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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 31MAY93	3. REPORT TYPE AND DATES COVERED technical: 01JUN92 to 31MAY93	
4. TITLE AND SUBTITLE Functionalized Polymeric Materials for Electronics and Optics			5. FUNDING NUMBERS C: N00014-90-J-1148 R&T Code: 4132016	
6. AUTHOR(S) S. Sengupta, J. Kumar, A. Jain and S. Tripathy			8. PERFORMING ORGANIZATION REPORT NUMBER 1148-93-13	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Massachusetts Lowell Department of Chemistry 1 University Avenue Lowell, MA 01854			10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research-Chemistry Division Code 1113 Department of the Navy Arlington, Virginia 22217-5000			16. SPONSORING / MONITORING AGENCY REPORT NUMBER	
<p><b>DTIC</b> <b>SELECTED</b> <b>JUN 15 1993</b></p>				
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Reproduction in whole or in part is permitted for any purpose of the United States Government. This document has been approved for public release and sale; its distribution is unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 Words) Polymeric materials are being developed to possess unique electronic and optical properties. A number of polymeric nonlinear optical polymers and electrically conducting polymers have been reported that also present significant processing and cost advantages. Design of new polymer materials for electronic and photonic applications rely on incorporation of molecular level functionalities into the polymer structure. These and other functionalities significantly impact the processing and fabrication characteristics of the thin film devices as well. Design, characterization and thin film fabrication aspects of candidate polymers are discussed.				
14. SUBJECT TERMS nonlinear optical polymer, electrically conducting polymers			15. NUMBER OF PAGES 26	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	

OFFICE OF NAVAL RESEARCH

GRANT N00014-90-J-1148

R&T Code 4132016

Technical Report No. 93-13

Functionalized Polymeric Materials for  
Electronics and Optics

by

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in

Chemistry of Advanced Materials (C.N.R. Rao, Ed.)  
Blackwell Scientific Publications, London (1992)

University of Massachusetts Lowell  
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Lowell, Massachusetts

May 31, 1993

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# 12 Functionalized Polymeric Materials for Electronics and Optics

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**Abstract** Polymeric materials are being developed to possess unique electronic and optical properties. A number of polymeric nonlinear optical polymers and electrically conducting polymers have been reported that also present significant processing and cost advantages. Design of new polymeric materials for electronic and photonic applications rely on incorporation of molecular level functionalities into the polymer structure. These and other functionalities significantly impact the processing and fabrication characteristics of the thin film devices as well. Design, characterization and thin film fabrication aspects of candidate polymers are discussed.

## 1 Introduction

The largest application of synthetic polymers has been in the replacement of structural materials such as wood, steel and aluminum, textile fibers like the natural polymers wool, cotton and silk and the natural elastomer rubber. Polymeric materials have played a steadily expanding role in the past five decades due to their relatively low cost, easy processability and wide range of performance capabilities. Starting with the development of nylons by Carothers, engineering plastics have found application where high performance is desired. The use of the term polymeric in the modern sense dates from its use by Carothers [1] in 1929.

More recently, there is increasing emphasis on engineered plastics or polymers where appropriate design features are incorporated at the molecular or morphological level to produce desired functionality. The role of polymers as the active component in electronic and optical devices is an area of research that has seen tremendous expansion during the past decade. The search for new electronic and optical materials has led to the development of new classes of polymers with emphasis on their rich molecular architecture and overall molecular organization.

Techniques that are relevant to molecular level manipulation are Langmuir-Blodgett (LB) film growth, spin coated large area films and polymeric thin film single crystals grown by confined solution growth techniques. In the LB films molecular systems are manipulated at thicknesses of molecular dimensions. Both polymeric and monomeric systems may be handled in this manner [2]. The monolayers may be designed to possess desired molecular architectures and functions and may be stacked into complex multilayered systems. The multilayer arrangement method was pioneered by Kathryn Blodgett [3] and may be used to introduce different functionality to different layers.

Polymerization in these mono- or multilayer systems leads to rugged multifunctional films and have been proposed as approaches to the development of intelligent polymeric systems. Biopolymers and other biological macromolecules may be

an integral part of these materials that can be designed to mimic the complex functions and attributes of living organisms. Numerous electronic, optical and molecular electronic devices have been proposed based on these structures.

Films with defined properties up to a few microns thick may be prepared simply by spin coating technique for many electronic and optical applications. This is ideally suited for glassy polymers where appropriate functional groups have been added to elicit the desired optical properties. For waveguide devices film thickness of the order of the light wavelength ( $\sim 1 \mu\text{m}$ ) is desirable and spin coating leads to such thickness in a one step process. The spun-on films are isotropic and have to be further processed if properties originating from ordering of the functional units are desired.

Large area thin film single crystals of polymeric systems have been recently developed. In addition to the higher degree of molecular order achieved in these crystalline systems, complex lattice structures may also be realized by appropriate molecular design. This technique of polymer crystal growth is most readily applicable to polydiacetylenes. Some of the largest nonresonant optical nonlinearities have been reported from these polymers [4]. Approaches such as electropolymerization may also be employed for growing films of functional polymers. Other techniques include thin film deposition of monomers and oligomers and subsequent polymerization. Molecular self-assembly, chemisorption, and chemical vapor deposition are some other approaches towards growth of polymeric thin films for electronics and optics application.

Several electroactive polymers have been prepared using these methods. These approaches focus on incorporating complex functionalities in macromolecular thin film systems directed towards novel devices. The trend towards miniaturization in electronics and optics has sparked the interest in the ultimate limit of molecular level function and organization.

In this chapter approaches to molecular design and thin film growth will be explored in the context of novel applications and properties. Polymeric materials as they are processed using these techniques will be discussed. Some of their properties will be investigated for application in electronic and optical devices. This chapter will touch upon some of the relevant issues of molecular design but will not provide an exhaustive review.

## **2 Nonlinear optical polymers**

### **2.1 General background**

The large scale application of optical techniques to communication, signal processing, and data storage and processing technologies has been both driven by and created a need for high performance optical devices such as lasers, electro-optical modulators, image processors, optical memories and harmonic generators. Most solid state optical devices are currently based on inorganic dielectric and semiconductor materials. While there is considerable development in materials technology there is still significant room for improvement. The promise of optical computing can be realized in practical form only by further developments in

optical device and materials technology. Growth of single crystals and subsequent processing and fabrication continues to be a difficult problem. Polymeric materials can be designed to have enhanced optical coefficients, better processability and fabricability and significant cost advantage. In many of the traditional optical applications polymers have already found extensive use. The use of polyacrylates and polycarbonates in plastic lenses and fibers is now widespread. The optical clarity achieved in some of these glassy polymers is excellent and wide variation in the index of refraction is possible.

The versatility of polymer technology is seen in its application to soft contact lenses, where good optical quality and permeability to water and oxygen has been achieved in the same material. Similarly, it is believed that the application of polymeric materials in active optical devices will be most advantageous. Active electronic and optical devices are beginning to be fabricated using polymeric materials [5]. In principle one could have complete opto-electronic systems based on polymeric materials technology. For device applications, the polymeric materials should possess excellent linear optical properties such as transparency at the desired wavelengths and appropriate index of refraction. In addition, for active optical devices appropriate nonlinear optical properties are desired.

There is distortion of the charge cloud in a nonlinear (NLO) medium under the application of an electric field. For weak electric fields, the applied electric vector  $\mathbf{E}$ , induces a polarization  $\mathbf{P}$  in the material, which is linearly dependent on the electric field.  $\mathbf{P}_{\text{linear}} = \chi^{(1)}\mathbf{E}$ , where  $\chi^{(1)}$  is the susceptibility tensor. The net polarization in the medium under the influence of several fields is a linear superposition of the effects of the same fields acting independently. The fields can interact with each other through the higher order terms in the polarization vector  $\mathbf{P}$ , which, can now be expanded as [6]

$$\mathbf{P} = \chi^{(1)}\mathbf{E} + \chi^{(2)}\mathbf{E}*\mathbf{E} + \chi^{(3)}\mathbf{E}*\mathbf{E}*\mathbf{E} + \dots \quad (1)$$

The nonlinear susceptibilities  $\chi^{(2)}$ ,  $\chi^{(3)}$ , . . . , of the medium represent the magnitudes of the higher order interactions with the applied fields. These properties are dictated by features at the molecular level; including electronic and molecular structure and the nature of the overall molecular packing. The optical device architecture is dictated by the magnitude and the nature of these NLO coefficients.

