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A Strategy for the Development of Macromolecular
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STRATEGY FOR THE DEVELOPMENT OF MACROMOLECULAR NONLINEAR OPTICAL MATERIALS

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ABSTRACT

Three convenient techniques to process second order organic nonlinear optical materials have been emphasized. Active moieties suffer from slow relaxation of the field-induced noncentrosymmetric alignment when processed with amorphous polymers or grafted to a flexible polymer backbone. Novel approaches to assemble the active molecules in preferred orientations in epoxy and phenol-formaldehyde resins are presented.

TEXT
MARGIN

I. INTRODUCTION

Theoretical and experimental investigations over the past two decades have characterized the organic compounds which exhibit strong asymmetric intramolecular charge transfer (ICT) through conjugated π -electron moieties under appropriate electromagnetic fields as the ideal materials for future optoelectronic applications¹⁻⁷. Major advantages of organic materials include large second order NLO coefficient, ultra fast response times, performance over a broad wavelength range and high laser damage threshold.

The origin of second order nonlinear optical (NLO) phenomenon in organic materials is significantly different from the conventional inorganic NLO materials. The extent of second order (quadratic) NLO effect such as second-harmonic generation (SHG) is determined by the coefficient $\chi^{(2)}$ which in turn depends on β , its molecular analog termed hyperpolarizability. Ease of ICT is a criterion of paramount importance for a large second order electro-optic effect in organic materials^{8,9}.

SAME

The most common approach to obtain high value of β is to incorporate moieties which promote ICT upon application of electric fields. This in turn is achieved by introducing strong electron donating groups such as NH_2 , NMe_2 , OH , etc. and electron withdrawing groups such as NO_2 , CN , CO_2H , etc. in a molecule possessing delocalized π -electron system such as benzene or polyene. This essentially results in asymmetric charge distribution and ICT in the excited electronic state. In addition, factors such as planarity and conjugation length also contribute towards increasing the molecular nonlinearity. In this context it is important to keep in mind that second order NLO effects can be observed only in a medium that lacks a center of inversion symmetry and by analogy, $\beta=0$ for a centrosymmetric molecule.

Organic NLO materials, despite having large second order parameters, require convenient fabrication techniques for potential applications, since bulk crystals of these materials are not easy to grow or to handle. In recent years, the processing of NLO molecules has been improved to a great extent either by mixing homogeneously with suitable amorphous polymers¹⁰⁻¹⁴ or by covalent attachment to polymers¹⁵⁻¹⁹. For a number of application this form of NLO materials is ideally suited.

The advantages of using amorphous polymers for NLO applications are their flexibility, controllable nonlinear index of refraction, high optical damage threshold, low optical loss in red and near-IR spectral regimes and significant compatibility with NLO molecules²⁰. Special features such as low-temperature operational capability, ease of microstructure fabrication and the availability of fabrication equipment for mass production are extremely useful for device applications.

TEXT
MARGIN

In the present work three different strategies are described towards better processing and improved organization of organic active molecules using polymeric materials. Relative advantages and deficiencies of the various systems are also described.

II. RESULTS AND DISCUSSION

Guest-Host System

Materials combining the advantages of organic NLO molecules and the superior processing characteristics of the amorphous polymers, known as guest-host system, have been reported¹⁰⁻¹⁴. Thin film materials of this combination can be obtained by casting (viz. spinning, dipping or other coating techniques) a solution of NLO molecule and amorphous polymer from a common solvent.

Amorphous polymers, in general, have a relatively open structure which allows NLO molecules to be retained in the matrix when cast as a thin film upto a certain concentration. Further, the active molecules are



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achieve higher densities, as high as 60 weight percent of nonlinear active groups and hence high nonlinear effects. A number of such systems composed of PMMA^{15,16}, PS¹⁷ and polysiloxane^{18,19} backbones have been reported recently. Covalently attached active molecules are orientationally ordered either by using corona poling technique in a similar manner as for the guest-host system (Figure 3) or by depositing mono or multilayered film by Langmuir-Blodgett(L-B) technique (Figure 4).

