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by

**W.H. Kim, B. Bihari, R. Moody, N. B. Kodali,
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SELF ASSEMBLED SPIN COATED AND BULK FILMS OF A NOVEL POLYDIACETYLENE AS SECOND ORDER NLO POLYMERS

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ABSTRACT

The polymer chains of a novel asymmetric polydiacetylene, namely poly{[[[8-butoxy carbonyl]methyl urethanyl] 1-(5-pyrimidyl)-octa-1,3-diyne}(BPOD), in the absence of nonlinear optically active chromophores and without recourse to poling assemble in an acentric stable polar organization upon spin coating or solution casting. Asymmetry of the side groups and the spontaneous alignment of the urethane side groups by means of hydrogen bonds appear to be responsible for this organization. An abrupt decrease of SH intensity at around 130 °C is found to be closely related to the breaking of noncentrosymmetry in the films in conjunction with the disruption of intramolecular hydrogen bonds. The changes observed were reversible below 130 °C but becomes irreversible above this temperature. Comparison of absorption spectra of the poly(BPOD) films before and after thermal treatment indicate that only a slight change occurred in the absorption characteristics of the polymer backbone. FT-IR and dielectric spectroscopy confirm the relaxation of the stable hydrogen bonded polar organization at higher temperatures. Activation energies involved in this process were found to be a little higher than hydrogen bonding dissociation energies calculated from polyamide and polyurethane.

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The larger activation energies observed here indicate the combined effect of the disruption of the hydrogen bonds followed by β relaxation.

INTRODUCTION

Polydiacetylenes (PDAs) are a class of conjugated polymers and one of the promising candidates for the nonlinear optical applications owing to their large third order susceptibilities ($\chi^{(3)} \sim 10^{-9}$ - 10^{-10} esu) [1] and ultrafast response [2,3]. For these reasons, PDAs have been investigated extensively as third order nonlinear optical materials. It has been suggested that PDAs with aromatic substituents directly attached to the main backbone will present novel properties for these applications since the number of π -electrons per repeat unit increases through π -conjugation between the backbone and the side groups [4-6]. In fact, $\chi^{(3)}$ of these PDAs are found to be almost one order higher than those without such groups [7-8]. Conjugating side groups may modify backbone electronic properties in other unique ways [9,10].

Second order nonlinear optical (NLO) properties in bulk crystals or thin films of PDAs have not been extensively studied presumably due to their centrosymmetric packing in these materials. Design and synthesis of diacetylenic monomers with potential noncentrosymmetric alignment, e.g., attachment of NLO active dyes, is not simple because they require multiple synthetic steps. Polymerization of diacetylenic monomers in the monomer single crystals is not always possible and it is not guaranteed that the noncentrosymmetric alignment is still maintained upon polymerization. For practical devices, it is extremely difficult to obtain polymeric crystals in a desired geometry and shape. Further, if large area thin films of the polymer are desired, the alignment is destroyed upon dissolution of the polymeric crystals (provided they are soluble in common solvents) and

upon casting or spin coating from the solutions isotropic or centrosymmetric films are formed. For these reasons PDAs have not been considered to be materials of interest for second harmonic application.

However electric field induced second harmonic generation(SHG) in PDA films [11] has been reported in which the symmetry is broken due to the external DC-field. Berkovic et al. [12] observed SHG in the monolayers of several diacetylenic monomers and polymers spread at the air-water interfaces in a Langmuir Blodgett(LB) trough. They believed that the SHG signals arise mainly from the side groups on the PDAs since the diacetylene core is centrosymmetric. Garito et al. [13] demonstrated electric-field-induced SHG from PDAs containing two different, highly asymmetric substituents (one is NLO active chromophore). They concluded that "the magnitude of the macroscopic NLO response in PDAs critically depend on the nature of the microscopic charge correlated π -electron states and also on the symmetry and the degree of the structural order".

Theoretical calculations have indicated donor-acceptor substituted PDAs to possess large second order nonlinearity and could potentially be among the best second order nonlinear optical materials [14]. PDAs, in fact, provide several advantages for second order nonlinear optical applications over other organic materials: (1) Since the polymer backbone is extensively conjugated, large optical nonlinearity is expected (2) Noncentrosymmetrically aligned polymeric single crystals can be obtained without recourse to poling by careful choice of the monomer single crystals if they are packed in a noncentrosymmetric manner although chances are low (3) PDAs have good thermal and mechanical stability and can be obtained in various forms for device fabrication. For practical applications, it is ideal to obtain good optical quality films with preferred

orientation as observed in poled polymeric systems. In a few cases when PDAs are soluble in common solvents isotropic or centrosymmetric films may be prepared by spin coating [15-17]. Spontaneous orientation of the polymer chains in the films which can be often seen in the spin coated films of polyimides [18,19] has not been observed in the films of PDAs. We may be able to break the centrosymmetric nature in PDAs by aligning the polymer chains by either chemical or physical means. Various techniques have been developed to induce orientation in the films. They include casting-stretching method of soluble PDAs [20], Langmuir-Blodgett method [21], and vacuum deposition-rubbing method [22]. These methods are known to produce homogeneous films and inplane backbone orientation.

