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A Relaxation Study of Poled Nonlinear Optical
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Spectroscopy

by

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A RELAXATION STUDY OF POLED NONLINEAR OPTICAL POLYMERS BY INFRARED REFLECTION-ABSORPTION SPECTROSCOPY

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SYNOPSIS

The relaxation of poled nonlinear optical (NLO) chromophores in polymer films was characterized by infrared reflection-absorption spectroscopy. Both a guest-host system and a photocrosslinkable polymer system were investigated. Polymethylmethacrylate (PMMA) doped with either 2-methyl-4-nitroaniline (MNA) or 4(4'-nitrophenylazo) phenylamine (DO3) was studied. The photocrosslinkable polymer system, polyvinylcinnamate (PVCN) doped with 3-cinnamoyloxy-4-[4-(N,N-diethylamino)-2-cinnamoyloxy phenyl azo] nitrobenzene (CNNB-R) was also investigated. Doped NLO active molecules were aligned using the corona poling technique. Infrared spectra as a function of time were used to monitor the relaxation behavior of the oriented dyes after poling. Relaxation of NLO molecules was followed at various characteristic vibrational frequencies. The relaxation of MNA was found to be faster than that of DO3. The NLO dye molecule, CNNB-R, was covalently bonded to the host polymer and formed a three dimensional crosslinked network after ultraviolet (UV) irradiation. Relaxation of NLO molecules in pristine and UV treated samples were compared. UV light induced crosslinking provided better temporal stability of molecular alignment in this system.

Keywords: nonlinear optical polymers, infrared reflection-absorption spectroscopy, relaxation of oriented dipoles, corona poling

INTRODUCTION

Amorphous polymers doped with organic chromophores with large second-order hyperpolarizabilities have become promising materials for nonlinear optical (NLO) applications. These materials are attractive because of their large nonlinear susceptibility and relative ease of processing. They have been proposed for use in many applications such as electro-optic switching and modulation, second harmonic generation (SHG), and optical signal processing.¹⁻³

Second order nonlinear optical properties can be obtained by the alignment of doped organic chromophores in a polymer in a noncentrosymmetric manner. Several classes of second order NLO polymers have been studied, such as Langmuir-Blodgett films^{1,4}, guest-host systems⁵⁻⁷, and materials containing NLO moieties covalently linked to either the side chains^{8,9} or the polymer main chains.^{10,11} Thermal^{12,13} or photochemically¹⁴⁻¹⁶ crosslinked systems, and materials incorporating NLO chromophores in quasi-organic matrices^{17,18} have also been investigated. Alignment of dipoles is usually achieved by applying a large electric field across the polymer film, namely poling. The electric field can be obtained by either corona discharge^{5,7,9,19} or applying an electric potential between two electrodes.^{7,13,20} Poling is usually carried out at a temperature near the glass transition (T_g) of amorphous polymers where the increased mobility of polymer chains eases the movement of

chromophores. The orientation of chromophores is retained by cooling down the temperature well below T_g in the presence of the field. Since poled ordered NLO chromophores in the polymers provide the second order NLO properties, it is important to study the orientation of these chromophores and the temporal stability of the poled order.

The degree of orientation of chromophores in poled polymers and their relaxation have been studied using a number of different techniques.^{5,6,19-26} SHG as a function of time, has been used to study the relaxation of oriented NLO dyes dispersed in amorphous polymers.^{5,6,20-23} The second harmonic coefficient which is proportional to the square root of the second harmonic (SH) intensity, is related to the angle between the poling field and the molecular axes of the poled dye molecules.^{6,27} Once the field is removed, this angle changes as the dipoles start to relax and lose their orientation. This leads to a decrease in the SH intensity. UV-visible spectroscopy was also used as a tool to study the orientation distribution of chromophores after poling.⁶ When polymer films are subjected to a large electrostatic field, the chromophores are aligned along the direction of the electric field. This results in an intensity change in their absorption spectra. Electrochromism, which results in a shift of the molecular absorption peaks as a large electric field is applied has also been reported for poled NLO polymer films.¹⁹ This is a result of a change in the dipole moment of the NLO molecules due to the poling field. Waveguiding experiments have been performed to study the anisotropy of refractive index of poled NLO polymer films.¹⁹ The decay of the field-induced anisotropy shows a relaxation of the aligned dipolar molecules. Dielectric spectroscopy studies on NLO polymers were also reported.²⁴⁻²⁶