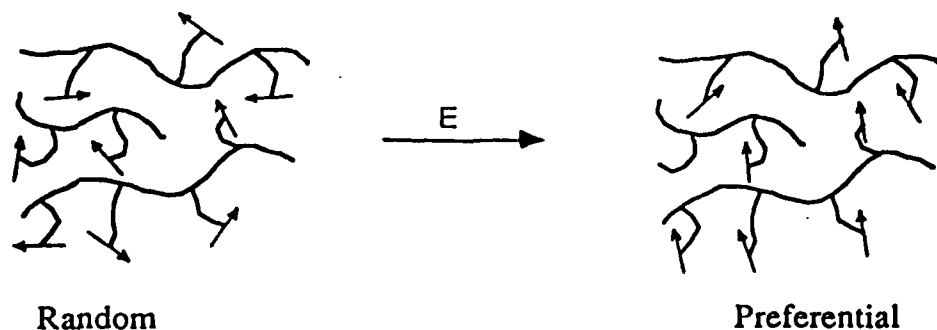


FIGURE 3. Alignment of active moieties in grafted system

L-B technique is capable of producing high quality, oriented films of organic materials by depositing the films one molecular layer at a time. The close control of layer thickness and molecular orientation achievable makes the technique particularly attractive for this application. The alignment of the chromophores can be achieved without the poling procedure which is essential for the guest-host system.

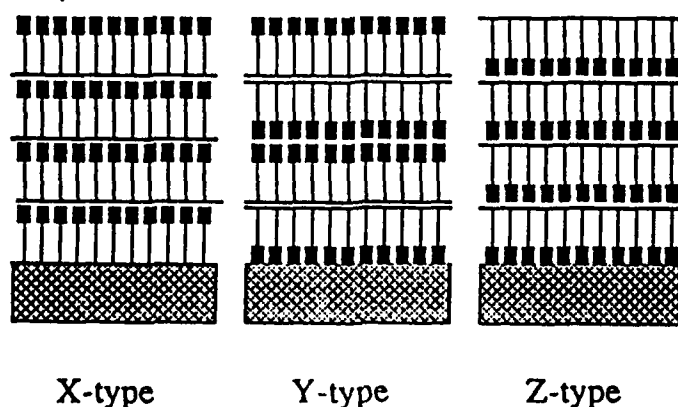


FIGURE 4. Various deposition modes of L-B multilayers

One of the difficulties associated with the use of organic chromophoric side groups relates to their deposition by L-B technique. Too close packing of the chromophores (steric crowding) results in a rigid film

A number of NLO molecules, for example, MNA(2-methyl-4-nitroaniline) and DR-1(disperse red-1) in PS or PMMA matrices have been studied extensively¹⁰⁻¹⁴. The results indicate that the second order parameters of the matrix are not consistent due to the relaxation of the guest and host molecules when the external poling field is off.

In our recent work molecular interactions between the guest and host molecules as a function of their molecular and electronic structure and molecular organization have been emphasized²³. It is understood that the mobility, polarity and the free volume of the polymer matrix, and the size, ground state dipole moment and the second order hyperpolarizability of the NLO molecules play an important role in designing novel guest-host systems.

A new copolymer host, namely, SAN(styrene acrylonitrile copolymer), was thus introduced for the first time to enhance the interaction between the guest and host molecules by controlling the distribution of available free volume resulting from different polar and nonpolar components. These investigations have established SAN (with 32-33 weight percent acrylonitrile content) as the best host material studied so far from the standpoint of high solubility of the active compound, strongest second-harmonic(SH) signal obtained for a number of active molecules and the short and long term stability of the poled guest-host system. Figure 2 describes the stability of MNA in different polymer matrices. It is anticipated that the nonlinear interactions may be further optimized by suitable control of the comonomer ratio and distribution in the copolymer. This also provides a convenient handle on the tailoring of the index of refraction of the complex.