Recently we have reported a soluble, asymmetrically substituted PDA, viz. poly{[[8-butoxy carbonyl]methyl urethanyl] 1-(5-pyrimidyl)-octa-1,3-diyne}(BPOD), in which an aromatic substituent is directly attached to the main backbone [23]. This polymer is highly soluble in chloroform (>1%) and optical quality films can be obtained by either spin coating or casting the solution. It has been reported that the effective conjugation length of poly(BPOD) in solutions is enhanced through conjugation between the main backbone and the aromatic sidegroups compared to poly(4-BCMU). Similar observation is also expected from the films. In figure 1, absorption spectra of spin coated film and solutions of poly(BPOD) is compared with those of poly(4-BCMU) in which $R_1=R_2=-(CH_2)_4OCONHCH_2COOC_4H_9$. The films of poly(BPOD) and poly(4-BCMU) show λ_{max} at 525/573 nm and 476/520 nm, respectively. The only structural difference in poly(BPOD) from that of poly(4-BCMU) is that the former has one of the flexible urethane side groups replaced by a rigid aromatic pyrimidyl group. Since the other side group in poly(BPOD) is a

polar flexible urethane containing moiety, we still expect a high degree of intramolecular interaction between these side groups possibly in the form of hydrogen bonds as observed in case of the poly(n-BCMU) series. In figure 2, the hydrogen bonded network of poly(BPOD) is shown. To our surprise, significant SHG activity is observed from the spin coated films of poly(BPOD) in the absence of the classical second order NLO chromophores (electron donor-acceptor groups separated by a π -conjugated bridge) and without the aid of electric field induced poling.

INSERT FIGURE 1

INSERT FIGURE 2

In this paper, we investigate the nature and mechanism of self assembly responsible for this second order NLO property in these amorphous spin coated films of poly(BPOD). The values we report here is surprisingly large considering that there is no traditional NLO active chromophore present and electric field induced poling was not carried out. We propose that acentric alignment necessary for the NLO properties observed here is mainly due to the combined effect of the asymmetry of the two side groups and the spontaneous alignment of the urethane moiety. This occurs in conjunction with the formation of intramolecular hydrogen bonds between the urethane side groups. The pyrimidyl side groups in conjunction with the conjugated backbone segment form the asymmetric anharmonic electronic oscillator.

EXPERIMENTAL

Synthesis and solid state polymerization of diacetylene monomer BPOD has been reported elsewhere [23]. Poly(BPOD) was dissolved in chloroform (~1% w/v) and the films were obtained by spin coating the polymer solutions on glass substrates at various speed to achieve appropriate film thickness followed by drying under vacuum overnight. Similar method was employed on a KBr crystal window for FTIR measurement. The film thickness was measured by using either an Ellipsometer or a Scanning Electron Microscope.

UV-visible spectra of the films were obtained on a Perkin-Elmer Lambda 9 UV/VIS/NIR spectrophotometer at different temperatures. FT-IR spectra of the polymer films were recorded at various temperature by using a Perkin-Elmer 1760X FT-IR. Measurements of the dielectric properties of the films were performed with a Hewlett Packard model 4284A multifrequency LCR meter. The instrument was operated at 10 discrete frequencies ranging from 30 Hz to 1 MHz. Mercury confined within an O-ring was used as the top electrode. Measurements were carried out at different temperature on a computer controlled hot stage with a constant heating rate. SHG measurements were carried out according to the method reported earlier [24].

RESULTS AND DISCUSSION

An estimate of the effective second harmonic generation coefficient (d_{eff}) for the spin coated films has been obtained by assuming the tensor properties of the films to be of a similar nature as the poled polymeric systems [25]. The d_{eff} for the spin coated films of poly(BPOD) are summarized in Table 1. For comparison, poly(4-BCMU) shows no measurable signals under the same conditions. These values are

significantly larger than any reported to date from ordered ferroelectric liquid crystalline NLO polymers [26].

INSERT TABLE 1

Transmission Electron Microscopy(TEM) and X-ray diffraction as well as Polarized Optical Microscopy studies indicate that the films are amorphous and no crystallinity is present. However, a couple of small humps at low angles of X-ray diffraction pattern suggest the presence of certain degree of orientation in the film. Two broad rings from the diffraction pattern from TEM also support the results of the X-ray study.