It was found that the relaxation behavior of poled NLO molecules with main chain chromophores is associated with the α -relaxation of the polymers.²⁵

IR and Raman spectroscopies have also been used as tools for studying the orientation of polymers.^{4,28-32} Samples with highly ordered molecular arrangements can be obtained using the Langmuir-Blodgett technique. Characterizations of the molecular orientation of these monolayers have been reported by using infrared dichroism.⁴ Liquid-crystalline polymers exhibit a variety of phase transitions which involve in the rearrangements of mesogenic units. Infrared spectroscopy was used to characterize the microstructures of liquid crystalline polymers in various mesophases.³²

A current project in our laboratory involves dielectric measurements on poled NLO polymer thin films.³³ Polymers are spin-coated onto a metal surface first before constructing a sandwich structure needed for the measurement. We have adopted a similar sample geometry to perform the IR reflection-absorption spectroscopy. This technique provides an opportunity for using the identical sample for both IR and dielectric measurements. In this paper, the investigation of the dynamics of the rotation of dopants dispersed in amorphous polymers was performed by means of polarized infrared reflection-absorption spectroscopy.

EXPERIMENTAL

Sample preparation

1g of polymethylmethacrylate (PMMA) and 0.2g of 2-methyl-4-nitroaniline (MNA) were dissolved in 10ml of 1,4-Dioxane and was filtered through filter membranes (pore size 0.2 μ m). The solution was spin-coated onto a glass slide coated with 1500Å Aluminum. The sample was soft baked at 50°C for 12 hours. PMMA doped with 4(4'-nitrophenylazo) phenylamine (Disperse Orange 3, DO3) samples were prepared in the same manner. MNA and DO3 obtained from Aldrich Chemical Co. were recrystallized once prior to use.

1g of polyvinylcinnamate (Polysciences, Inc.) and 0.3g of 3-cinnamoyloxy-4-[4-(N,N-diethylamino)-2-cinnamoyloxy phenyl azo] nitrobenzene (CNNB-R) were dissolved in 15ml of 1,4 Dioxane. The synthesis of CNNB-R has been reported previously.³⁴ The solution was first filtered and then spin-coated onto a glass slide coated with 1500Å of aluminum. Subsequently, the sample was baked at 80°C for 18 hours.

The sample is poled by applying a high electric potential (~3kvolts) across a sharp tungsten needle and the grounded heating stage which supports the sample. The heating stage provides thermal control during the poling process. The corona discharge results in the accumulation of surface charges on the top of the polymer film. These charges produce a static field across the film which is responsible for the alignment of the dipoles. The aluminum layer was grounded during the poling process. Poling of the PMMA doped with MNA or DO3 were performed at 70°C for 15 minutes. The samples were quenched to room temperature in the presence of the corona field. IR measurements were performed as a function of time at room temperature for 20 hours.

PVCN doped with CNNB-R samples were poled at 70°C for 15 minutes. The sample was quenched to room temperature and then exposed to UV radiation for 20 minutes with the poling field left on. A multi-ray UV lamp (Gates, Inc.) was used for photocrosslinking. An intensity of 2mw/cm² at 254 nm was chosen. The IR spectrum was recorded immediately after the poling process. The sample was then placed in an oven with a preset temperature of 70°C. After a certain period of time, the sample was taken out and quenched to room temperature before an additional IR measurement was taken. The sample was again placed back into the oven after the measurement. This heating and cooling cycle was repeated throughout the relaxation study of the photocrosslinking system.

FTIR spectra were collected with a Perkin-Elmer 1760 FTIR spectrometer at 4 cm⁻¹ resolution as a function of time. A Perkin-Elmer variable angle specular reflectance accessory was used to obtain the reflection-absorption spectra. An incident angle of sixty degrees was chosen for this study. A wire grid polarizer was used to obtain the desired polarization. For time dependent reflection-absorption spectroscopy, an incident polarization parallel to the plane of the sample was chosen. Figure 1 shows the experimental setup for obtaining reflection-absorption spectra and the sample geometry for the measurement.