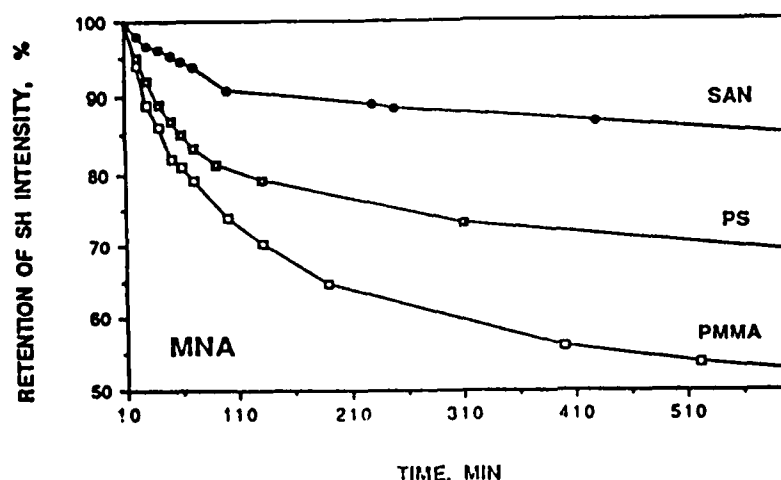


FIGURE 2. Retention of SH properties of various poled guest-host systems with time

Grafted System

In this approach relaxation of the active molecules is taken care of by fixing the nonlinear moieties covalently in the side chains of the polymer molecules. An advantage of using this system is that one can

homogeneously spread in an amorphous matrix. Therefore, the size and the solubility of the NLO molecules in the solid polymer solution are very important for obtaining a film with good optical quality. Unwanted crystallization and phase segregation of the NLO molecules lead to losses as a result of optical scattering from the resultant two phase film. What is desired is the largest possible concentration and optical orientation of the active molecules without introducing any optical losses in the material's transparent regime.

PMMA(polymethyl methacrylate) and PS(polystyrene) have been traditionally used as the host matrices due to their ease of processing and good linear optical properties. PMMA matrix is significantly polar compared to PS. Consequently, the compatibility of the polar active molecules is expected to be more in PMMA than in PS. On the other hand the relaxation subsequent to poling of the PS matrix is much better than PMMA because of structural rigidity. One severe disadvantage is that the PS matrix accommodates only low concentration of the active molecules. In fact, homogeneous thin film of PMMA can be obtained with the NLO molecules having concentration upto 30 weight percent.

As expected optically responsive molecules are randomly oriented in the polymer matrix although a small amount of residual anisotropy is sometimes seen as the asymmetric molecules are spin coated onto the substrate. Poling of such molecules is essential since the second order parameters are directly proportional to the orientational order of the optically responsive molecules in the matrix. Necessary polar alignment is induced by the application of external electric field in a method defined as poling^{21,22}. Effective poling requires the temperature of the matrix to be close to the glass transition temperature, T_g , as the electric field is applied and subsequent cooling down of the sample and freezing-in of the noncentrosymmetric order below T_g . Figure 1 describes the schematic representation of NLO molecules during the poling process.

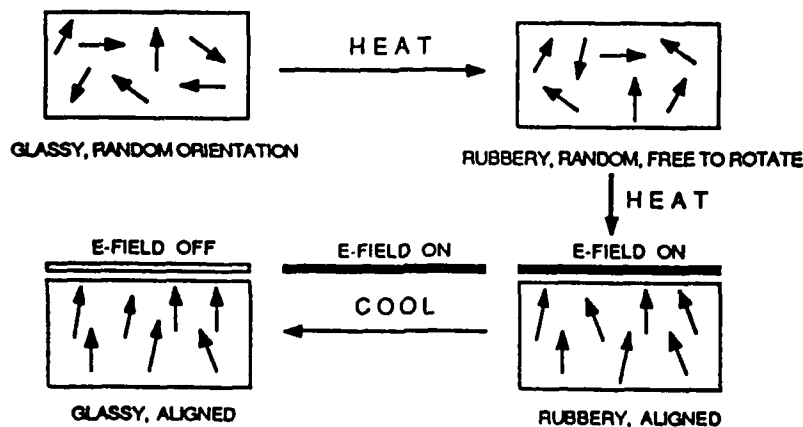
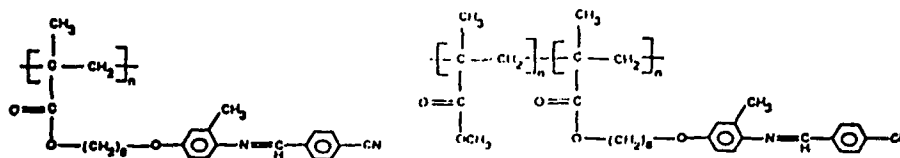


FIGURE 1. Alignment of active molecules in the polymer matrix during poling process

which is undesirable as a degree of flexibility is required to enable the film to survive the stress it suffers during deposition. For instance, polymer 1 shows an excellent isotherm (Figure 5) which is ideal for deposition of monolayer but, in practice, it is very difficult to fabricate multilayer structures²⁴.