## 2.2 Second-order NLO polymers

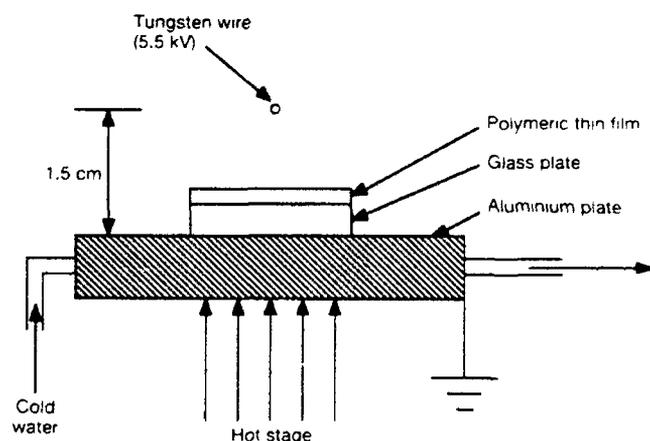
The design of NLO moieties and NLO polymers has been approached from both theoretical and experimental vantage points. The general view that has emerged is that both a large charge separation (and hence a large dipole moment) and a large molecular polarizability is required. This can be accomplished best by coupling strong donor and acceptor groups through a conjugated electron system like an aromatic ring. The resultant systems exhibit strong intramolecular charge-transfer transitions, so that transparency and high NLO coefficients need to be carefully traded off against each other [7,8].



For applications such as second harmonic generation (SHG) the choice of NLO chromophore is dictated by transparency at the fundamental and second harmonic frequencies. Molecular polarizabilities can be measured in solution by electric field induced second harmonic generation (EFISH) [7,9–11], and solvatochromic [12] techniques. For second-order nonlinearity, acentricity is required at the molecular and macroscopic levels. In molecular crystals, acentricity is determined by the crystal structure, which is difficult to control, since in most highly polar molecules, a centrosymmetric packing is usually energetically more favorable. However, a number of molecular crystals with noncentrosymmetric structures leading to large optical nonlinearity have been identified. The problems of crystal growth and processability remain the major stumbling blocks to be overcome for these systems.

In polymer systems, acentricity is readily achieved by alignment of the NLO moieties in an electric field (electric field poling). In addition, polymers possess excellent mechanical properties and processability. Thus, the fabrication of devices from fragile molecular crystals can be replaced by planar integrated optics technology using large area NLO polymer films cast or spun-on from solution or processed from a melt. Polymer properties are readily modified by making changes in the structure such as, altering the molecular weight distribution or appropriate chemical modification.

Electric field poling for the creation of macroscopic acentricity in NLO polymer systems was introduced by Meredith *et al.* [13]. Singer and coworkers extended this work [14–16] and at present it is a standard procedure used to process second-order NLO polymers. A very useful variant of the parallel electrode poling technique is corona poling (Fig. 12.1) [17].



**Fig. 12.1** Experimental set-up for corona poling.

This has the advantage that electrodes do not have to be deposited on the polymer film and breakdown under large electric fields may be avoided. Also very high fields (of the order of MV/cm) over a large surface area are readily obtained. A corona discharge is a partial ionization of air, usually at atmospheric pressure. During the corona poling process, charges deposit on the polymeric film when the applied voltage is higher than the corona discharge voltage. These charges give rise to a large local field given by:  $E = \sigma/\epsilon$ . The local electric field is dependent on  $\sigma$  (surface charge density) and  $\epsilon$  (dielectric constant). The value of field obtained by corona poling is usually much larger than that from parallel plate poling. For unpoled polymeric thin films, the NLO active molecules are randomly placed in the polymeric matrix, although a small amount of residual anisotropy is sometimes seen as the asymmetric molecules are spin coated on the substrate. Noncentrosymmetric order in the thin films is introduced by the alignment of the NLO molecules. The second-order NLO properties are proportional to the orientational order of the optically responsive molecules in the matrix.

In general, poling is carried out at temperatures close to the glass transition temperature,  $T_g$ , in order to allow sufficient molecular motion. The simplest polymeric system as a second-order NLO material consists of two components: an NLO chromophore (referred to as guest) dispersed in a glassy polymer matrix (referred to as host). The advantages of such a system are obvious. A wide variety of NLO molecules can be used, since acentric crystal growth is no longer a requirement. The polymer host imparts excellent processability and ease of fabrication. However, limited solubility of the guest in the host matrix leads to dilution of the NLO effect. The concentration of the guest molecule is limited by phase segregation at higher concentrations. This phase segregation at high concentrations leads to large scattering losses. Another difficulty encountered in the two component system is the thermal relaxation of the ordering of the NLO molecules. While this problem is common to all poled polymer systems, it is particularly acute for guest-host media. Higher stabilities can be obtained by using high  $T_g$  matrices. For example, a polyimide-dye system (Pyralin 2611D-Eriochrome Black T) has been described with a  $T_g$  of 320°C, where optical nonlinearity was found to be stable at 150°C [18]. Higher NLO dye concentration may be achieved without the associated phase segregation problem by designing compatible dye-host systems.

The problems associated with the two component systems may be alleviated by direct covalent attachment of the NLO dye to the polymer host. The NLO moiety may be attached either to the side chain or incorporated into the main chain itself. In either case, much higher loadings of the NLO units are possible, since they are chemically attached to the polymer. Side chain NLO polymers may be easily prepared by designing a suitable NLO moiety containing monomer. Alternately, NLO units may be derivatized to the side chains of an existing polymer. For example a copolymer of methylmethacrylate (MMA) and 4-[4-(methacryloxy)octyloxy-2-methylphenyliminomethyl] cyanobenzene has been synthesized [19]. In general, grafted systems are considerably more stable than guest-host systems. In Fig. 12.2 the relaxation behavior of second harmonic intensity which is a measure of the order in the system is plotted versus time.



thermally cross-linked to yield fairly large NLO coefficients and excellent temporal stability [22,23]. Cross-links between the polymer chains restrict the molecular motion of the segments and hence prevent the randomization of the ordered NLO molecules. This approach was reported by Eich *et al.* [22] in an epoxy system in which the NLO moieties are incorporated either in the multifunctional epoxy or amine components or in both. A low molecular weight prepolymer is made to impart adequate flexibility to the NLO components. Long term poling and thermally induced cross-linking are performed simultaneously in order to obtain a three-dimensional NLO polymer network. The problem of slow relaxation which is an inherent property of NLO-dye doped and NLO-dye functionalized side chain polymers [16,17,24–27], is eliminated. A high degree of loading of NLO molecules is also possible without the problem of phase segregation. In addition the cross-linked system is expected to possess enhanced thermal stability due to its network structure.

A group at the University of Lowell has adopted solid state photochemistry as a vehicle to obtain cross-linked three-dimensional networks containing NLO units. The principle is based on the 2 + 2 photodimerization reaction between the photoreactive carbon-carbon double bonds which are substituted in both the NLO-dye and the polymer. In this section some of the physical characteristics of the photocrosslinkable systems derived from a cinnamate functionalized NLO-dye and the photoreactive polymers polyvinylcinnamate (PVCN) and polyvinylstyrylacrylate (PVSA) are discussed.

The structures of one of the NLO-dye and some of the polymers are shown in Fig. 12.4. The azo dye, 3-cinnamoyloxy-4-[4-(*N,N*-diethylamino)-2-cinnamoyloxy phenylazo] nitrobenzene (CNNB-R), has the appropriate design features including the photocrosslinking groups [28]. Solutions of the polymer and the dye in an appropriate solvents are spin coated over substrates such as glass, quartz and indium-tin-oxide (ITO) coated glass at speeds depending on the desired film thickness. The samples are then baked in a vacuum oven to remove excess solvents. These films can be poled by corona poling technique to impart the second-order NLO properties [17]. Lamps with the spectral peak at 254 and 366 nm can be used as the source of UV radiation in order to cross-link the PVCN and PVSA matrices respectively. The exposure time for desired cross-linking may be established from the UV-Vis spectra of the doped polymer films.