RESULTS AND DISCUSSION

Figure 2 shows changes in the IR reflectance spectra as a result of poling and relaxation of MNA in PMMA. The IR measurement was performed after poling, at 60° incident angle with a polarization parallel to the

polymer film. After the sample was poled, the molecular dipoles of the MNA molecules tend to be aligned along the direction of the electric field. Therefore, these dipoles are preferentially oriented vertical to the substrate which reduces the overlap between the IR radiation E field and the transition dipole moment. This leads to a decrease in absorbance, or in other words an increase in the measured reflectance. As the relaxation of dipoles starts, the reflectance decreases continuously. Sublimation of MNA was observed at elevated temperatures and must occur to some extent during the poling process. This physical loss of the chromophore also contributes to the increase of measured reflectance. An undoped PMMA film was also poled for comparison. The carbonyl peak at 1735 cm^{-1} showed an increase in reflectance after poling. Besides, it was found that the baseline of the spectrum was slightly shifted. For our analysis of the NLO molecules, we have found that the magnitude of the reflectance changes due to the poling of the host polymer is negligible. Reflectance changes due to relaxation of dipoles were also observed in other functional groups. The results are summarized in Table 1. Figure 3 shows several vibrational modes for a triatomic functional group. The atomic vibrations shown here are all in the same plane.

The transition dipole moments of the nitro group for both symmetrical (ν_s) and asymmetrical stretching (ν_{as}) vibrations are perpendicular to each other.⁴ When the NLO dyes are oriented, the transition dipole of ν_s tends to move away from the plane of the sample. Therefore, during the dipolar relaxation a decrease of reflectance due to the increased absorbance is observed as shown in Figure 4(a). Since the molecules are not perfectly oriented, the plane normal of the nitro group

does not have a specific direction associated with the substrate normal. In addition, the transition dipole of ν_{as} does not have a preferred direction with respect to the polarization of the incident IR radiation. We did not observe a significant intensity change for ν_{as} of DO3 compared to the case of ν_s as shown in Figure 4(b). Moreover, it was found that the ν_{as} peak shifted from 1522 cm^{-1} to 1520 cm^{-1} after poling. The peak shifted back towards the original value during the relaxation process. Similar results were obtained in the case of MNA. In addition, the reflectance of ν_{as} increased during the relaxation process which is opposite to the case of ν_s . The observed changes are smaller than the reflectance changes of ν_s . The reason for the field-induced peak shift is not clear at this stage. However, the different relaxation behaviors between ν_s and ν_{as} of the nitro group may suggest a method for assisting the peak assignment in the IR spectra.

Figure 5 shows normalized reflectances vs. time after poling at wavenumbers corresponding to NH_2 scissoring of both MNA (1640 cm^{-1}) and DO3 (1632 cm^{-1}) molecules. The reflectance of the samples right after poling was assigned to be unity. The reflectances measured at different time periods were normalized accordingly. MNA shows a faster relaxation rate at the initial stage than DO3. In addition MNA shows a larger percentage of decrease in reflectance over a period of 20 hours. This result is similar to that obtained from the SHG measurement.⁵ The reason that the relaxation of MNA is faster than DO3 is mainly due to the size difference of the molecules. The spatial rotation of the chromophore during relaxation is affected by the distribution of the local free volume around the dye molecules in these polymers. Therefore, MNA rotates more easily

than DO3 in the PMMA matrix which leads to a more rapid decrease in reflectance for MNA than DO3.

For the photocrosslinkable system, relaxation of poled NLO dyes were found to be extremely slow at room temperature due primarily to the large molecular size of CNNB-R. Therefore, the relaxation of the photocrosslinking system was performed at 70°C. Figure 6 shows the FTIR spectra of PVCN doped with 30% CNNB-R, before and after poling without UV treatment. A polarization perpendicular to the incident plane was chosen for monitoring the relaxation behavior. The spectra show a significant reflectance increase after poling since the dipoles tend to orient in the direction normal to the polymer film. During the annealing process at 70°C, the sample showed a rapid change of reflectance at the initial stage of annealing followed by a further gradual decrease toward the original intensity before poling.

In comparison, Figure 7 shows the FTIR spectra of poled PVCN doped with 30% CNNB-R with subsequent 20 minutes of UV irradiation. A rapid relaxation was also observed after annealing at 70°C for 5 minutes. However, after this initial change the reflectance at 1609 cm^{-1} remained fairly constant during further annealing. Our studies have shown that during UV irradiation, a certain degree of degradation took place which resulted in a decrease of absorbance and hence a corresponding increase of reflectance. UV induced degradation complicated the interpretation of the experimental results. Therefore, SHG measurements were used to support our analysis. A weak SHG signal was observed for both UV treated and untreated samples after 3 hours of annealing at 70°C. However, after an additional 24 hours of heat treatment at 70°C, SHG signal of the sample

treated with UV radiation was still quite evident. In contrast, the sample without UV irradiation showed no SHG signal at all. The result confirmed that the stability of the photocrosslinked sample was improved through the UV crosslinking reaction.