Polymer 1

Polymer 2

In view of this difficulty a random copolymer is proposed (polymer 2) in order to improve L-B multilayer deposition and to exhibit nonlinear optical properties. In this molecule the structural rigidity or steric crowding between the chromophore and the backbone is eliminated by the flexible PMMA spacers. Octamethylene spacer unit in the side group may further enhance the nonlinear susceptibilities arising from the cooperative order of the side chains which are capable of showing liquid crystalline(LC) behavior independently²⁵. This spontaneous molecular orientation enhances the NLO susceptibilities five times or more²⁴⁻²⁸.

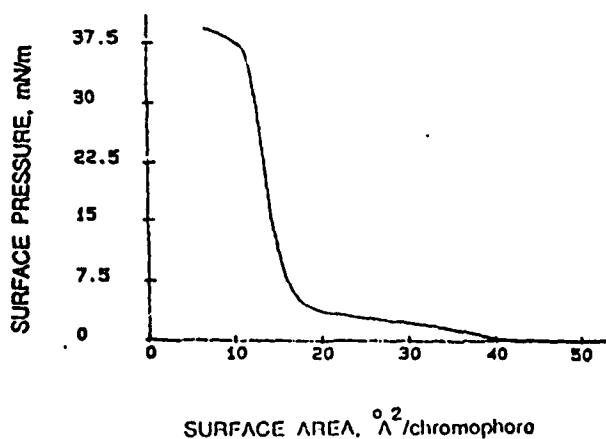


FIGURE 5. Isotherm of polymer 1; pH = 8.1, temperature 15.3°C

Taking advantage of the increased orientation imparted by corona poling or even better crystalline order by L-B technique and the hindered motion of the nonlinear optical moiety in the side chain of the polymer leads to substantial improvements in both the magnitude and stability of nonlinear optical susceptibilities compared to guest-host polymer systems ordered by poling.

Cross-Linked System

Grafted system, although significantly more stable than the guest-host systems, still suffers from slow relaxation of the field-induced noncentrosymmetric alignment and hence the nonlinearity. It was believed that a stable film could be obtained by processing the active molecules in a manner similar to the guest-host system with a curable polymer in which the active molecules are supposed to remain firmly embedded in the pores of the polymer network after curing. Our investigation using small and large active molecules and a curable epoxy polymer has established a number of shortcomings for this process. Shrinkage of the matrix even after curing at room temperature is the dominant problem in such a process.

It is, therefore, necessary to fix the active molecules in the polymer matrix in such a manner that the molecular movements are restricted in the curing stage. Such structures can be achieved by linking covalently with thermosetting resins which are known to possess excellent processability in the prepolymer stage. Unfortunately, after curing or cross-linking most thermosetting resins become translucent or opaque²⁹.

Epoxy and phenol-formaldehyde(PF) resins are the only curable polymers which are compatible with conventional processing techniques in the prepolymer stage and possess adequate optical transparency after curing. The chemistry and technology of epoxy³⁰ and PF³¹ resins are well established. Structural considerations play an important role in designing a suitable matrix since they differ chemically and hence in their curing approach.

Epoxy system is usually cured with a bi-functional primary amine which at lower temperature forms a linear processable polymer (commonly referred to as 'prepolymer') with a bi-functional epoxy monomer. Curing is done by heating the prepolymer to a higher temperature subsequent to processing. In this stage the secondary amino groups, formed during the prepolymer stage, react further with the epoxy end groups to generate a three-dimensional network.

Active molecules can be chemically functionalized to the epoxy polymer network by three different ways as proposed in Figure 7. Depending upon the linear and nonlinear optical requirements the right strategy can be adopted. In the first approach the active molecules themselves act as cross-linking agent which means that two NH_2 groups must be present opposite to the electron withdrawing group (e.g., NO_2) so that the net dipole moment is nonzero (Figure 7a). Recently, a fairly stable epoxy matrix in which the active molecules act as the curing agent (4-nitro-1,2-phenylenediamine) has been reported³². It is important to mention that the diamino active molecules having extended π -conjugated system through $-\text{N}=\text{N}-$ or $-\text{N}=\text{CH}-$ linkage are not sufficiently

reactive for cross-linking to occur. Hence, this class of active molecules having large second order nonlinear susceptibilities can not be used in this approach.