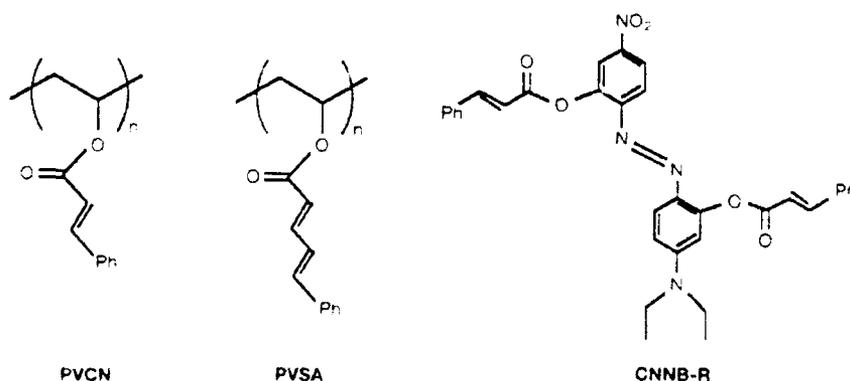


Fig. 12.4 Photocrosslinkable polymers and NLO-dye.

NLO molecules were also incorporated in the main chain while photocrosslinkable chromophores were covalently attached as pendent side groups. This system allows high concentration of NLO moieties. The synthesis of this type of photocrosslinkable polymers may be done in two steps: synthesis of functionalized NLO prepolymer and the chemical attachment of photoreactive groups. The prepolymers may be prepared by reacting an epoxy and an NLO chromophore consisting of an amine group. Epoxy compounds shown in Fig. 12.5, with the nonlinear species (1) have been used to prepare the polymer. Appropriate photoreactive groups are then attached to the prepolymer (2). Two photoreactive groups, cinnamoyl and styrylacryloyl, differing in reactivities have been used to investigate the photocrosslinking behavior (the nonlinear species is indicated by the dotted line). The synthetic route for obtaining the photocrosslinkable polymers (3, 4) is schematically shown in Fig. 12.5. The mechanism of cross-linking via the photocrosslinkable group is schematically shown in Fig. 12.6.

The most significant advantage of these systems is the photoprocessability. The poling and cross-linking processes are separated. Cross-linking is dose dependent and can be achieved in minutes. The level of cross-linking can be controlled easily by controlling the radiation dose. An index change of 0.02 or more between the cross-linked and uncrosslinked regions can be easily achieved. Therefore, writing of channel structures and phase gratings is possible by selective photo-irradiation.

The alignment of NLO moieties can also be achieved without the poling procedure using the LB technique. The LB method is a convenient technique for

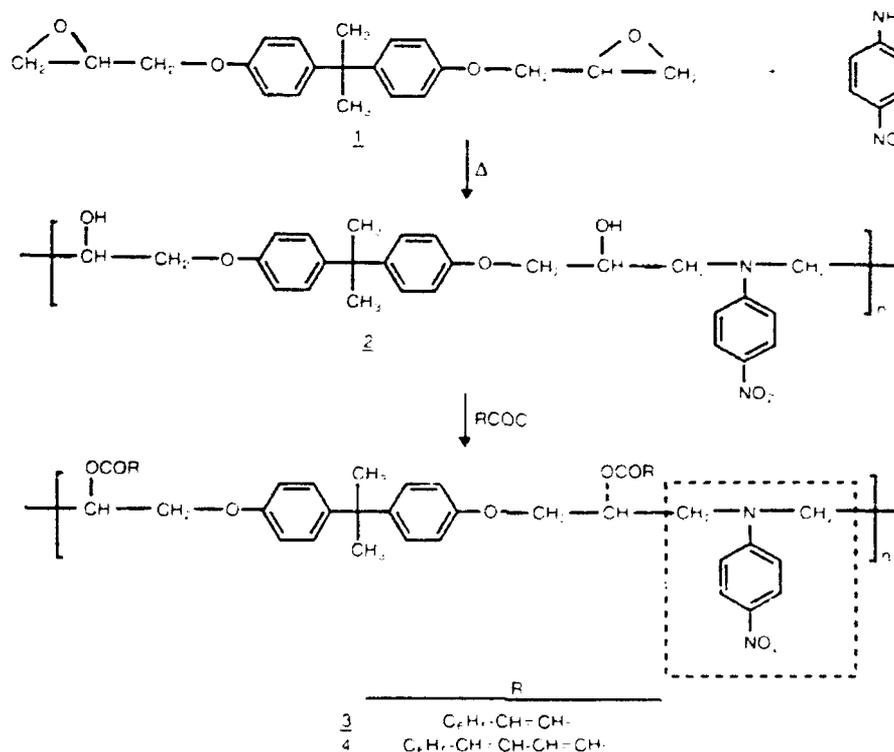


Fig. 12.5 Synthesis of photocrosslinkable main-chain NLO polymers.

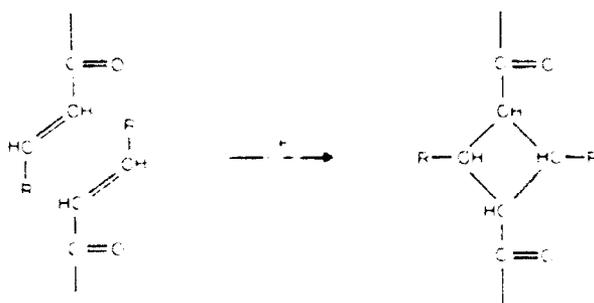


Fig. 12.6 Mechanism of photocrosslinking.

producing very thin films that can be controlled to molecular dimensions. The close control of layer thickness and molecular orientation makes this technique particularly attractive for organization of NLO moieties. Molecules that are most suitable for LB manipulation are linear molecules with a hydrophilic head group and a hydrophobic tail [2]. These type of molecules are spread at the air-water interface of an LB trough and a monolayer is formed as the surfactive head groups associate with the water subphase, while the hydrophobic tails stand away from the water surface. The molecules may be aligned and organized in a compact monolayer by compressing the molecules, using moving barriers. The monolayer thus formed is inherently noncentrosymmetric. Multilayers may be prepared from the monolayer by successive transfer to an appropriate substrate. This may be achieved in a number of different ways. Horizontal transfer with a hydrophobic substrate or vertical transfer, where head-to-head and tail-to-tail transfer is avoided, will lead to noncentrosymmetric multilayer films. In a typical vertical transfer process a single monolayer is deposited in both downstroke and upstroke and head-to-head alignment of the amphiphiles occur. This type of multilayer though thermodynamically most stable, leads to the cancellation of polarizabilities and hyperpolarizabilities for each bilayer.

These multilayer LB films usually have centrosymmetric alignment of molecules on the macroscopic level. Much effort has been invested to organize the material in a noncentrosymmetric film architecture [29–32]. *X*, *Y* and *Z* type multilayers are schematically shown in Fig. 12.7. If the surfactive molecules contained an NLO

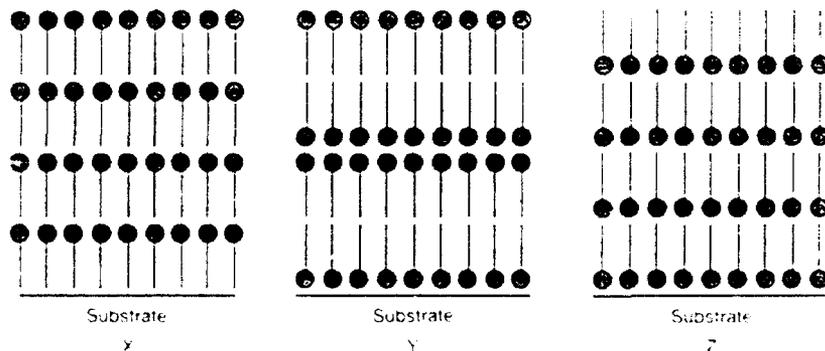


Fig. 12.7 Langmuir-Blodgett multilayers.

unit, with a large molecular hyperpolarizability, a large nonlinear response is expected from both *X* and *Z* type multilayers. As mentioned earlier, in the LB film fabrication process, distinct yet complimentary functionality may be introduced in the separate monomolecular layers forming the multilayer. A *Y* type structure may be designed with interleaving monolayers with NLO units only in one of the monolayers. This generates a thermodynamically stable structure with a bulk second-order NLO response.