CONCLUSIONS

Reflection-absorption IR spectroscopy was demonstrated to be a technique useful for the study of the relaxation of poled NLO molecules. Relaxation can be monitored at various vibrational frequencies. Field-induced peak shifts were found for the asymmetrical stretching vibration of the nitro groups. MNA, with a smaller molecular size shows a faster and larger relaxation than DO3 in the PMMA polymer host. In PVCN doped with CNNB-R system, UV irradiation induces a crosslinking reaction between the polymer host and the NLO dye which enhances the stability of the orientation of the NLO dye.

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Legend to the Table

Table 1. Relaxation observed at the various frequencies and the corresponding molecular vibrations for the functional groups of MNA.

cm ⁻¹	Assignments	Reflectance changes during the relaxation
3464	$\nu_{\text{as}}(\text{NH}_2)$	increases
3383	$\nu_{\text{s}}(\text{NH}_2)$	decreases
1640	$\delta_{\text{s}}(\text{NH}_2)$	decreases
1608, 1588	Aromatic ν (C-C)	decreases
1486	$\nu_{\text{as}}(\text{NO}_2)$	increases ^a
1313	$\nu_{\text{s}}(\text{NO}_2)$	decreases

^a A peak shifted to higher wavenumbers was observed.

Legend to the Figures

Figure 1. Experimental setup for reflection-absorption infrared measurements. Polymers were spin-coated onto a glass slide coated with 1500Å aluminum. A wire grid polarizer was used.

Figure 2. IR spectra of MNA in PMMA. Curves shown from top to bottom are: right after poling, 120 minutes after poling, and pristine.

Figure 3. Molecular vibrational modes for (a) scissoring (δ_s) of NH_2 (b) symmetrical stretching (ν_s) of NO_2 (c) asymmetrical stretching (ν_{as}) of NO_2 .

Figure 4. IR spectra show the relaxation of the nitro group for DO3 in PMMA as a function of time. (a) symmetrical stretching. Curves shown from top to bottom are: right after poling, 40, 120, 570 minutes after poling, and pristine. (b) asymmetrical stretching. Curves shown from right to left are: right after poling, 570 minutes after poling, and pristine.

Figure 5. Reflectance changes at wavenumbers which correspond to NH_2 scissoring as a function of time after poling for PMMA doped with MNA and DO3.

Figure 6. Relaxation of poled PVCN doped with 30% CNNB-R at 70°C. Curves shown from top to bottom are: right after poling, 5,10,20,80 minutes of annealing, pristine.

Figure 7. Relaxation of poled and UV irradiated PVCN doped with 30% CNNB-R at 70°C. Top and bottem curves are right after poling and pristine samples respectively. Overlaped curves which are shown in the middle are for 5,10,20,80 minutes of annealing after poling.

