

## Spectroscopic studies of paranitroaniline (PNA) doped in polymeric matrices PMMA and PVA

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**Abstract** : The absorption spectra of paranitroaniline (PNA) doped in thin films of PMMA (polymethyl methacrylate) and PVA (poly vinyl alcohol) have been reported. The extents of poling have been estimated by changes in absorption spectra. The changes appear mainly in the form of shifts in the position of band maxima and absorption coefficients. This understanding is necessary for the development and design of second-order nonlinear optical polymeric devices.

**Keywords** : Paranitroaniline, absorption spectra, poling.

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Poled polymer films doped with optically non-linear organic chromophores have been the subjects of extensive studies in recent years [1–3]. These polymers have attractive mechanical properties, high damage thresholds, large non-linear coefficients and ease of processing relative to crystalline materials that facilitate their use in practical devices. When these doped polymers are poled, the chromophores are aligned in a particular direction to provide high nonlinearities [4,5]. Significant changes are observed in the optical properties of these polymeric films *viz.* shifts in the absorption and emission peaks as well as changes in the intensities when they are poled. A quantitative analysis of these spectroscopic changes can be utilized to determine the extent of poling. In the present work, we report the optical properties of poled PNA doped thin films of PMMA (polymethyl methacrylate) and PVA (poly vinyl alcohol) by absorption spectroscopy. The effect on the absorption characteristics on poling the films has also been discussed.

Paranitroaniline (PNA) was taken from Aldrich and used without further purification. The host polymers PMMA (polymethyl methacrylate) and PVA (poly vinyl alcohol) were also from Aldrich. Solutions of these in appropriate

proportions were made in chloroform and acetone respectively. Thin films of (2–3  $\mu\text{m}$ ) thick were prepared by cast method. Organic solvents for spectroscopic measurements were of spectroscopic quality and were used without further purification. The absorption spectra of the films were measured on JASCO V-500 UV-visible spectrophotometer.

Corona poling method [3,6,7] was used to align chromophore in the polymeric films. The experimental arrangement for corona poling is schematically shown in Figure 1. A sharp tungsten needle at high state potential was positioned above a grounded electrode onto which the polymer film was coated. Onset of discharge occurs at a particular voltage, depending on the diameter of the needle tip and atmospheric conditions. Ions are created and deposited on top of the bare surface of the polymeric film. This creates an electric field which is defined by the surface potential and the film thickness. The major advantage of this method is the fact that only the bare, low conductivity polymer surface is charged. Impurities, defects and pinholes, therefore, cause only relatively small local currents and do not result in short circuiting the whole sample. The 8–10 KV power supply has been used for applying high voltage. In each case, films are

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poled for 30 minutes at a temperature slightly higher than room temperature.

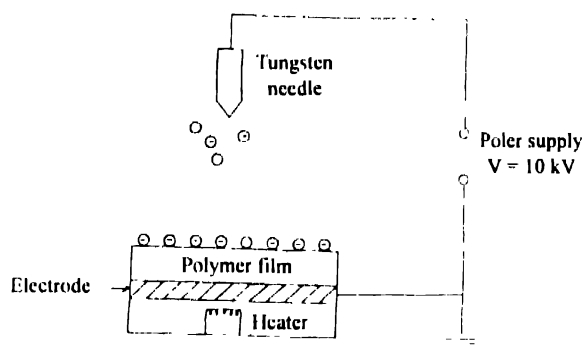


Figure 1. Corona poling setup

Figure 2 shows absorption spectra of unpoled and poled PMMA doped film of PNA, recorded under similar geometrical conditions. The spectrum is broad banded and is analogous to the spectrum in methanol [7]. The absorption

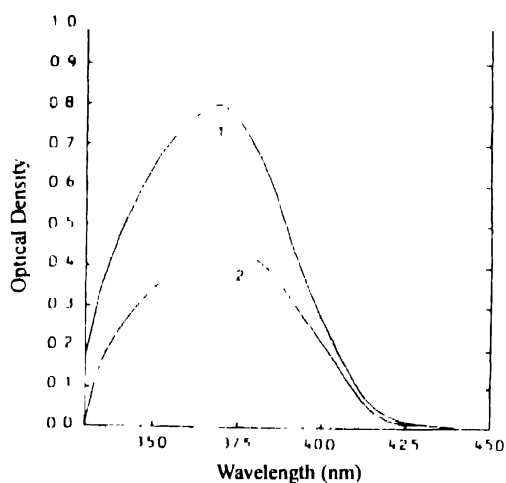


Figure 2. Absorption spectra of PNA in PMMA (1) before poling, (2) after poling

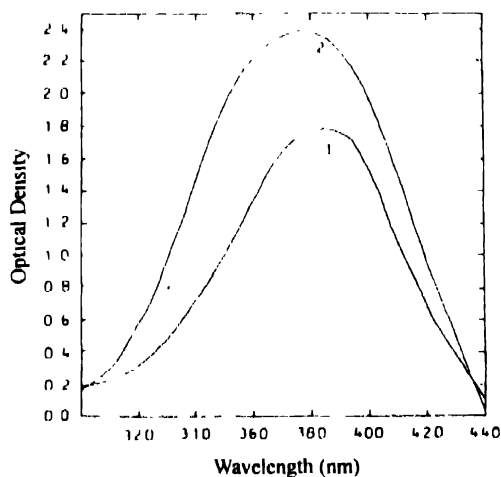


Figure 3. Absorption spectra of PNA in PVA (1) after poling, (2) before poling

peak lies at 372 nm. Absorption spectra of unpoled and poled PVA doped film on PNA are given in Figure 3. The absorption peak in this matrix is at 384 nm, the spectral features are same as in PMMA. Band positions, alongwith the shifts and the intensity ratios before and after poling in different matrices are given in Table 1.

