmonic generation) experiments. We use a recently developed setup which allows EFISH experiments on solutions of non-absorbing as well as of absorbing compounds. The molecular origin of optical nonlinearity is due to the electrical polarization of a molecule as it interacts with electromagnetic radiation. These interactions may change the frequency, phase, polarization or path of incident light. Dyes are predisposed for NLO applications because the mobile electrons that are responsible for the absorption of visible light also bring along the polarizability of the molecules, which is necessary for second harmonic generation (SHG). When it comes to practical applications of compounds with nonlinear optical properties, a major synthetic challenge is to construct noncentrosymmetric molecular systems with suitable processability. Amorphous polymers with covalently attached chromophores can meet this goal.[11,15]

2. Brief Background

The origin of second order non linear optical effects in organic molecules is traced to the presence of strong donor-acceptor interactions. In 1970, Davydov and his coworkers reported a strong

SHG in organic molecules having electron donor and acceptor groups connected with benzene ring. This discovery led to an entirely new and useful concept of molecular engineering to synthesize new organic materials for the SHG studies. From 1980 onwards tremendous growth occurred in design and development of organic materials for second order non linear optics.[12,13]

3. Nonlinear optics (NLO)

It is the branch of optics that describes the behavior of light in *nonlinear media*, that is, media in which the dielectric polarization 'P' responds nonlinearly to the electric field 'E' of the light. This nonlinearity is typically only observed at very high light intensities such as those provided by pulsed lasers. Nonlinear optics gives rise to a host of optical phenomena.[3]

3.1 Non linear optical effects and Applications[1]

Basic equation to govern optical effects in molecular systems is as;

$$P = \alpha E + \beta E2 + YE3 + \ldots$$

Where P is the polarization induced in a molecule of electric field E.
For macroscopic systems the equation changes to

$$P = x(1)E + x(2)E2 + x(3)E3 + \ldots$$

The first term represents the linear effects and is associated with the refractive index. It is the second and the higher terms which represent the non linear effects. The most important is the second order term βE2. The most important use of nonlinear optical materials would be to convert the infrared radiation to visible radiation by frequency doubling, thus enabling easier detection of the signals.

4. Dyes used in NLO

Organic dyes appropriate for the polymers include those having;

- at least one hydrosilation reactive carbon-carbon double bond
- absorption maxima between 300 and 2000 nm or, more particularly, between 300 and 700 nm and extinction coefficients, at the absorption maxima, greater than about 2x103 L/mol cm.

Two or more organic dyes can be used in combination. Preferred moieties for providing hydrosilation reactive carbon-carbon double bonds are pendant alkenyl chains particularly those where the carbon-carbon unsaturated bond is in the terminal position and strained endocyclic bicycloalkenyl groups, because these carbon-carbon double bonds are highly reactive for hydrosilation. Suitable such alkenyl chains are the vinyl, allyl, and 3-butenyl groups; appropriate strained endocyclic bicycloalkenyl moieties. 4,5 Particularly suitable dyes are those including;

- an electron donor group
- an electron acceptor group and
- a delocalized Pi electron system linking these two groups especially where the combination of these groups exhibits an NLO response.

The absorption band of an organic colorant can be tailored by

- either increasing the pi-conjugation length or
- by substituting donor-acceptor groups to a conjugated system

As a result the absorption characteristics of the UV-visible spectrum can be shifted and will have either bathochromic (red shift toward a longer wavelength or hysochromic shift (blue shift toward a shorter wavelength).[12]

4.1 Molecular Polarizibilty[1]

Molecules capable of high polarization (hyperpolarizability) i.e. high β values give the best nonlinear effects. In order for the effect to be realized practically, the molecules must align themselves correctly in the macroscopic state, i.e. in a noncentrosymmetric arrangement. (Ref. figure 1)