Incident IR radiation

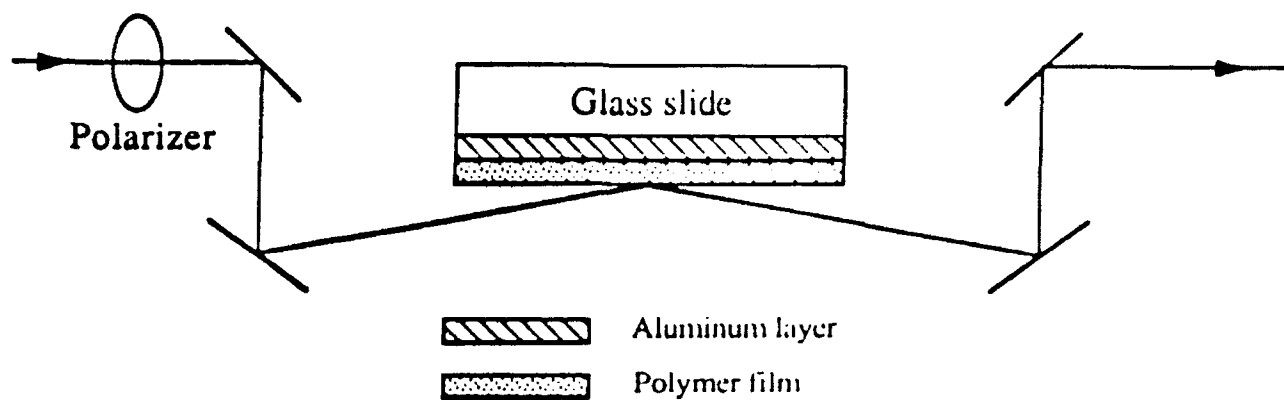


Fig 1

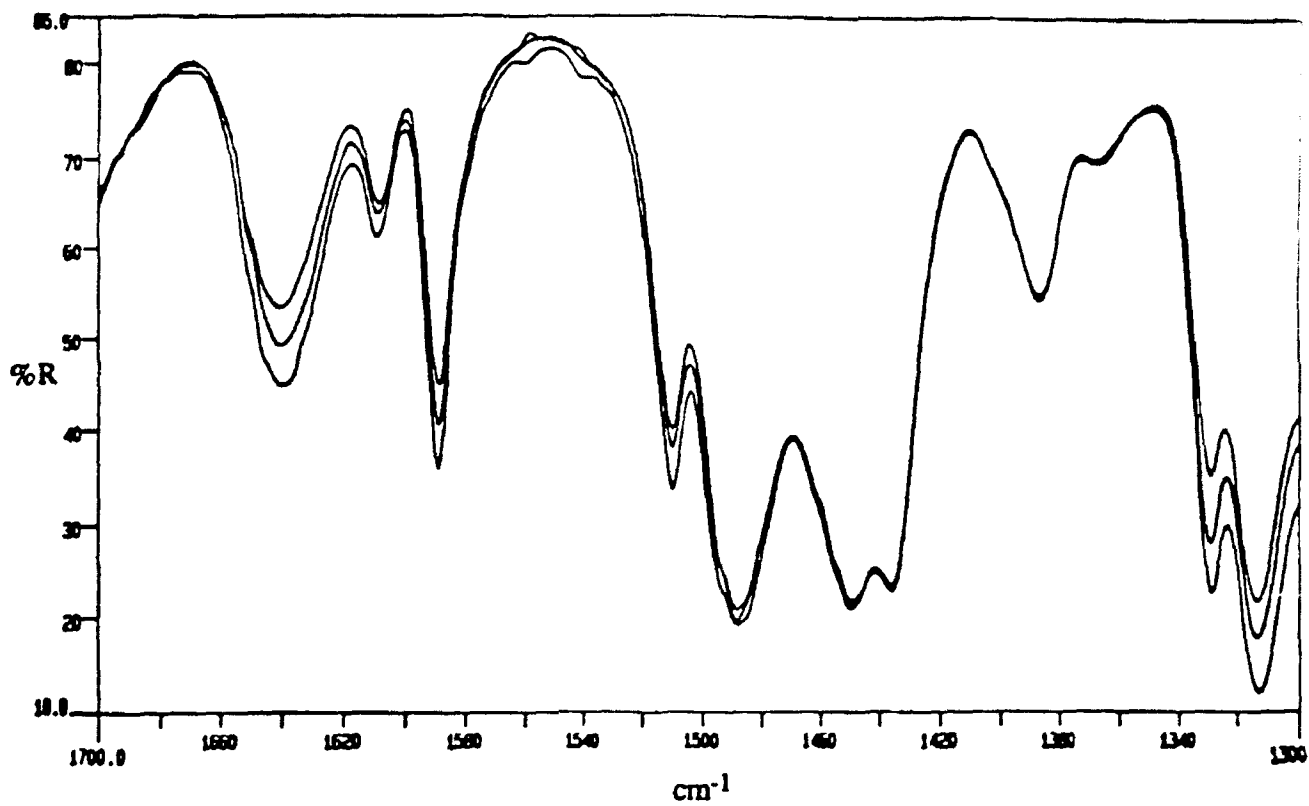


Fig 2

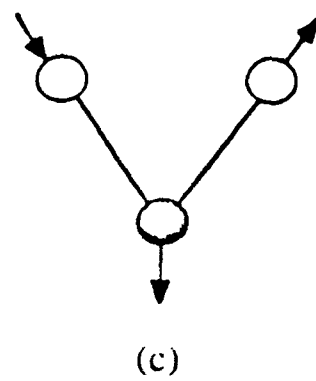