Table 1. Absorption peak positions and intensity ratios of PMMA and PVA films doped with PNA before and after poling

| Compound | Polymeric matrix | Absorption peak ( $\text{cm}^{-1}$ ) |              |       | Ratio of intensity |
|----------|------------------|--------------------------------------|--------------|-------|--------------------|
|          |                  | Before poling                        | After poling | Shift | Before/after       |
| PNA      | PMMA             | 26881                                | 26737        | 144   | 1.88               |
|          | PVA              | 26041                                | 25974        | 67    | 1.37               |

It is seen from the figures and the table that on poling, thin films of both PMMA and PVA show two electrochromic effects: First, decrease in absorbance, and second, red shift in the absorption maxima. The absorption shift is higher in PMMA ( $144 \text{ cm}^{-1}$ ) than in PVA ( $67 \text{ cm}^{-1}$ ). The intensity ratios are 1.88 in PMMA and 1.37 in PVA respectively. The order parameter is a standard scale to measure the orientation of the chromophores. The ordering parameters of a poled polymeric film is defined by  $(1 - A/A_0)$ , where  $A$  and  $A_0$  are absorbances after and before poling, respectively, and is commonly used to describe the poling efficiency [8]. The ordering parameters are 0.53 and 0.72 for PMMA and PVA doped film of PNA, which suggest that these polymers are efficiently poled. No emission studies of PNA doped films could be possible because the films were nonfluorescent at room temperature.

Paranitroaniline (PNA) is a well known second-order nonlinear optical material in which one donor ( $\text{NH}_2$ ) and acceptor ( $\text{NO}_2$ ) are located at the opposite ends of the conjugated system [9]. The substituents donate or accept  $\pi$ -electrons from skeletal benzene ring thereby removing the center of symmetry and exhibiting large nonlinear effects. The second-order polarizability ( $\beta$ ) for PNA has been calculated by various techniques. By EFISH technique,  $\beta$  for PNA is  $38 \times 10^{-30} \text{ esu}$  [10] while the Solvatochromic technique gives a value of  $\beta$  equal to  $18 \times 10^{-30} \text{ esu}$  [11] by using two-level model. A comparison with ortho and metanitroaniline ( $\beta$  values are approximately  $4 \times 10^{-30}$  and  $10 \times 10^{-30} \text{ esu}$  [9] respectively) suggest that PNA is highly non-linear and is a better molecule for non-linear applications.

The reduction in absorption and the red shift in the absorption peaks in PMMA and PVA films doped with PNA might be due to various non trivial and trivial mechanisms. These are (i) unidirectional alignment of the molecules, (ii) aggregation effects and (iii) electrochromic effects. In the

case of unpoled films the molecules are randomly oriented, the scattering losses of light during the course of travelling through the film are expected to be higher. However, poling of films creates a unidirectional alignment of the chromophores, which can reduce the scattering losses. The result will be an increase in the amount of the transmitted light (or in other words decrease in the absorption profile). With the reorientation of the molecules to a more perpendicular arrangement with regard to the film surface, the transition moments of the chromophores are oriented, in general more normal to the film. Since transmitted light normal to the surface has its electric vector parallel to the film, its interaction with the normal chromophores is reduced and the resulting spectra show both a decrease in intensity and a slight wavelength shift. The energy distribution from the interaction of the dipole moment and the electric field causes an electrochromic shifts of both the ground and excited state energy levels. Since the excited state dipole moment is usually greater than the ground state dipole moment the overall shift is to lower energy *i.e* longer wavelength. Similarly, other reasons like the chromophore decomposition due to heat, oxidation or molecular aggregation under the corona poling conditions may cause the reduction of absorption as well as shift in the absorption peak.

Theoretical expressions for dichroism and electrochromism of macromolecules in solution from a semiclassical treatment of polarized absorption of molecules oriented by Yamaoka and Charney [12] with particular emphasis on rigid molecules having axial symmetry. The parameters *viz.* reduced dichroism and reduced electrochromism were calculated under various field conditions. Page *et al* [8] have also made electrochromic waveguide studies of corona poled electro-optic polymer films. They have also observed changes in absorption and the electrochromic shifts in the absorption spectra of DANS, phenol blue and disperse red 1. They have used the model in which the chromophores are supposed be dissolved uniformly in the polymer host of static dielectric constant and the oriented forces are assumed to due only to the dye molecule. Also it was assumed that during optical absorption (of charge transfer band) the change in dipole moment occurs

in the direction of ground state dipole moment. In the frozen oriented sample application of an electric field causes a shift of the charge transfer band frequency, leading to a change in the refractive index. In the present case also similar effects have been obtained for PNA in both PMMA and PVA. However, further investigations, mainly polarization studies, will be required for the detailed investigations of both the orientation and electrochromic effects.

Optical nonlinear organic materials doped into thin polymeric films can be highly useful for future nonlinear applications. Poling of these films increases their efficiency. Spectroscopic studies like the absorption spectroscopy can be used to measure the extent of poling of these films. In the present investigation, PMMA and PVA films doped with PNA show a decrease in absorption as well as shift in the absorption peaks. A more quantitative investigation is underway.

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