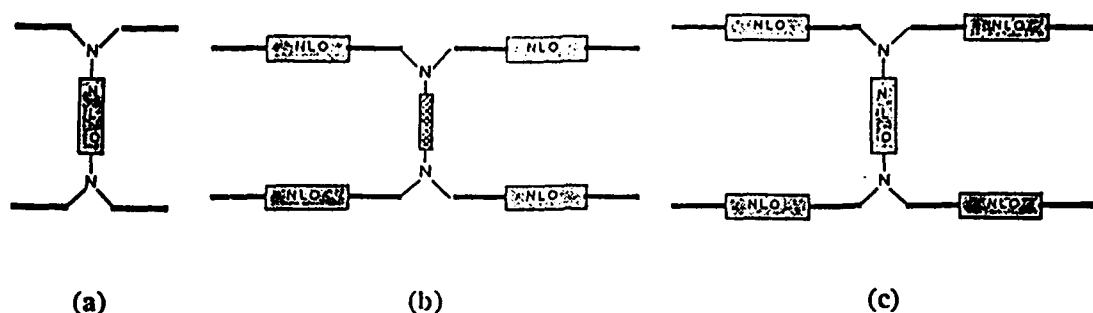


FIGURE 7. Functionalization of active molecules with an epoxy system

Alternative approach to obtain an epoxy matrix having efficient active molecules involves the incorporation of nonlinear moieties in the epoxy monomer itself. In this case an extended π -conjugated system substituted with strong donor (e.g., NH_2) and acceptor (e.g., NO_2) groups in appropriate positions can be used. In addition, two or more hydroxyl groups which do not contribute much towards net dipole moment may also be used to couple with epichlorohydrin (Figure 7b). Cross-linking may be done either by aliphatic diamine or by the active diamine used in the first approach. The latter has the advantage of optimizing nonlinear properties by using appropriate active molecules in the epoxy monomer as well as the curing molecule (Figure 7c).

PF resins are normally prepared by two different methods. One involves a base catalyst with an excess of formaldehyde over phenol. The initially formed product (called a 'resole') which contains several hydroxymethyl groups can be cured to a thermosetting polymer (called 'resite') simply by heating during which new ether linkages are formed. The other method utilizes an excess of phenol over formaldehyde in the presence of an acid catalyst. In this case, the initial product (called a 'novolac') requires the addition of more formaldehyde or, more commonly, the addition of paraformaldehyde or hexamethylene tetraamine (HMTA), to affect curing. Linear prepolymer having *ortho-ortho* linkages predominates (referred as *o,o'*-novolac) when the condensation is carried out in the presence of divalent metal catalysts, particularly zinc acetate in acetic acid³³.

Unlike the epoxy system active molecules are difficult to attach with the traditional cross-linking agents used to cure the PF prepolymers (resole

or novolac). Moreover, the reactivity of phenol decreases drastically as an electron withdrawing group such as NO₂ is introduced in to the phenyl ring. However, it may be possible to substitute the *para* positions of *o,o'*-novolac with nitro groups by electrophilic substitution (nitration) of the linear prepolymer. Cross-linking can thus occur through the unsubstituted *para* positions.

Apart from phenol itself, resorcinol is the most important phenolic compound used to modify phenolic resins. It is considerably more reactive than phenol and is used, therefore, to increase the rate of cure. Nitro group substituted resorcinol which is expected to form linear prepolymer can thus be used as a precursor for the nonlinear active molecule. Inter chain cross-linking through the phenolic hydroxyl groups using inorganic polybasic acids, such as phosphoric, boric, and phosphorous acids, which is known to improve the flame retardant properties of phenolic resins, can be used to cure linear PF prepolymers³⁴.

III. CONCLUSION

Investigations based on guest-host and grafted systems have established the need for a cross-linked system to prevent the initial decay in second order parameters subsequent to field-induced alignment. An introduction to obtain a stable matrix based on epoxy and phenol-formaldehyde resins is presented.

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