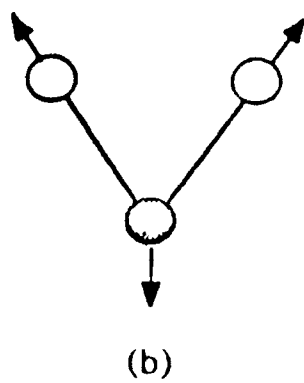
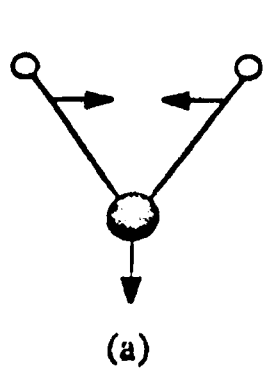
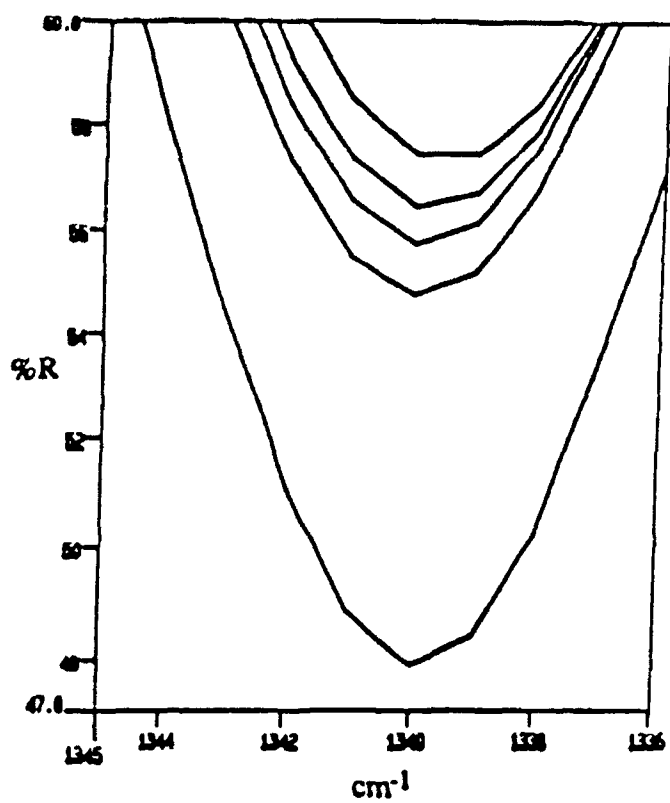
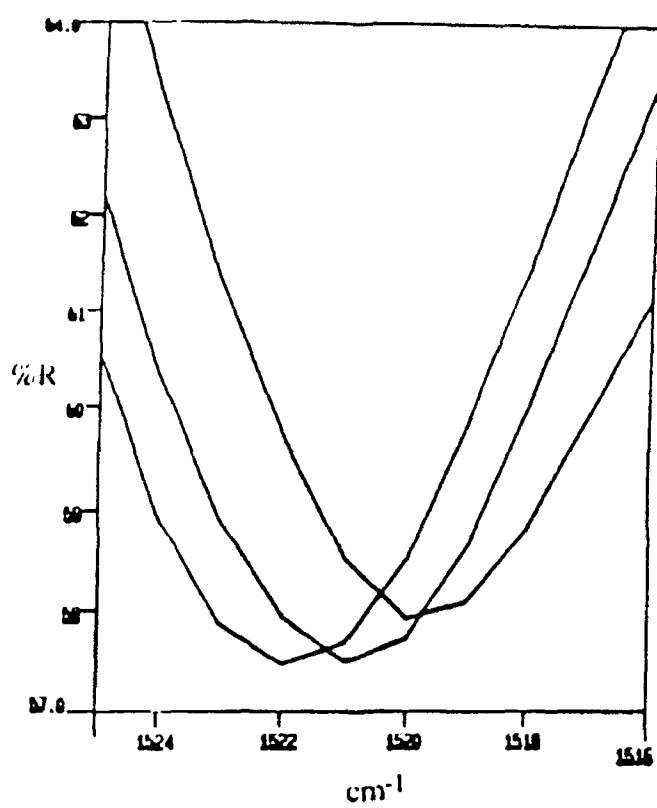


Fig 3



(a)



(b)