The s- and p-polarized absorption spectra of the spin coated film are shown in figure 3. No difference in the intensity between the two polarization was observed when the incident light is in the normal direction to the substrate. However, significant difference was observed when light is incident on the film at 45° to the substrate. This indicates that the films are isotropic in in-plane direction but anisotropic in through-plane direction. Similar observation was made from the angular and polarization dependence of the second harmonic signal from the poly(BPOD) thin films. They show a behavior similar to the poled second order nonlinear polymers. Figure 4 shows the SH intensity as a function of the polarization angle(ϕ) of the incident fundamental beam for a spin coated film. The second harmonic polarization was selected as p-polarization. The angle of incidence for fundamental beam was kept at 45° . The values shown in figure 4 gives a nearly perfect fit to a function of $(A\sin^2\phi + B\cos^2\phi)^2$ which indicates that these films have in-plane isotropy. Angular dependence of the second harmonic signal from spin coated poly(BPOD) is shown in Figure 5. SH intensity reaches a maximum when the incident

fundamental beam is at 55° with respect to the substrate normal. No second harmonic response is expected for the fundamental beam incident normal to the substrate if the film exhibits polar order similar to poled polymers. The SHG experimental results indeed confirm the existence of polar order with the symmetry axis perpendicular to the substrate. We conjecture that the alignment of the urethane side groups (in their hydrogen bonded form) in conjunction with the pyrimidyl groups in a direction near normal to the substrate give rise to the polar symmetry.

INSERT FIGURE 3

INSERT FIGURE 4

INSERT FIGURE 5

Figure 6 shows the changes in SH signal as a function of temperature. SH intensity starts to drop abruptly between $125-130^\circ\text{C}$ and decreases only slightly below 130°C . However, on heating the film to temperatures well above 130°C the signal approaches nearly zero and becomes irreversible. Differential scanning calorimetry (DSC) studies of poly(BPOD) shows no endothermic transitions upon heating and degradation starts at around 231°C . Furthermore, no significant thermochromic behavior was observed [27,28]. This suggests that the changes observed in SH signals upon heating is not due to thermal transitions or segmental motion of the backbone. Figure 7 shows the changes in absorption spectra of poly(BPOD) film as a function of temperature. A relatively small blue shift and decrease in intensity in the absorption spectra was observed upon

heating which also indicates that the PDA backbones are not significantly influenced by the thermal treatment.

It is believed that the chromic transitions shown in poly(4-BCMU) in solid as well as in solution are the result of an order-disorder conformational change of the backbone which are mainly caused by the formation and disruption of intramolecular hydrogen bonding of the urethanyl side groups. Distortions of the backbone in the form of static deformations of bond lengths and/or bond angles are easily generated in the PDAs containing long, flexible side groups upon environmental changes such as temperature and solvent system. A small distortion is known to significantly influence the electronic states of the π -electrons of the backbone and result in a dramatic change in the absorption spectra. Typically the disorder created by thermal treatment displays a very broad, ill-defined absorption band which indicates a highly deformed conjugated backbone with limited interchain interactions. Thus the small changes observed in the absorption spectra upon heating suggests that poly(BPOD) possesses a very rigid backbone due to the presence of bulky aromatic side groups and resists conformational changes which are often seen in a number of alkyl-urethane side groups. We propose that acentric alignment necessary for the NLO properties observed here is due to the combined effect of the asymmetry of the two side groups and the spontaneous alignment of the urethane moiety. This occurs in conjunction with the formation of intramolecular hydrogen bonds between the urethane side groups. Structural transitions in the side groups are intimately connected with the transitions in the NLO properties.

INSERT FIGURE 6

INSERT FIGURE 7

Figures 8 and 9 show the FT-IR spectra of spin coated film of poly(BPOD) as a function of temperature. Since we believe the alignment of the urethane side groups by means of intramolecular hydrogen bond is largely responsible for acentric alignment necessary for the NLO properties, only two spectral regions of interests are discussed here. They are N-H stretching and carbonyl stretching in the urethanyl moiety. Figure 8 shows the spectral changes in the N-H stretching region upon heating (left) and subsequent cooling to room temperature (right). N-H stretching band in between 3100 and 3500 cm^{-1} shows a relatively sharp peak centered at around 3257 cm^{-1} with a small shoulder at higher wavenumber at room temperature. Consistent with other urethane substituted PDAs this clearly indicates the presence of hydrogen bonded N-H groups with a small fraction of non-hydrogen bonded N-H moiety. This peak broadens and intensity dramatically decreases at temperatures around 130 °C and a new band appears at higher wavenumber at higher temperature. The SH signal drops abruptly in the temperature region and can not be recovered upon cooling above this region. The spectral changes observed in this region suggest the breakage of the hydrogen bonds and development of free N-H groups which, in turn, results in a disruption of the acentric organization.

Upon cooling to room temperature, this band returns to its original shape and intensity which indicates the reformation of the hydrogen bonds. On the other hand, the shoulder assigned as the free N-H band, becomes sharp and more intense as the sample is cooled from temperature above 130 °C. The hydrogen bonds are not recoverable when the sample is cooled from higher temperatures as a result of extensive randomization of

the side groups. This prevents the necessary proximity of the adjacent urethane linkages to form hydrogen bonds.