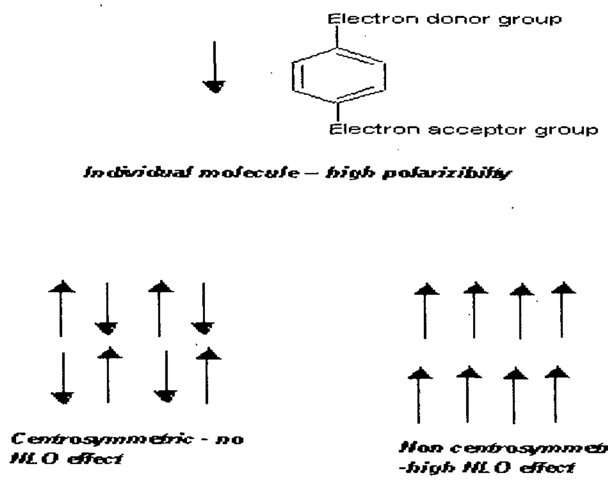


Figure 1. Important of molecular alignment on NLO effects

4.2 Molecular alignment

Although the molecules have high β values, they do not arrange themselves correctly in macroscopic state. Hence major challenge is to obtain media (polymers, crystals) in which these molecules are correctly aligned to express their high β values. 1 The organic structures offer tremendous possibilities of chemical modification and thus their nonlinear optical properties can be tailored. Thus a new science, nonlinear optics, for which functional organic dyes are the key elements, is in vogue. Organic molecular materials have become potential candidates for application in nonlinear optics. Important reasons for this;

- The high nonlinear response and optical damage resistance observed in some organic molecular materials.
- The prospect of chemical modifications to optimize the material properties,
- The possibility of theoretical prediction to guide seeking improved materials.13

4.3 Conjugated pi- systems[5,12] Benzene, azobenzene, stilbene, biphenyl, benzylidene, heterocycle or polyenes.

4.4 Electron Donor Groups[5,12] hydroxy, alkoxy, acyloxy, alkyl, amino, thioalkoxy and dithiolylidene groups; the halogen substituents —Cl, —Br, and—I are also suitable. Of these, the hydroxy, alkoxy, amino, thioalkoxy and dithiolylidene groups, and the indicated halogen substituents are preferred. More preferred are the amino groups, especially tertiary amino groups having two alkyl groups attached to the amine nitrogen.

4.5 Electron Acceptor Groups[5,12] sulfonyl, alkoxycarbonyl, alkoxysulfonyl, acyl, nitro, 2-nitrovinyl, cyano, 2-cyanovinyl, 2,2-dicyanovinyl, tricyanovinyl, and perfluoroalkyls including trifluoromethyl and trifluoromethylsulfonyl groups. Of these, nitro, dicyanovinyl, tricyanovinyl, sulfonyl, and perfluoroalkyl groups are preferred.

The above electron donor and acceptor groups tend to cause bathochromic shifts accompanied by interest in the intensity of absorption.

5. Particularly preferred dyes[5]

- the aryl and heteroaryl dyes
- the azo, bis(azo), tris(azo), tetra(azo) and penta(azo) dyes
- the stilbene, bis(stilbene), and tris(stilbene) dyes
- the azomethine and azostilbene dyes
- the quinone and anthraquinone dyes
- And the polymethine dyes generally referred to as neutrocyanine dyes, examples of which are the coumarins, the indophenols, the indoanilines, the phenazones, the phenothiazones, and the phenoxazones.
- Also isometric nitro anilines are studied simple organic molecules. Meta nitro aniline and para nitro aniline are closely similar but para nitro aniline crystallizing in centro symmetric structure while meta nitro aniline does has non zero second order susceptibility.[12]

5.1 Further included among the preferred dyes[5]

- the diphenoquinodimethane dyes
- the quinodimethane dyes
- the naphthoquinodimethanes
- the pyrenoquinodimethanes
- the polymethine dyes derived from the condensation of aromatic aldehydes with isophorone and malononitrile

5.2 Preferred aryl and heteroaryl dyes phenyl, biphenyl, naphthyl, anthracyl, and pyridinyl dyes, as well as the 2,3-dihydroperimidines, thiazoles, pyrazoles, benzthiazoles, isothiazoles, imidazoles, and pyrroles.

5.3 Useful nature of the dyes used[5] The organic dyes be preferably nonionic. Such dyes are advantageous, because they tend to be more soluble than ionic dyes in the cyclic polysiloxanes. Nonionic dyes also exhibit lower conductivities in polymeric matrices than ionic dyes, yet further, such nonionic dyes, or at least certain of these, are less susceptible to dielectric breakdown than ionic dyes. The dyes can have just one hydrosilation reactive carbon-carbon double bond. However, where the dyes have two or more such carbon-carbon double bonds, polymerization can be effected between such dyes and the cyclic polysiloxanes, without requiring the polyenes. Of such dyes having at least two hydrosilation reactive carbon-carbon double bonds, these bonds can be of differing hydrosilation reactivity. Moieties having carbon-carbon double bonds which are less reactive to hydrosilation include the methacrylate, cyclopentenyl, cyclohexenyl, and styryl group.