Fig 4

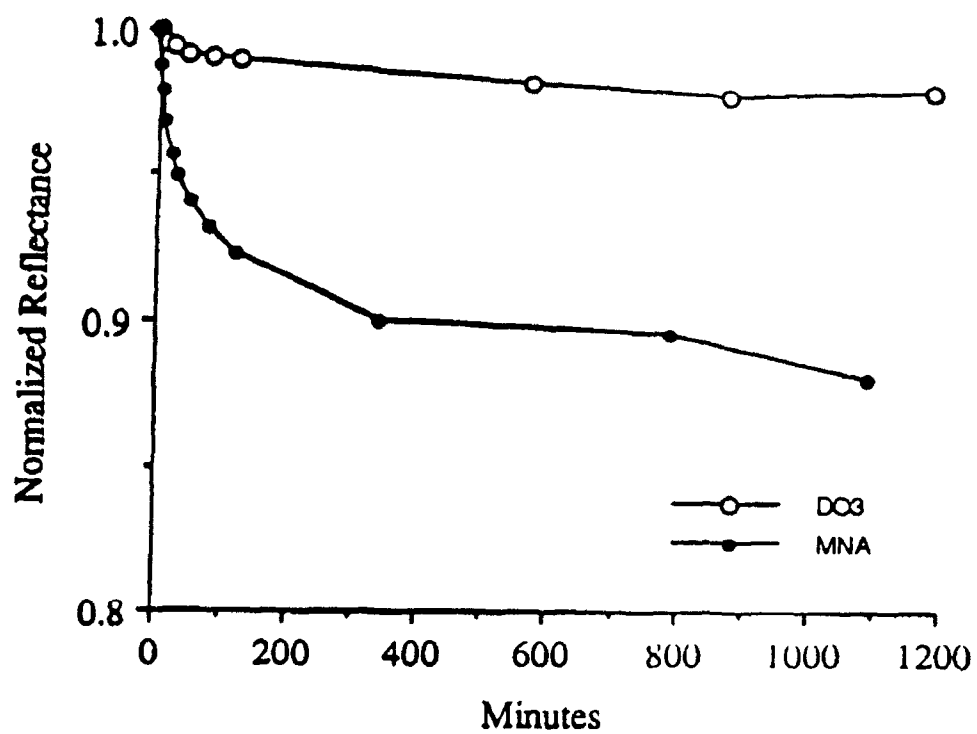


Fig 5

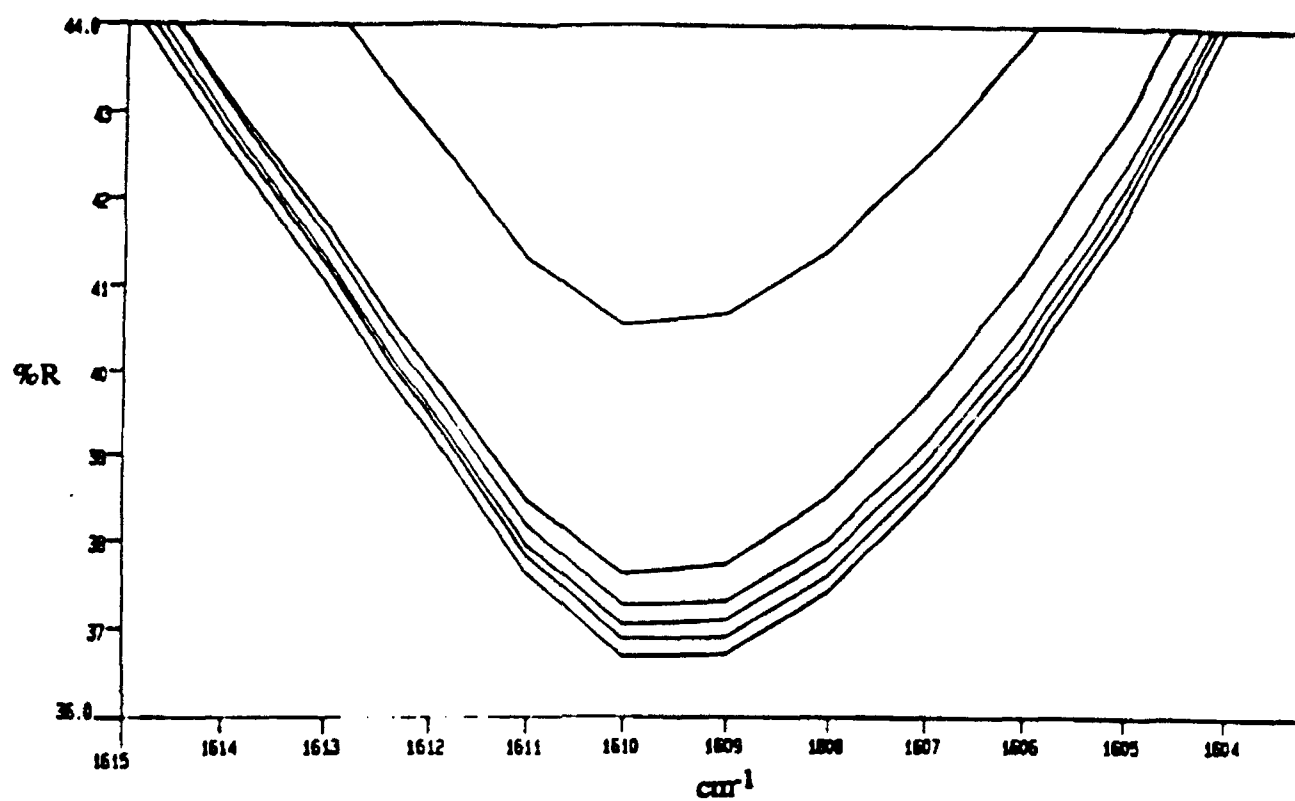