INSERT FIGURE 8

Spectral changes are also expected in the 1600 and 1800 cm^{-1} region of the spectra from the urethanyl substituted polymers due to the sensitivity of the ester and urethane carbonyl groups on hydrogen bonds although they may be far less dramatic than corresponding N-H bands. Figure 9 shows the spectral changes in this region upon heating (left) and subsequent cooling to room temperature (right). The peaks appearing at 1745 and 1717 cm^{-1} are assigned to vibrations of the ester carbonyl and hydrogen bonded carbonyl of the urethane moiety, respectively. The peak at 1717 cm^{-1} is relatively shifted to a higher wavenumber compared to the other symmetric urethane substituted PDAs such as poly(4-BCMU) in which the urethane carbonyl is appearing below 1700 cm^{-1} . It is believed that the intensity and the degree of the hydrogen bond in poly(BPOD) is largely reduced with respect to those of poly(4-BCMU) since only one urethane group per repeat unit is present in the former, hence results in a shift to a higher wavenumber. As temperature increases, ill-defined bands in addition to the original ones develop and turn into a broad peak centered at higher wavenumber at the temperature above 130°C . The new band appearing between 1730 and 1740 cm^{-1} is assigned to the free urethane carbonyl stretching although two peaks between 1680 and 1710 cm^{-1} are not well established. The spectral changes occurred during heating are reversible upon cooling but irreversible above 130°C . This is also well in agreement with observations made from the N-H stretching region in the FT-IR spectra as well as the absorption spectra.

INSERT FIGURE 9

Dynamic behavior of the molecular dipolar organization in the film at various temperatures is further investigated by dielectric spectroscopy. Figure 9 shows temperature dependence of the dielectric constant of the poly(BPOD) film at various frequencies. No significant segmental motion from the main chain is expected at moderately high temperatures due to the rigidity of the PDA backbone. The changes seen in the dielectric response at high temperatures is caused by the increase in the mobility of the dipolar units in the side groups. Dielectric constant starts to increase dramatically around 125-130 °C at 30Hz. Again, this is the temperature region at which SH signal drops abruptly and becomes irreversible above this temperature. This is a good indication that the restricted mobility of the side groups which was caused by the hydrogen bonding now begins to relax and randomize at this temperature. Figure 10 shows temperature dependence of the $\tan\delta$ of the poly(BPOD) film at various frequencies. Activation energy involved in this process was calculated from the Arrhenius plot of angular frequency and inverse T_{\max} (where T_{\max} is defined as the temperature where the $\tan\delta$ peak reaches maximum for each frequency), and it was found to be 18-20 kcal/mol. Hydrogen bond dissociation energy of polyurethane and polyamide are known to be in the range of 8-14 Kcal/mol [29-31]. The larger activation energies observed here indicate the combined effect of the disruption of the hydrogen bonds followed by β relaxation. The motion of the side groups would result in the loss of the noncentrosymmetric structure which was "locked" in place by the hydrogen bonding.

INSERT FIGURE 10

INSERT FIGURE 11

CONCLUSIONS

Polymer chains of a novel asymmetric polydiacetylene, BPOD, self assemble in an acentric stable polar organization upon spin coating. Spontaneous alignment of the urethane moiety caused by the intramolecular hydrogen bonds between the side groups appear to be responsible for this organization. An abrupt decrease of SH intensity at around 130 °C is found to be closely related to the breaking of noncentrosymmetry in the films in conjunction with the disruption of these intramolecular hydrogen bonds. The changes observed were reversible below 130 °C but become irreversible above this temperature. Dielectric and infrared spectroscopy confirm the relaxation of the stable hydrogen bonded polar organization at higher temperatures. Pyrimidyl substituted conjugated segment of the polydiacetylene is the second order NLO chromophore. The pyrimidyl group can serve as an electron acceptor. It will be very instructive to calculate the molecular hyperpolarizability of the present asymmetric electronic oscillator. The invention of this bulk self assembling second order NLO polymer also opens up numerous possibilities in molecular design for further optimization of properties.

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FIGURE CAPTIONS

Table 1. d_{33} values obtained from poly(BPOD) spin coated films at incident wavelength of 1.064 μm .

Figure 1. Absorption spectra of poly(4-BCMU) and poly(BPOD). (A) and (B); in chloroform. (C) and (D); in chloroform/hexane. (E) and (F); spin coated films, respectively.

Figure 2. Hydrogen bonded network of poly(BPOD).

Figure 3. Polarized absorption spectra of spin coated film of poly(BPOD). Top; vertical polarization Bottom; horizontal polarization. Sample was placed 45° tilted with respect to the incident light.

Figure 4. Plot of polarization angle vs SH intensity of spin coated film of poly(BPOD).

Figure 5. Plot of angle of incidence vs SH intensity of spin coated film of poly(BPOD).

Figure 6. Temperature dependence of SH intensity of spin coated film of poly(BPOD).

Figure 7. Absorption spectra of spin coated film of poly(BPOD) recorded at various temperatures. From top to bottom; 25 °C, 50 °C, 80 °C, 130 °C, and 170 °C.