In order to fabricate LB films which are thermally and mechanically stable over long periods of time, it may be preferable to employ polymers rather than low molecular weight organic molecules. LB films prepared from polymers are expected to be stable and transfer onto a substrate without serious disruption in the oriented structure. The polymers synthesized for this purpose should possess amphiphilic groups. Polymers with hydrophobic backbone structure and polar NLO moieties in the side groups have been synthesized.  $-\text{CN}$  and  $-\text{NO}_2$  groups attached to the NLO moieties are sufficiently polar to render them hydrophilic. There have been a number of research reports on nonlinear optical polymer LB films [33–36].

Recently, polymers in which the NLO moieties separated by flexible methylene spacer are covalently attached in the side chain of polymethacrylate (PMA) backbone [19] have been fabricated into monolayer films. Aromatic Schiff bases substituted with appropriate donor and acceptor groups were chosen because of their large ground state dipole moment and large molecular hyperpolarizability [37,38]. Alternatively, NLO chromophore functionalized surfactive monolayers may also contain a polymerizable group. An NLO monomer monolayer may be assembled and subsequently polymerized in the solid state to form a rugged film. Diacetylene functionalized NLO surfactive monomers have been synthesized and NLO polymer monolayers have been formed from these structures [39].

This approach to monolayer formation and preparation of heterostructure assemblies need not necessarily use the LB technique. Functionalized molecules may be self-assembled, where thermodynamically stable organizations with desired symmetry are realized. Molecules may then be 'stitched' together and overlaid to form superlattices that are NLO active. Recently for example, Li and coworkers [40] have reported a self-assembled superlattice structure consisting of alternate layers of an NLO chromophore and a silicone spacer with an additional transverse polyvinyl alcohol layer for structural stability.

The NLO chromophore (Ch), 4-[*N,N'*-bis(3-hydroxypropyl)amino]styryl-4'-pyridine, was used and resulted in one of the largest multilayer NLO responses reported. Figure 12.8 is a schematic of that arrangement where Cp is the coupling agent (shown in Fig. 12.9), Ch is the chromophore and *X*'s and *Y*'s are methylene spacer units. The first step in generating these structures involves binding of the coupling agent to the free hydroxyl groups on the glass substrate to form a siloxane layer. The chromophore is then reacted with the bound methylene iodide groups. The free hydroxyl groups in the chromophore layer are in turn reacted with a silylating agent such as  $\text{Cl}_3\text{SiOSiCl}_2\text{OSiCl}_3$  to form a second siloxane layer. A polyvinylalcohol layer is now added for structural stability. Additional layers of coupling agent, chromophore, siloxane are added in the same sequence to form multilayers. These multilayer films adhere strongly to the glass substrate, show

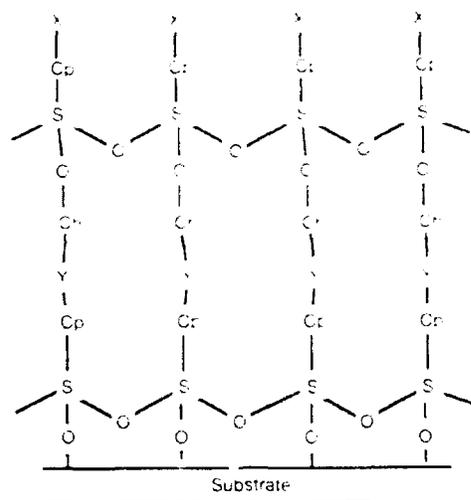


Fig. 12.8 Self-assembled multilayer with NLO properties.

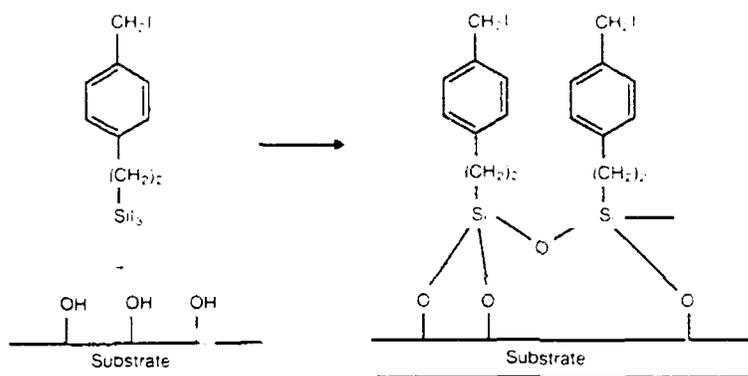


Fig. 12.9 Binding of coupling agent to substrate surface.

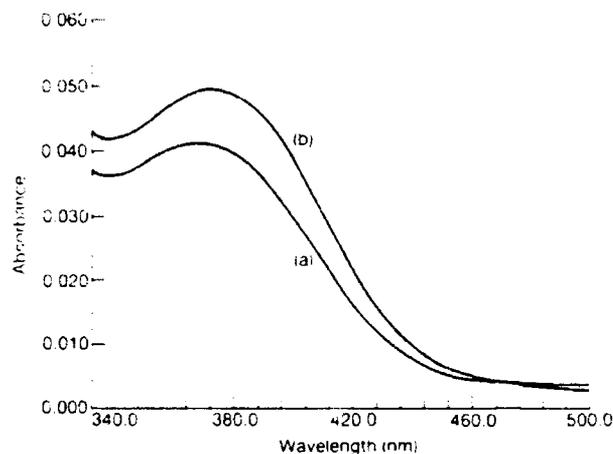
excellent chemical resistance and a high degree of order as evidenced by the NLO properties.

### 2.3 Investigation of linear and second-order NLO properties

Linear and NLO properties of these polymeric systems are investigated for two purposes. Linear optical properties such as absorption and refractive index are crucial parameters for device design. Second, these properties are used as diagnostics to identify whether the desired molecular structures and organizations were realized in the macroscopic medium.

#### 2.3.1 UV-VIS NEAR IR SPECTROSCOPY

Since many of the proposed NLO devices using these polymeric materials are expected to function in the 0.4–1.5  $\mu\text{m}$  spectral range, it is important to investigate the UV-Vis near IR absorption characteristics of the polymers. For example, a



**Fig. 12.10** Polarized UV-visible spectra of 11 layers of a side chain NLO polymer where the backbone is polymethylacrylate (a) *p*-polarization, (b) *s*-polarization.

polymer to be used for SHG must be transparent for both the fundamental and the second harmonic frequencies. A desired application is frequency doubling of diode laser sources, operating in the blue-green region of the spectrum. Due to intramolecular charge transfer NLO moieties have their characteristic electronic absorption in the near UV or visible spectral regime. Orientation of these NLO groups may be established by obtaining polarized absorption spectra with the incident electric vectors oscillating parallel and perpendicular to the substrate.

Polarized UV-visible spectrometry is an effective tool to examine the molecular orientation in LB films [41–43]. Figure 12.10 shows the polarized UV-visible spectra at 45° incidence from a multilayer of a side chain NLO polymer. The absorption of the *p*-polarized spectrum is weak in comparison with the *s*-polarized spectrum. This result indicates that the NLO moieties are oriented at a shallow angle to the substrate.

The orientation of NLO moieties in the LB film were evaluated using a dipole model. Taking the ratio between the absorbances due to the *s*- and *p*-polarized lights, the molecular tilt angle was calculated. For 11 and 5 layers of this polymer, the value of  $\theta$ , the molecular tilt angle was estimated to be 60°. Methylene units are expected to orient away from the substrate surface due to their hydrophobic character. Molecular orientation in this type of a monolayer is schematically illustrated in Fig. 12.11.

Orientation of the NLO unit in the poled and unpoled state may also be determined by measuring the relative absorbance of the films at the absorption peak of the NLO chromophore. Figure 12.12 is a UV-Vis spectrum of polyvinyl cinnamate film doped with 10% of the cross-linkable NLO azo dye CNNB-R.

The spectrum for the poled polymer film indicates a significant decrease in absorption at the characteristic absorption wavelength with respect to the unpoled film. Stability of the poled polymer films may be monitored by measuring the absorption spectrum over a period of time. As the aligned chromophores relax the reduced absorption at the characteristic wavelength creeps back to the original value obtained for the unpoled sample. On the other hand, if the poled film were

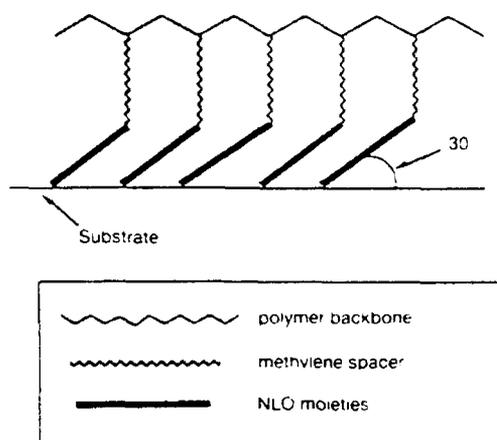


Fig. 12.11 Molecular orientation in a polymeric LB monolayer.