Fig 6

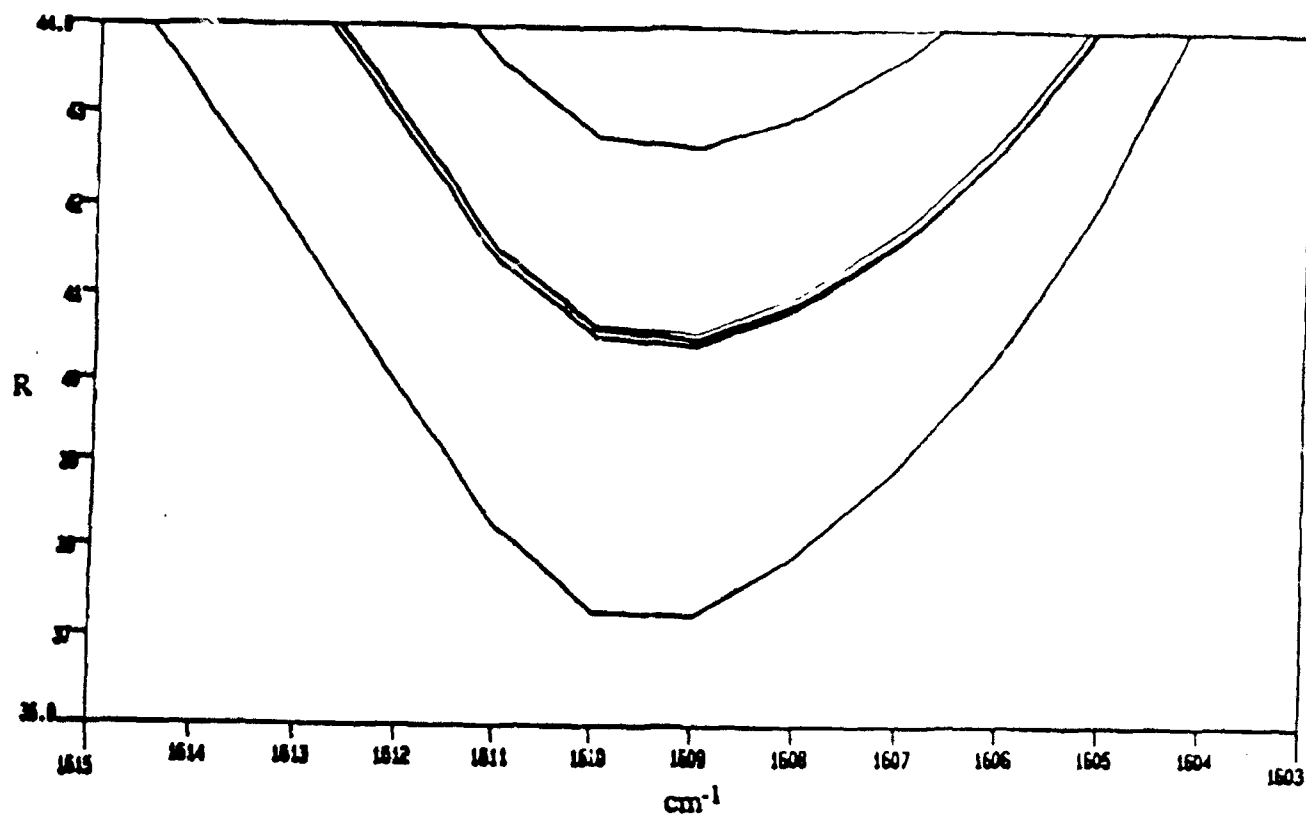


Fig 7