Figure 8. FT-IR spectra of spin coated film of poly(BPOD) in 3000-3500 cm^{-1} region. Left; recorded at various temperatures. Right; recorded after cooled to room temperature. From top to bottom; 25 °C, 50 °C, 80 °C, 110 °C, 130 °C, and 150 °C.

Figure 9. FT-IR spectra of spin coated film of poly(BPOD) in 1600-1800 cm^{-1} region. Left; recorded at various temperatures. Right; recorded after cooled to room temperature. From top to bottom; 25 °C, 50 °C, 80 °C, 110 °C, 130 °C, and 150 °C.

Figure 10. Temperature dependence of dielectric constants of spin coated film of poly(BPOD) at various frequencies.

Figure 11. Temperature dependence of $\text{Tan}\delta$ of spin coated film of poly(BPOD) at various frequencies.

table 1

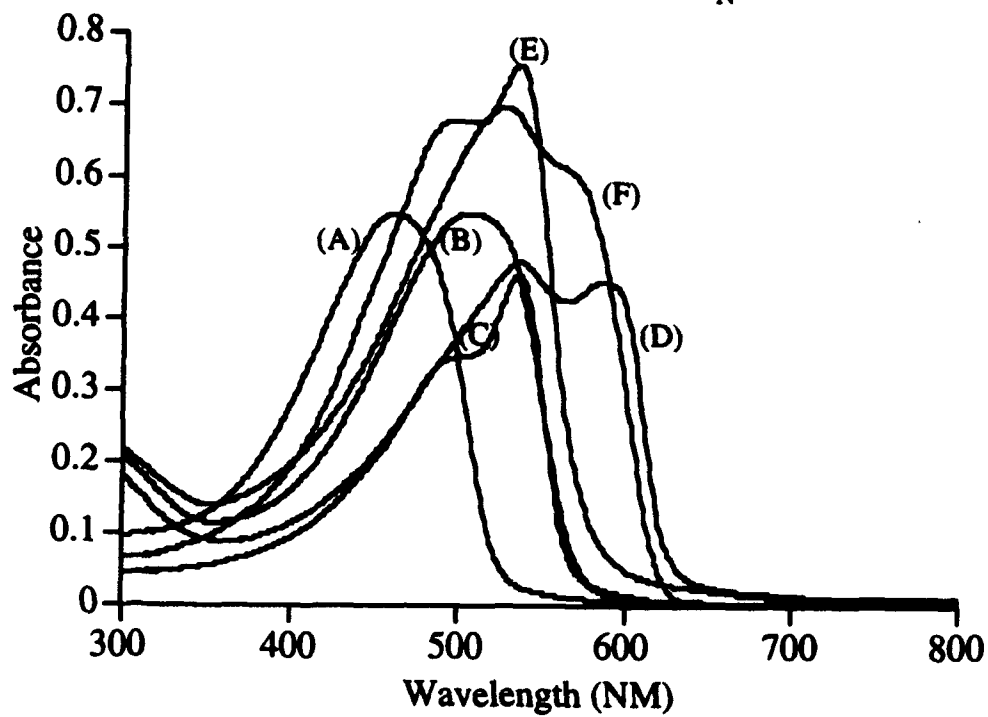
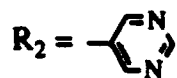
Film thickness (μm)	d_{33} (pm/V)	
	w/o abs. correction	with abs. correction
0.31	0.74	5.57
0.25	0.78	4.43
0.19	0.88	3.32

Poly(4-BCMU)

$R_1 = R_2 = (CH_2)_4OCONHCH_2COOC_4H_9$

Poly(BPOD)