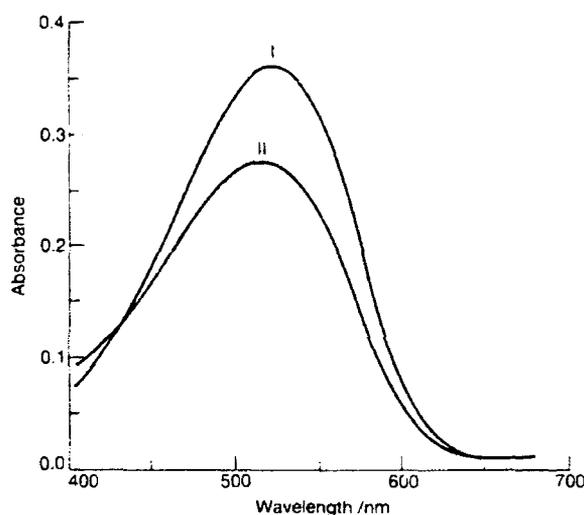


Fig. 12.12 UV-Vis spectra of PVCN film doped with 10% CNNB-R. I = unpoled and uncrosslinked; II = poled and cross-linked.

photocrosslinked subsequent to poling the absorption spectrum remains constant in time.

The order parameter obtained from anisotropic absorption in poled films is defined by  $f = 1 - A_p/A_0$ , where  $A_p$  and  $A_0$  are the absorbances of the poled and unpoled film respectively. This order parameter is a measure of the degree of poling of the NLO chromophore and can be used to compute second-order NLO susceptibility  $\chi^{(2)}$  [17].

### 2.3.2 WAVEGUIDE MEASUREMENTS

Thin film waveguides of NLO polymers may be fabricated on glass, fused quartz, and other suitable substrates by spin coating from a polymer solution. Planar and channel waveguide structure have been fabricated using these spun-on films. Approaches such as prism and grating coupling techniques have been used to

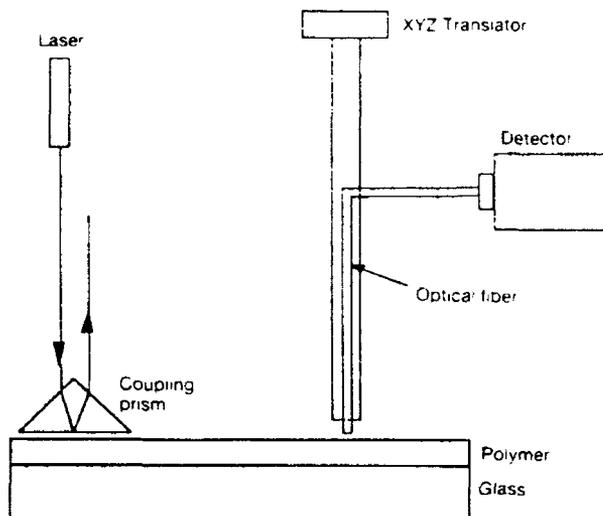


Fig. 12.13 Waveguide loss measurement system.

couple laser beams into the waveguide structures. Propagation and coupling into the various waveguide modes provide information about the thickness, index of refraction and optical losses in the polymer waveguide [44].

In order to measure waveguide loss, light scattering out of the waveguide from a propagating mode can be collected by a fiber bundle. The fiber bundle facing the waveguide plane is held by a xyz translator as shown in Fig. 12.13. The other end of the fiber bundle goes into a detector. The fiber is scanned along the streak formed by the guided beam and light collected by the fiber is detected as a function of its position. As the fiber is moved along the waveguide streak, the collected intensity is proportional to the light intensity in the guide at that point. The waveguide loss can thus be determined as a measure of difference in intensity along the waveguide streak [38]. The index of refraction and thickness may be measured by this technique as well. Ellipsometric techniques may also be used to determine the index of refraction in these polymeric films.

### 2.3.3 SECOND HARMONIC GENERATION

The NLO coefficients  $d_{ij}$  of the polymeric optical materials can be obtained by SHG measurements. The standard calculations of the  $d_{ij}$  coefficients follow Jerphagnon and Kurtz's method [45]. For uniaxial polymeric films, SHG power is given by

$$P_{2\omega} = \frac{512\pi^3}{A} t_{\omega}^4 T_{2\omega} d^2 P_{\omega}^2 R(\theta) \left[ \frac{\sin^2 \varphi(\theta)}{(n_{\omega}^2 - n_{2\omega}^2)} \right] \quad (2)$$

where  $A$  is the area of the laser beam spot.  $P_{\omega}$  is the incident laser power.  $t_{\omega}$  and  $T_{2\omega}$  are the Fresnel-like transmission factors [46].  $n_{\omega}$  and  $n_{2\omega}$  are the refractive indices at the indicated frequencies.  $R(\theta)$  is the multiple reflection correction, and  $\varphi(\theta)$  is the angular dependence of the second harmonic power resulting from interference between free and bound waves.

A widely used technique for the measurement of the second-order nonlinear susceptibility is one that compares the SHG intensity of the unknown sample with that of a reference material with known  $d$  coefficients, like crystalline quartz (Y cut) whose  $d_{11}$  coefficient is accurately known. Second harmonic intensity of the polymeric films relative to the reference material (quartz), neglecting multiple reflections [45, 46] is:

$$\frac{P_{2\omega}^s}{P_{2\omega}^q} = \frac{d_s^2(t_{\omega}^s)(T_{2\omega})_s R_s(0)(n_{\omega}^2 - n_{2\omega}^2)_s^2 \sin^2 \phi_s p_s^2}{d_q^2(t_{\omega}^q)(T_{2\omega})_q R_q(0)(n_{\omega}^2 - n_{2\omega}^2)_q^2 \sin^2 \phi_q p_q^2} \quad (3)$$

where  $d_s$  and  $d_q$  are second harmonic coefficients of the polymeric film and quartz respectively and  $p_s$  are projection factors. Kleinman [47] symmetry (i.e.  $d_{31} = d_{15}$ ) is used here, and for small values of the poling field  $d_{33}/d_{31}$  is assumed to be 3. The rate of relaxation of orientational order and hence, second-order nonlinearity can thus be conveniently monitored by following the temporal decay of the intensity of the second harmonic.

#### 2.3.4 ELECTRO-OPTIC PROPERTIES

The electro-optic coefficient is an important parameter for the design of the electro-optic modulators and several measurement techniques have been developed [48–51]. An interferometric technique is employed to measure any changes in the refractive index when a modulating electric field is applied across the film. These techniques are relevant for both linear and quadratic (Kerr) electro-optic effects. In the case of linear electro-optic effect the modulated intensity of the light beam is at frequency  $\omega$ , where  $\omega$  is the frequency of the modulating electric field. In the case of quadratic electro-optic effect the modulated intensity from the interferometer is at  $2\omega$ . In Fig. 12.14 the experimental arrangement of the Michelson interferometric technique is shown schematically. The interferometer with phase-sensitive detection is used to measure the EO coefficient of the polymeric thin films [52]. For this

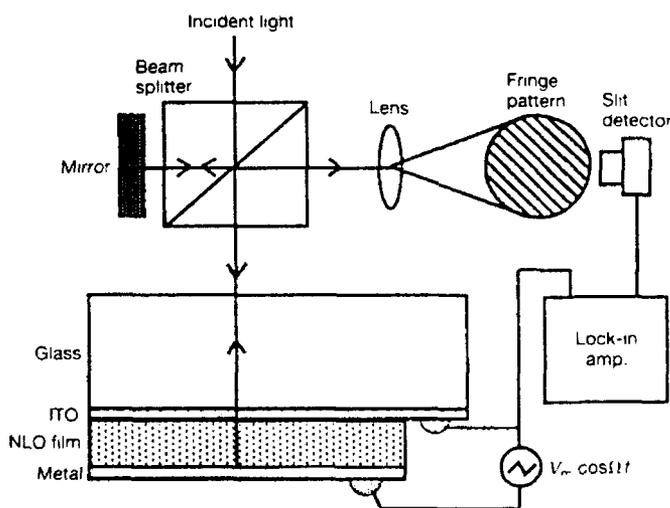


Fig. 12.14 Michelson interferometer.

configuration, sample preparation is simple and effects of air current, vibrations and temperature fluctuations are much smaller than those for a Mach-Zender interferometer.