6. Examples[5]

Table 1 :- Preferred substituted phenyl azo and bis(azo), and stilbene dyes, and examples of dyes having carbon-carbon double bonds of different hydrosilation reactivity.

7. New developments in this field

7.1 Nonlinear optical elements are disclosed which comprise a polyimide which is solution and/or melt processible, and a poled NLO dye[4]

Here a number of modifications can be studied in non linear optical materials. The invention includes a variety of features as follows.
A nonlinear optical element comprising: a blend of

- a processible polyimide having a glass transition temperature Tg below its thermal decomposition point; and
- an NLO dye having a molecular hyperpolarizability of greater than about 10 electrostatic units

Wherein the NLO dye is aligned in conformance with an externally applied electric field and wherein said processible polyimide has a repeat unit selected from the group consisting of (Ref. Figure 2).

The nonlinear optical element NLO dye is selected from the group consisting of (Ref. figure 3)

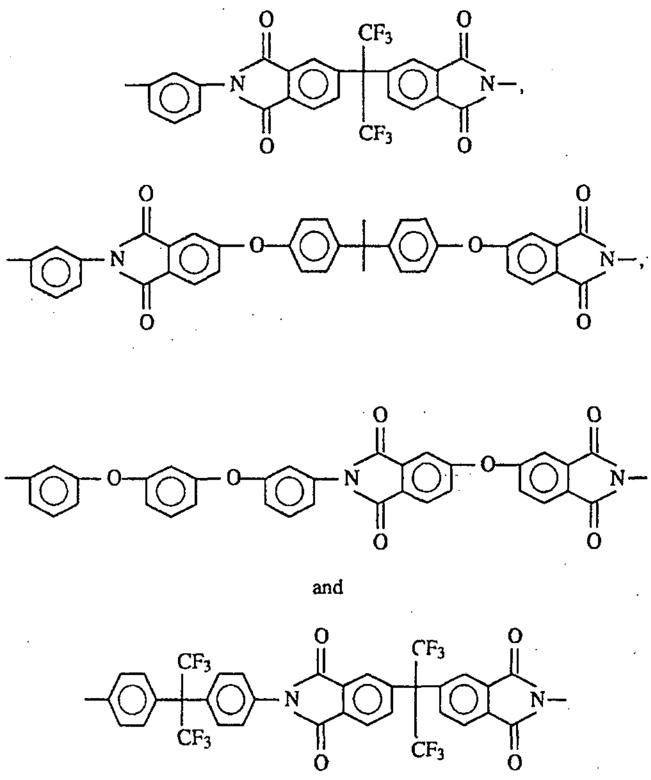
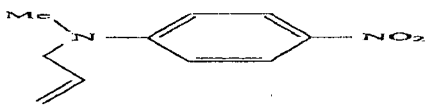
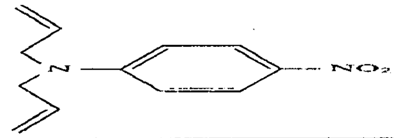
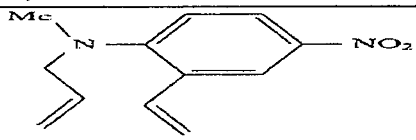
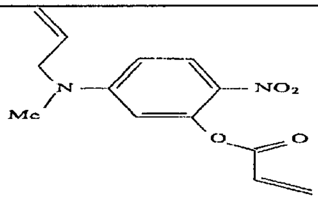
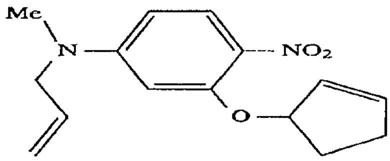
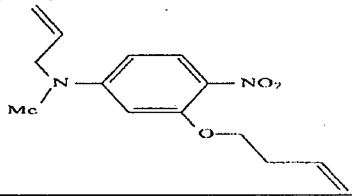
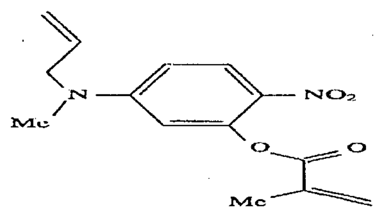
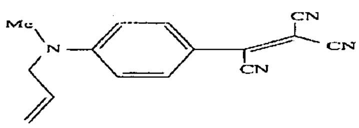
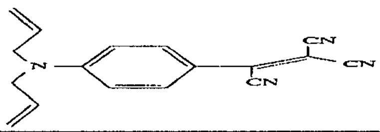
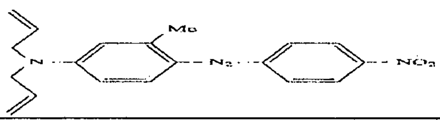
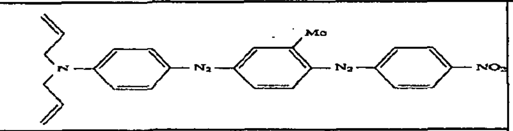
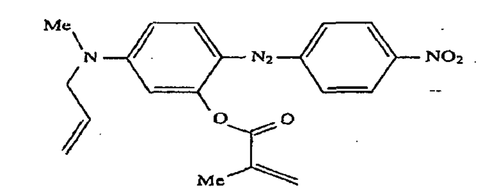
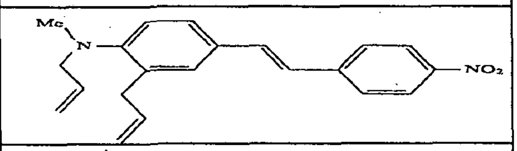
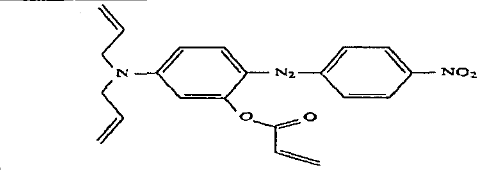
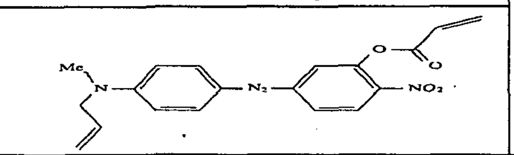
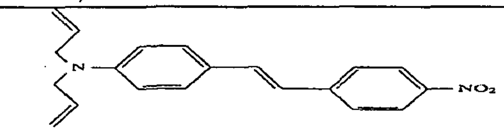
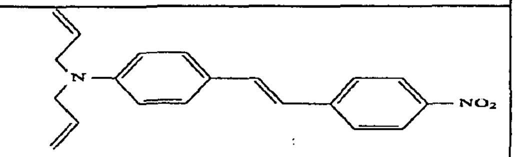
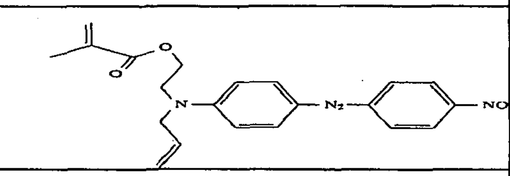
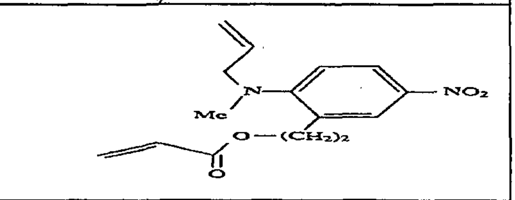
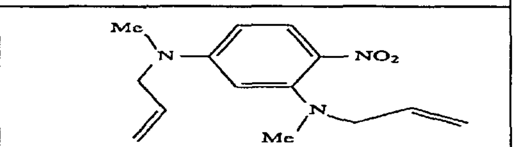


Figure 2:- Processible polyimide

Table 1 :- Preferred substituted phenyl azo and bis(azo), and stilbene dyes, and examples of dyes having carbon-carbon double bonds of different hydrosilation reactivity.