$R_1 = (CH_2)_4OCONHCH_2COOC_4H_9$



f. 2

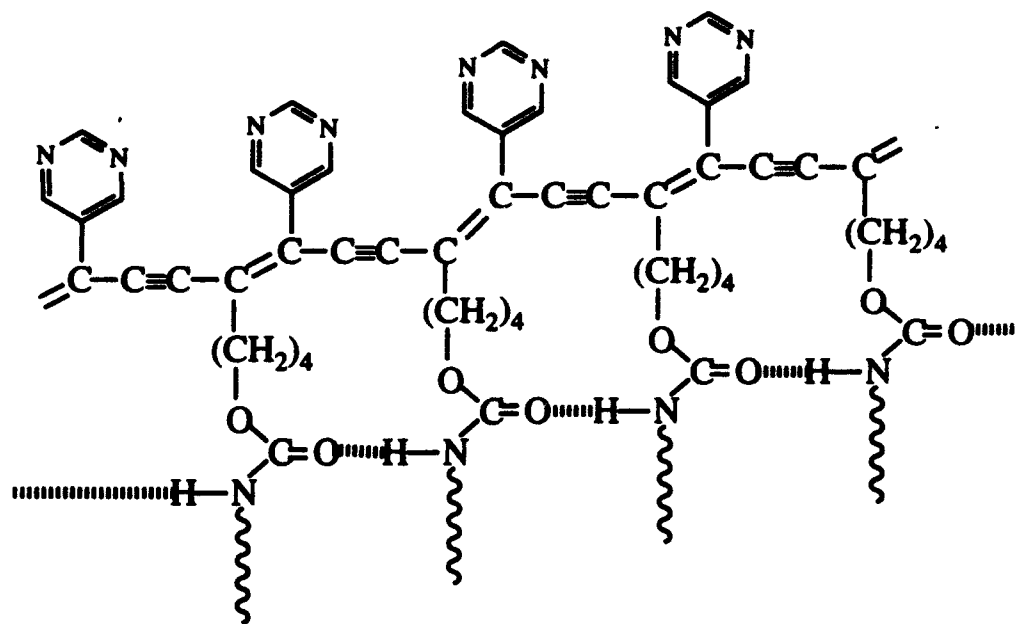
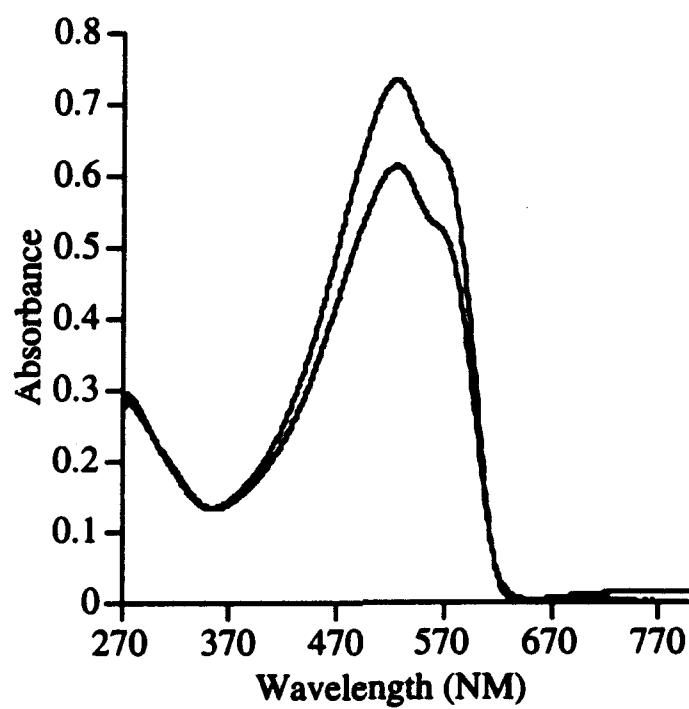
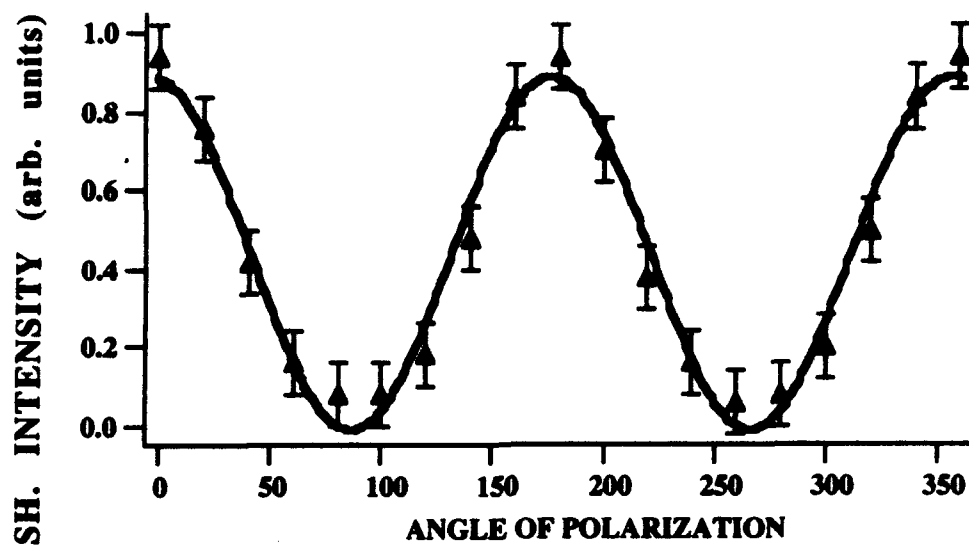