In the sample arm, a laser beam propagates through an ITO-coated glass substrate, a thin NLO polymer film, and is then reflected back by a metal electrode. The linear EO coefficient is measured using the phase shift introduced by the modulating voltage.

#### 2.4 Third-order NLO polymers

Polymeric materials with large second-order nonlinearity may also possess large third-order nonlinearities, regardless of packing symmetries in the bulk material. Thus NLO guest-host systems with large dye concentrations have been shown to possess large third-order nonlinearities. However, the largest third-order nonlinearities have been observed in polymers with extensive  $\pi$ -conjugation along the polymer backbone. Large third-order optical nonlinearities have been demonstrated in conjugated polymers including polyacetylene, polythiophene and polyphenylene vinylenes [53-56]. These conjugated polymers may be oxidized to form conducting polymers as well, a topic that will be discussed in a later section.

The third-order NLO properties of polydiacetylenes are best defined among the conjugated polymer systems currently under investigation. Polydiacetylenes may be grown as discussed earlier in the form of Langmuir monolayers and subsequently polymerized to form a polymer monolayer. Multilayers may be formed by repeated deposition of the monomer monolayer and subsequent polymerization in the film. Alternatively, polymerized monolayers may be transferred using the dipping techniques discussed earlier. Third-order NLO susceptibility  $\chi^{(3)}$  as large as  $10^{-9}$  esu has been reported for these multilayer films. The response time of this electronic nonlinearity has been determined to be faster than tens of femtoseconds in the transparent regime.

Polydiacetylenes form a unique class of polymers as polymerization is carried out in the solid state [57]. The lattice-controlled polymerization in the single crystal monomer leads to a single crystal polymer. The monomer single crystals are usually transparent but take on an intense color upon polymerization. The third-order nonlinear response also increases by several orders of magnitude as a conjugated backbone is formed [58].

Third-order nonlinearity in NLO dye incorporated systems is of considerable interest. This interest stems from the excellent processability of glassy polymer based guest-host systems. It is relatively easy to fabricate planar or channel waveguide structures in spun-on films of these materials. There is in addition a tremendous flexibility in the design of the nonlinear molecular systems. In fact dye molecules may be approximately tailored to be compatible with the host polymer. However, most guest-host systems suffer from the usual problem of phase segregation at large concentrations of the NLO dye. As discussed earlier, NLO dyes may be attached as side chains to polymers to eliminate the phase segregation problem and obtain a high degree of loading.

## 2.5 Investigation of third-order NLO polymers

There are a number of techniques that may be employed to measure the third-order NLO coefficients in a polymeric thin film system. These techniques include third harmonic generation, four wave mixing, EFISH, Kerr measurements, and electroreflectance and absorbance measurements. Time resolved nonlinear spectroscopy and pump probe experiments may be used to measure the response time of the nonlinearity.

### 2.5.1 THIRD HARMONIC GENERATION

Conceptually, the simplest experiment to carry out to measure third-order susceptibility is third harmonic generation. While SHG is limited to noncentrosymmetric systems, any medium can give rise to a third harmonic signal. Therefore in addition to the polymeric sample of interest, any intervening medium, such as air, or supporting substrate will contribute to the third harmonic signal. In spite of these problems, experimental techniques allow unambiguous determination of  $\chi^{(3)}$  from these measurements [56,58].

An experimental arrangement very similar to the one used for measuring SHG coefficients may be used to study the generation of third harmonics. Some of the early experiments on third harmonic generation from conjugated polymers were carried out by Sauteret *et al.* [58]. Comparison of results from single crystals of diacetylene monomer and polydiacetylene indicated more than a couple of orders of magnitude enhancement in the nonlinear response. This is a result of polymerization leading to a conjugated backbone which is responsible for the large nonlinearity. In the polymer single crystal  $\chi^{(3)}$  along the polymer chain direction was found to dominate the other  $\chi^{(3)}$  components by two orders of magnitude. Third harmonic generation from a number of conjugated polymers such as polyacetylene, polyphenylene vinylene and polythiophene have also been carried out.

### 2.5.2 KERR EFFECT MEASUREMENT

Application of large electric fields can result in a significant perturbation of the electron cloud in a polymeric material in a nonlinear fashion. This is manifested in a change in the index of refraction and can be written as  $\Delta n = n_2 E^2$ . The constant  $n_2$  is directly related to the effective third-order NLO susceptibility of the material. Such index change resulting from third-order nonlinearity is proportional to the square of the applied electric field.

Kerr measurements under large electric and optical fields have been carried out in several polymers in the film form in different configurations. Optical Kerr measurements in polydiacetylene LB multilayers were carried out by Carter *et al.* [39]. The variation of refractive index with incident intensity in the polydiacetylene multilayers fabricated on silver coated gratings on a silicon wafer were measured. Coupling angle is a sensitive measure of the index of refraction of the polymeric overlayer. Change in the index of refraction is measured as a function of the incident laser intensity by measuring the shift in the grating coupling angle.

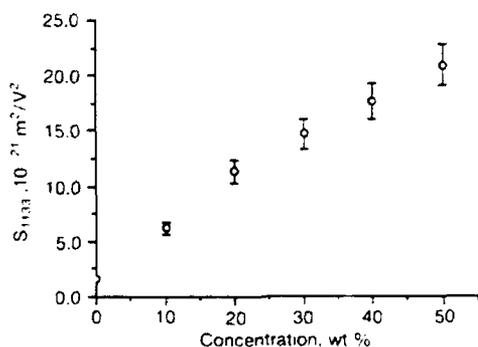
Electric field induced changes in the index of refraction may be measured using interferometric techniques in a manner analogous to the measurement of linear electro-optic coefficient. The nonlinear optical polymer confined between two transparent electrodes is inserted in one arm of a Mach-Zender interferometer. Phase shift introduced by the change in the index of refraction as a result of the applied field is recorded and is a measure of the change in the index of refraction. In the case of quadratic electro-optic effect the modulated intensity is at a frequency  $2\omega$ , where  $\omega$  is the frequency of the modulating electric field.

A number of dye doped guest-host systems have been investigated for their third-order properties in this manner. Kuzyk *et al.* [50] have reported on a guest-host system with PMA as the host and an azo dye as the nonlinear guest, using the Mach-Zender configuration. Similar experiments have been carried out with side chain polymers with azomethine pendant groups by Kumar *et al.* [59]. More recently, CNNB-R-doped PVCN system has been investigated for its third-order properties in the unpoled isotropic phase by Li *et al.* [60]. The experimental arrangement in this case is similar to the set-up for the investigation of the linear electro-optic effect shown in Fig. 12.14. For this measurement, the polymer film was spin-coated on an ITO-coated glass plate where the ITO layer was used as an electrode. A gold layer was thermally evaporated onto the polymer film to form the second electrode. An a.c. modulating field (about 5 kHz) was applied across the polymer film. A detector was employed to measure the modulations at two half-intensity points of a selected interference fringe at  $2\omega$ , noted as  $I_{2\omega+}$  and  $I_{2\omega-}$ . The quadratic electro-optic coefficient,  $S_{1133}$ , as a measure of the third-order optical nonlinearity is then given by:

$$S_{1133} = (1/\pi n^3) [(I_{2\omega+} - I_{2\omega-}) / (I_{\max} - I_{\min})] (\lambda d / V_m^2) \quad (4)$$

where  $n$  is the refractive index,  $\lambda$  is the laser wavelength,  $d$  is the thickness of the film,  $V_m$  is the modulating voltage, and  $I_{\max}$  and  $I_{\min}$  are the maximum and minimum intensities of the selected fringe, respectively.

The measured quadratic electro-optic coefficient as a function of dye concentration is shown in Fig. 12.15. The quadratic electro-optic coefficient exhibits an approximately linear relationship with the dye concentration. This indicates that there is no dye aggregation in the polymer film at concentrations as high as 50%.



**Fig. 12.15** Quadratic electro-optic coefficient as a function of NLO dye concentration in the polymer.

The quadratic electro-optic coefficients in this system are large compared with those reported by Kumar *et al.* [59] based on azomethine dyes and those reported recently by Kuzyk *et al.* [50] at the same dye concentration.