Dye name	Structure	Explanation
N-allyl-N-methyl-4- nitroaniline		The arrangement of various electron acceptor and donating groups (as stated earlier) have effect on the hyperpolarizabilities of the molecule. Powerful electron withdrawing group like nitro is conjugated with various electron donating groups. The para substituted isomer is more effective followed by ortho isomer and then by meta isomer. They have large β values. Also isometric nitro anilines are studied simple organic molecules. Meta nitro aniline and para nitro aniline are closely similar but para nitro aniline crystallizing in centro symmetric structure while meta nitro aniline does no and has non zero second order susceptibility.
N,N-diallyl-4- nitroaniline		
N-allyl-N-methly-2- vinyl-4- nitroaniline		
N-allyl-N-methyl-3- acryloyloxy- 4- nitroaniline		
N-methyl-N-allyl-3- (2- cyclopentenyloxy)-4- nitroaniline		
N-methyl-N-allyl-3-(3- butenyloxy)- 4- nitroaniline		
N-allyl-N-methyl-3- methacryloyloxy- 4- nitroaniline		
N-allyl-N-methyl-4- tricyanovinylaniline		Powerful electron withdrawing group like tricyanovinyl is conjugated with various electron donating groups . Mono azo and bisazo dyes having nitro group conjugated with various electron donor groups. Also we have tris (azo), tetra(azo) and penta (azo)
N,N-diallyl-4- tricyanovinylaniline		
NN-diallyl-4-(4- nitrophenylazo)- 3- methylaniline		

N,N-diallyl-4-[4-(4"- nitrophenylazo)-3-methylphenylazo]aniline		dyes in this class. Conjugated pi- systems like azobenzene , stilbene etc. have being used in this category.
N-methyl-N-allyl-4-(4- nitraphenylazo)-3- methacryloyloxyaniline		
N,2-diallyl-N-methyl-4-[2-(4-niaophenyl) ethenyllaniline		
N,N-diallyl-4-(4- nitrophenylazo)-3- acryloyloxyaniline		
N-methyl-N-allyl-4-(4- nitro-3-methacryloyloxyphenyl azo)aniline		
4-(N,N-diallylamino)- 4-nitrostilbene		The stilbene, bis(stilbene), and tris(stilbene) dyes with various electron donor and acceptor groups.
N-ally-N-(2- menthacryloyloxyethyl) 4-nitrobenzenamine		
N-allyl-N-(2- methacryloyloxyethyl) 4-(4-nitrophenylazo) benzenamine		Conjugated pi- systems like azobenzene ,benzene. Diamino benzenes having nitro or any other strong electron acceptor group. Different electron donor groups are also used here.
N-allyl-N-methyl-2-(2-acryloyloxyethyl)-4- nitrobenzenamine		
N,N-diallyl-N,N dimethyl-4-nitro- 3-benzenediamine		

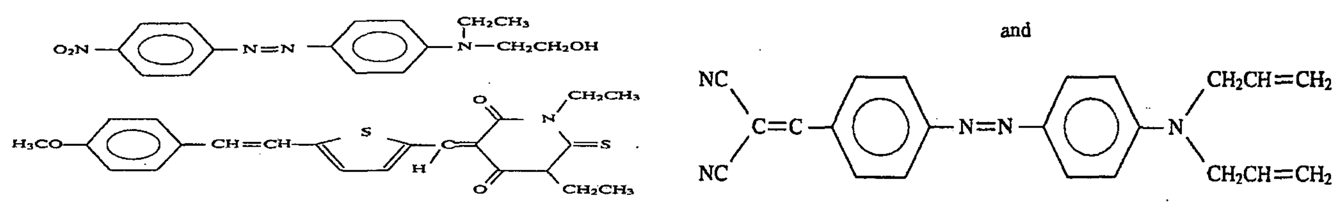


Figure 3:- Nonlinear optical element, NLO dye

The peculiar feature is nonlinear optical element in the form of a film. A nonlinear optical device capable of second harmonic generation which comprises a nonlinear optical element, a source of coherent radiation, and a means to direct the radiation emerging from the source into the nonlinear optical element, characterized by: the nonlinear optical element being a nonlinear optical element.

7.2 Langmuir–Blodgett film and second harmonic generation of a new type of amphiphilic non-linear optical bis-chromophore complex dye[12]

A bivalent zinc complex anion: bis(2-thione-1,3-dithiol-4,5-dimercapto)zinc, balances several non-linear optical (NLO) dye cations. The Langmuir film-forming properties of such complex dyes at the air/water interface, the stability and second-order non-linear optical properties of the monolayer and Langmuir–Blodgett multilayer films were studies and results showed that both the film-forming properties and NLO efficiencies were improved greatly when the zinc complex anion was incorporated into four types of NLO-active organic dyes.