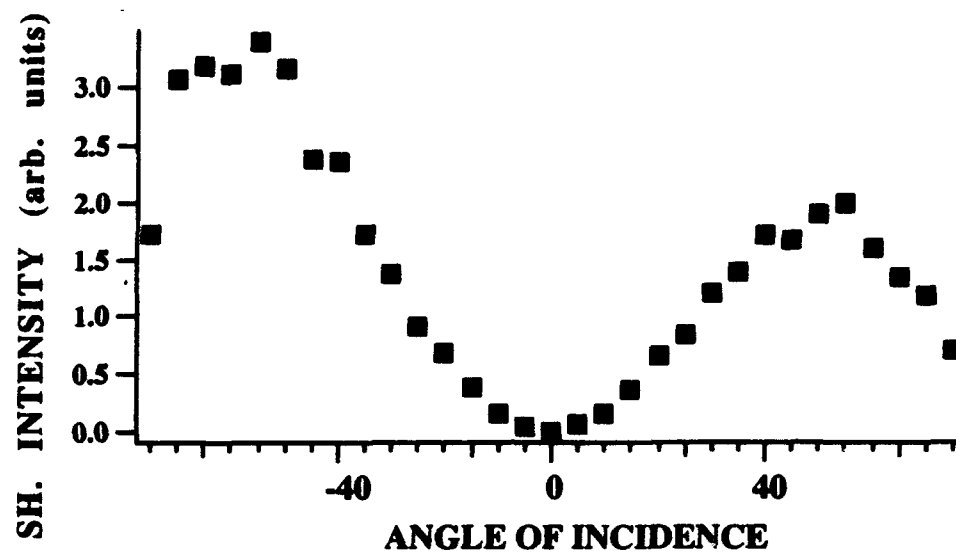
Fig 3



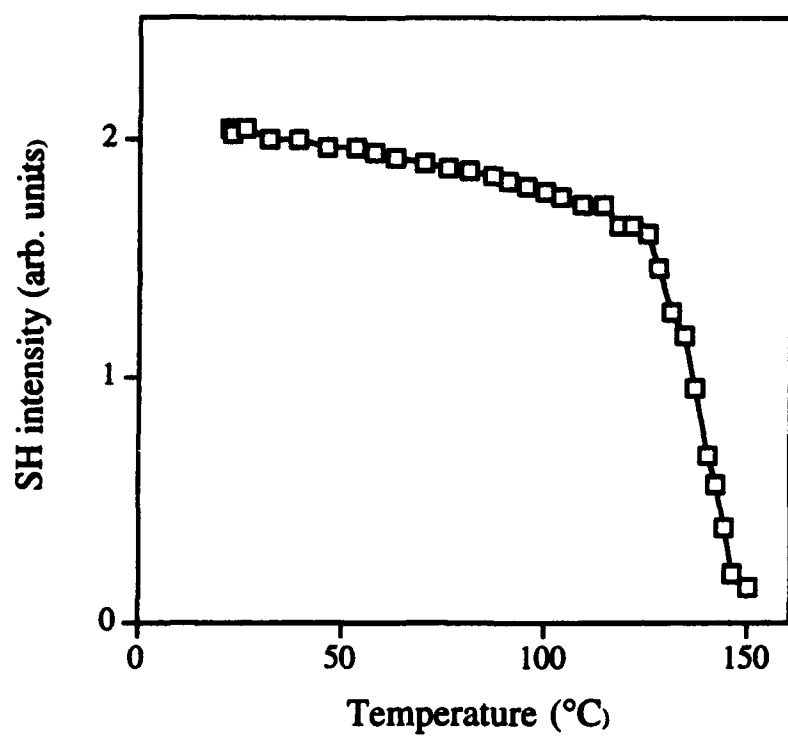
f34



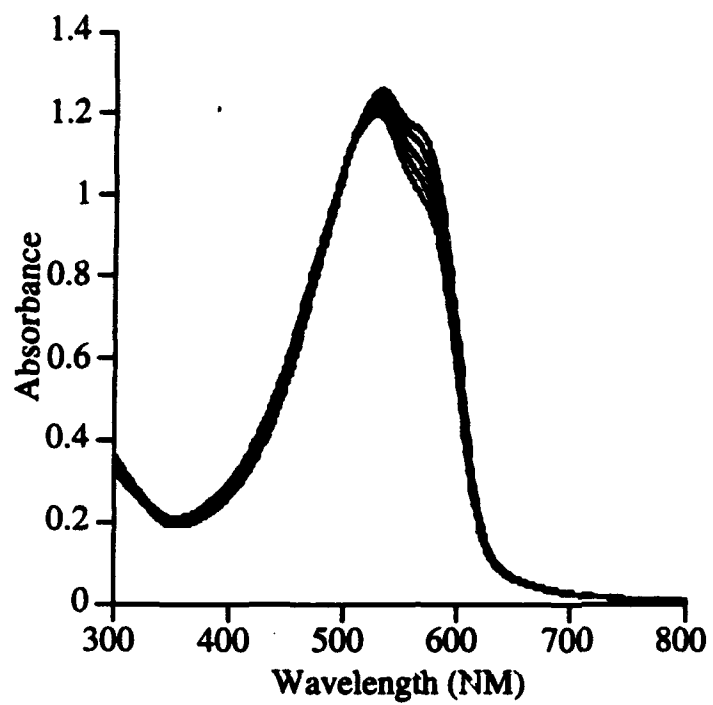