Degenerate four wave mixing experiments have been carried out on dye incorporated as well as conjugated polymer system [4]. These measurements may be interpreted as diffraction of a probe beam from an index grating created by interfering two write beams. The index grating is brought about through the intensity dependent refractive index of the polymer. The diffraction efficiency of the grating provides a measure of the third-order nonlinearity.

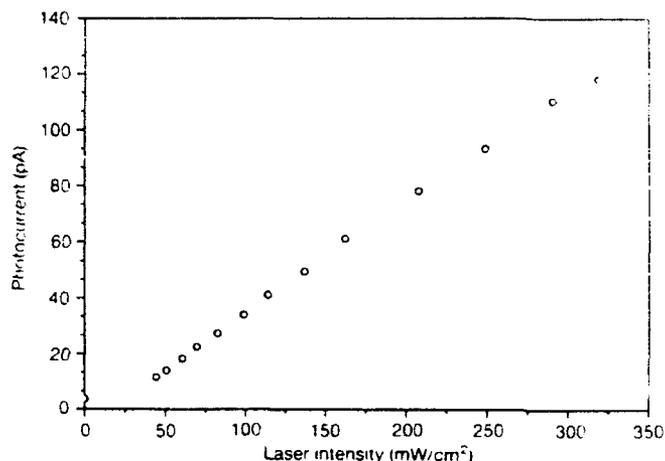
### 2.5.3 PHOTOREFRACTIVE EFFECTS IN POLYMERS

A photorefractive material is one in which an incident light pattern induces a corresponding index pattern. For example, if two coherent beams are interfered in a photorefractive material a sinusoidal index pattern results. This occurs because the light pattern induces a space charge field  $f_{SC}$  in the material by photogeneration of charge carriers from the bright areas which subsequently diffuse or drift into the dark areas where they tend to get trapped. The space charge field leads to an index change via the linear electro-optic effect and is given by  $\Delta n = 1/2n^3rf_{SC}$ . Unlike the Kerr effect where index changes are brought about through the third-order nonlinearity, the photorefractive effect is mediated by linear electro-optic effect. Optical energy is absorbed in the process and using very low laser power it is possible to produce large refractive index modulations [61].

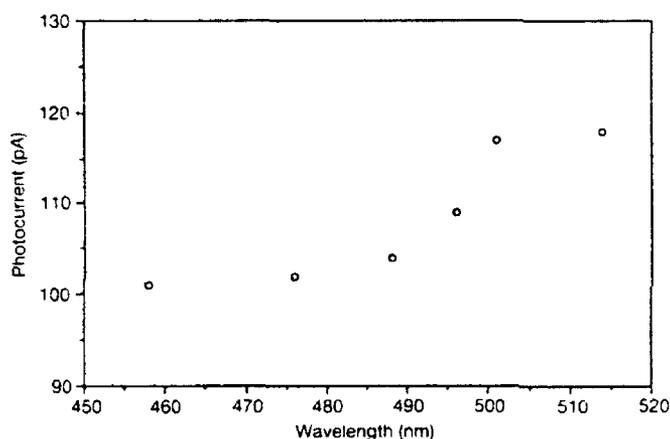
Until recently many of the potentially useful phenomena of NLOs such as optical phase conjugation and real time holography have been demonstrated with inorganic photorefractive crystals [62, 63]. These inorganic photorefractive crystals are slow, difficult and expensive to process and are relatively fragile. Further, it is not possible to process these in the form of large area single crystals. It is for this reason polymeric photorefractives that can be processed as films are of interest. For a photorefractive polymer large and stable electro-optic coefficient and photoconductivity are desired in the same material. Dark conductivity in the material should be significantly smaller than photoconductivity, otherwise the photoinduced grating will be thermally erased.

Recently Ducharme *et al.* [64] have been able to demonstrate photorefraction in 100  $\mu\text{m}$  thick films of electro-optic polymers based on the epoxy system discussed earlier [23]. A suitable hole transporting agent (for photoconduction), diethylaminobenzaldehyde diphenylhydrazone (DEH) was incorporated into the polymer. In these films significantly large diffraction efficiencies have been observed in nondegenerate four wave mixing experiments. This class of photorefractives could be further improved if phase segregation due to the presence of incompatible components could be avoided. Li *et al.* [60] have recently reported large photoconductivity in the photocrosslinkable second-order material PVCN/CNNB-R discussed earlier. In Fig. 12.16 photocurrent as a function of light intensity is plotted. Photocurrent as a function of wavelength of incident light is plotted in Fig. 12.17.

The photorefractive diffraction efficiency figure of merit  $Q = n^3r/\epsilon$  for this system was estimated to be 12 pm/V where  $n$  is the index of refraction,  $r$  the



**Fig. 12.16** Photocurrent in PVCN/CNNB-R as a function of laser intensity at 514 nm with 10 V bias.



**Fig. 12.17** Photocurrent in PVCN/CNNB-R as a function of laser wavelength at 10 V bias with laser intensity of 0.3 W/cm.

electro-optic coefficient and  $\epsilon$  the dielectric constant of the medium. This value is quite competitive with the values of figure of merit for most inorganic crystalline materials including the semiconductors. It is anticipated that cheap and efficient polymeric photorefractive will have benefits in image enhancing and motion sensing devices, in addition to uses in optical signal modulation and routing.

### 3 Electrically conducting polymers

During the past decade there has been an explosive growth in the research involving electronically conducting polymers. This started with the report on polyacetylene whose conductivity was increased by about ten orders of magnitude as a result of doping [65]. A large number of conducting polymers has since been developed. These conducting polymers are characterized by a  $\pi$ -conjugated polymer backbone with the ability to support a delocalized electronic charge defect.

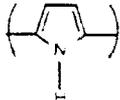
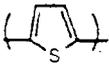
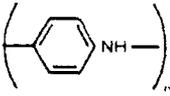
POLYMER	STRUCTURE	DOPING MATERIALS	D.C. conductivity, SCM
Polyacetylene	$(CH_2)$	$BF_4^-$ , $Li^+$ , $Na^+$ , $AsF_6^-$	1000-100000
Polypyrrole		$BF_4^-$ , $ClO_4^-$ , tosylate	500-7500
Polythiophene		$BF_4^-$ , $ClO_4^-$ , tosylate $FeCl_4^-$	1000
Polyaniline		HCL	200

Fig. 12.18 Electronically conducting polymers.

The charge defect may be introduced in the backbone by the removal or addition of electrons (oxidation and reduction). Overall, the conducting polymer system remains neutral as the backbone charges are compensated by the dopant counterions. The nature and extent of doping has a strong influence on the electronic and optical properties of the candidate conducting polymers. Figure 12.18, adapted from Kanatzidis [66], shows a number of the better known materials.

The electrical properties of conducting polymers have been the subject of intense interest and research in the past decade. This has been driven both by the interest in practical applications and the desire to elucidate the mechanisms behind the conductivity of these materials. In particular the frequency and temperature-dependent conductivity has been extensively studied, extending from d.c. to optical regions.

### 3.1 Electropolymerization and dielectric behavior

Several of the conducting polyheterocyclic polymers such as polypyrrole and polythiophene are most conveniently prepared in film form by electropolymerization [67]. The monomer is usually polymerized by anodic oxidation in the presence of an organic salt which provides electrolytic conductivity and counterions. An organic solvent such as acetonitrile is used, or the monomer itself may serve as the solvent. This method of synthesis has the advantage that the polymer is deposited on the anode in an uniform thin film, and is already in the oxidized conducting state. If the reduced form is desired, it can be produced by reversing the current flow in the electrolytic cell. Polyaniline can be similarly prepared from aqueous solutions containing aniline and hydrochloric or sulfuric acids. A very useful review of synthetic methods for conducting polymers has been given by Naarman and

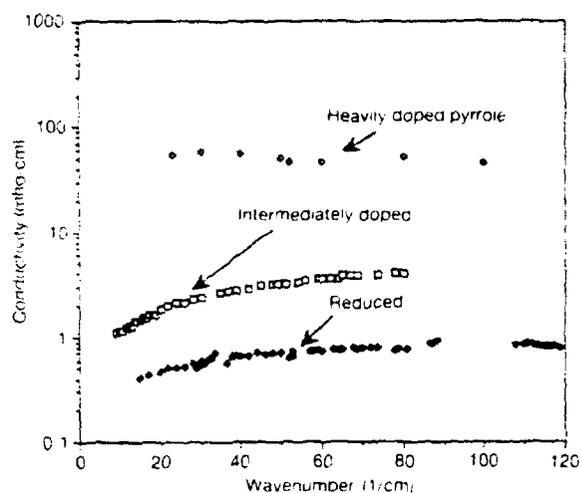


Fig. 12.19 Conductivity of polypyrrole as a function of doping level.