7.3 Langmuir–Blodgett films of non-linear optical dyes with chiral centers in matrices of amylose esters[14]

The structure and second harmonic generation of a dye belonging to a new class of NLO dyes. The pure dye did not form a stable monolayer at the air-water interface. Hence the dye was mixed with amylose acetate which resulted in a stable monolayer when the amount of dye did not exceed the 50 base mol%. The mixture of the dye and amylose acetate consisted of domains. The domains of the dye are crystalline and can be considered as H-aggregates. The mixed monolayer can be transferred on to solid substrates. FT–IR and UV-vis spectroscopy were used to determine the molecular orientation in the multilayer. Second harmonic generation signals were detected in the reflection mode. The multilayer as deposited showed SHG signals when the primary beam is p-polarized resulting in an s-polarized SHG signal. When the monolayer was heated above the melt temperature of the dye and cooled down again, the signal was strongly enhanced and a p-polarized fundamental beam resulted in s and p polarized SHG

8. Polymers[15]

The polymers include organosilicon crosslinked polymers and crosslinkable prepolymers. Further, they include hydrosilation products cyclic polysiloxane, organic dye and optionally, polyene, they can include one or more of each of these components. If polyene is not present, the dye must have at least two hydrosilation reactive carbon-carbon double bonds; where polyene is included, and then dyes with only one such double bond are also appropriate. The polymers specifically include those having both one and more organic dyes, each with one or more hydrosilation reactive carbon- carbon double bonds and one or more of the polyenes.

9. Market Potential[1,11]

Nonlinear optical dyes (organic molecules having large nonlinear polarizabilities) have been recognized as potentially useful as components of the optical elements in optical frequency converters and in electro optic devices. Generally, in order for the NLO dyes to exhibit the large second order optical susceptibilities essential to nonlinear optic applications, the molecules must be constructively arrayed in a noncentrosymmetric configuration. Such molecules have been crystallized in a noncentrosymmetric space group, but this method does not work for all potentially useful molecules, and the resulting shape and properties are limited by the very nature of a crystal. The NLO dyes have been used, for example, in combination with glassy polymers to provide nonlinear optical elements. The choice of the dye molecule and glassy polymer affects the stability of nonlinear optical effect obtained, because the dye molecules have a tendency to "relax" over time, thereby losing the configuration necessary for the enhanced nonlinear optical properties. The electrical properties and chemical stability of a glassy polymer used in optical elements are important, since these characteristics are relevant to the efficient functioning of devices in which the nonlinear optical elements are generally employed. Thus, when choosing a host polymer for NLO dyes pertinent properties for consideration include

- low water absorption
- thermal and chemical stability
- dielectric constant
- Thermal coefficient of expansion.

Polyimides are often used in electronics applications since many of their properties makes them especially suited for such uses. Certain NLO dyes have great stability of nonlinear optical effect.

10. Applications [1,3,11]

- Components of the optical elements in optical frequency converters and in electro optic devices and Electronics.
- Nonlinear optical dyes (organic molecules having large nonlinear polarizabilities) have been recognized as potentially useful as components of the optical elements in optical frequency converters and in electro optic devices.
- They are used in photonic technologies which are analogous to the field of electronics.
- They can be hybridized for making devices and interconnects.
- They are used as high performance electro-optic polymer thin films in opto-electronic integrated circuit fabrication in existing microelectronic device manufacturing facilities.
- They are used in ophthalmic lenses, compact discs, and laser discs.
- Nonlinear effects used in telecommunication and optical data storage.

11. Conclusion

Nonlinear optics is a dynamic research field vigorously investigated by numerous chemists, physicists and electrical engineers. Non linear optical effects refer to the observations that interaction between light and certain materials not only depend linearly on electric field strength, but also on other parameters that can be described with second or third power functions. Organic materials that have been investigated for second order non linear optical effects can be summarized into several categories such as single crystals, Langmuir-

Blodgett (LB) films, polymers, guest (NLO dyes) - host (polymer matrix) systems, NLO –chromophore functionalized polymers , self- assembled systems, and liquid crystals. In recent years growth has been in the development of organometallic molecules and polymers for nonlinear optics in which role of metal to ligand bonding is used to optimize optical non linearity's.

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