f₈₅

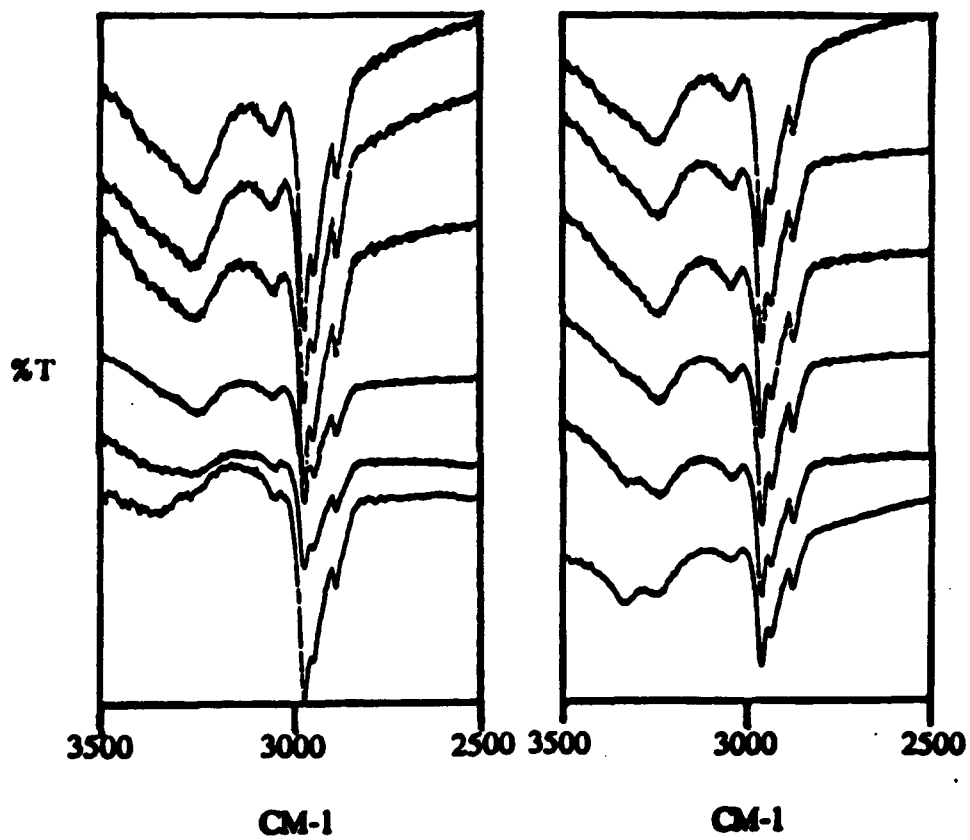


fig



f87





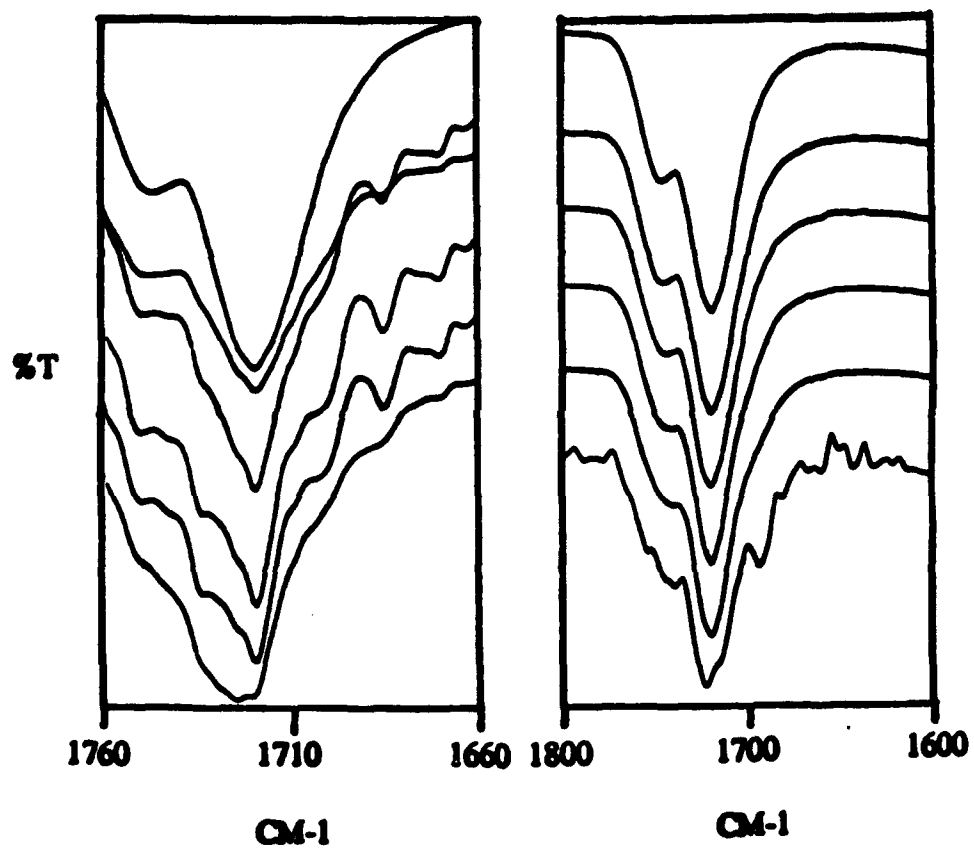


Fig 8