Theophilou [68]. These films have been extensively studied for their electrochemical, electronic, electrochromic and optical properties and applications.

Recently Phillips and coworkers have reported measurements on the microwave and far infrared properties of polypyrrole tosylate [69,70]. Thin films ranging in thickness from 5 to 50  $\mu\text{m}$  were prepared electrolytically in the fully oxidized form and then some of the samples were partially reduced by passing a reverse current through the electrolytic cell. As may be expected, the high frequency conductivities correlate with the d.c. conductivities and both are a function of the degree of oxidation (doping level).

The high frequency conductivities could be varied by more than two orders of magnitude by adjusting the doping level as shown in Fig. 12.19. Both the real ( $n$ ) and imaginary ( $k$ ) parts of the refractive index and hence also the dielectric constants [ $\epsilon_1 = n^2 - k^2$  and  $\epsilon_2 = 2nk$ ] show pronounced dispersive behavior for the more heavily doped samples. The real and imaginary parts of the complex dielectric constant are plotted in Fig. 12.20.

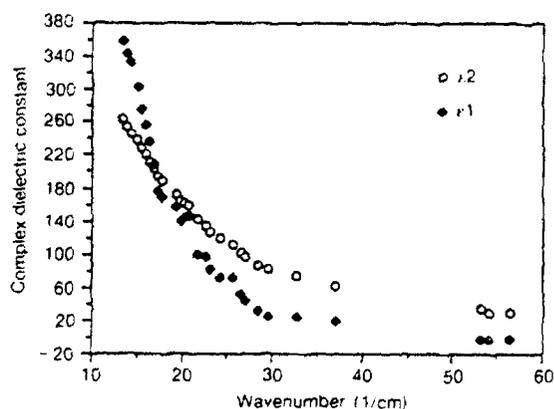


Fig. 12.20 Complex dielectric constants for a doped polypyrrole sample with  $\sigma = 50 \text{ S/cm}$ .

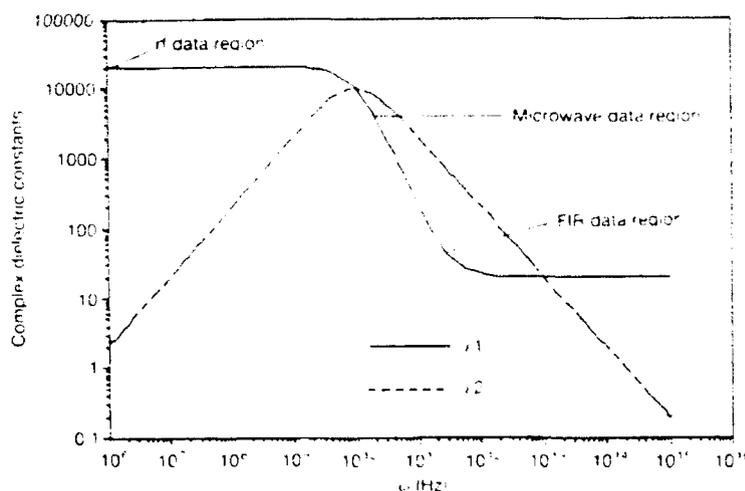


Fig. 12.21 Plot of  $\epsilon_1$  and  $\epsilon_2$  for a polypyrrole sample.

The overall behavior was found to be in accord with a Debye type model. Figure 12.21 is a fit to a Debye model where experimental data in the microwave and the far infrared region were available. Zuo *et al.* [71] have successfully fit low frequency (10 Hz–1 MHz) data for polyaniline (emeraldine form  $\sigma = 5$  S/cm) to the Debye model as well. Since polypyrrole can be obtained in large area films, and is relatively stable, and readily modified by doping, it may be useful in the fabrication of devices such as filters in the infrared and microwave spectral range [69].

### 3.2 Monolayer electrically conducting films and heterostructures

Recently, LB techniques have been used quite extensively to prepare and study films of conducting polymers. It has been used as a technique for fundamental studies in these materials. LB films of conducting polymers are of particular interest for molecular electronics device applications [72,73]. Conducting polymer monolayers have been prepared in a manner analogous to the NLO polymers. Surface active monomers may be set up in a monolayer and simultaneously polymerized and oxidized to form a conducting monolayer. Alternately, soluble conducting polymers mixed with a surface active host such as stearic acid may be spread on the LB trough. The conducting polymer need not possess surfactive character in order to form a good monolayer film.

Monolayers based on the poly(3-alkyl pyrroles) and poly(3-alkyl thiophenes), were manipulated in a number of different ways [74–79] to produce monolayers and multilayers in complex organizations. Mixed monolayers of 3-hexadecylpyrrole and pyrrole were polymerized at the air–water interface in the presence of ferric chloride as the oxidizing agent to yield conducting monolayers and studied by electron microscopy and diffraction techniques. LB films of polymerized 3-alkyl pyrrole and unsubstituted pyrrole prepared by this technique and mixed monolayers of stearic acid and poly-3-alkyl thiophenes were studied by near edge X-ray absorption fine structure spectroscopy (NEXAFS) using a synchrotron radiation source.

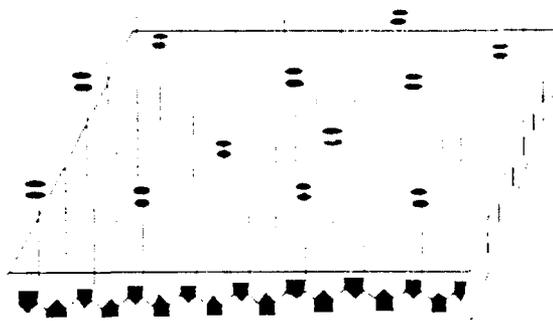


Fig. 12.22 Schematic of the two-dimensional polypyrrole lattice with mixed alkyl and ferrocene-derivatized unit extended into the third dimension.

The polarization dependence of the spectrum was interpreted to estimate the degree of ordering of the hydrocarbon chains, and the conducting components. A particularly interesting study of a ferrocene-derivatized pyrrole surfactant system has been done [80]. The molecule 3-(13-ferrocenyl, 13-hydroxytridecyl) pyrrole (Fc-Py), which consists of a pyrrole group at one end of a 12 carbon aliphatic chain and a hydroxyl ferrocene at the opposite end was used. While structurally similar to 3-n-hexadecylpyrrole (3HDP), Fc-Py does not form a stable monolayer by itself. However, mixed monolayers of Fc-Py and 3HDP were readily prepared and transferred as mono- and multilayers to suitable substrates. Conducting polymerized films could be obtained as before, in the presence of unsubstituted pyrrole and ferric chloride. The NEXAFS spectra indicated that the hydrocarbon chains are highly ordered and normal to the substrate, in these films. This information, together with the pressure-area isotherm data suggests the schematic arrangement shown in Fig. 12.22, with the 3HDP inducing vertical orientation of the Fc-Py monomer units.

It was demonstrated by cyclic voltammetry that the redox behavior of the ferrocene moiety is completely preserved in these mixed polypyrrole films. This provides additional indirect evidence to support the proposed structure, indicating that the ferrocene moieties are not buried within the polypyrrole layer and free to interact with the external environment. It was further demonstrated that this reversible behavior of the ferrocene-ferrocenium couple could be utilized, to create thin-film amperometric glucose biosensors [81].

#### 4 New directions

Research over the past decade has clearly established molecular and polymeric materials as candidates for application in electronics and optics technologies. Polymeric materials provide access to new process technologies for active electronic and optical devices. Further, the possibilities of incorporating the desired functionalities are immense. Search and incorporation of these functionalities in artificially structured polymeric materials will continue. Polymers will be designed, taking into account the arrangement of these functionalities, to provide ease of processing and fabrication and long term stability. Biological systems may serve as

models for the design and development of these new materials. Well-established planar microfabrication technologies on the other hand will provide approaches to device design and fabrication. Polymers are expected to be mostly used in the film form for these applications.

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