Electrical and optical studies of corona poled 4-hydroxy-4′-nitroazobenzene doped polymethylmethacrylate films

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Guest-host polymeric systems with 4-hydroxy-4′-nitroazobenzene as guest and polymethylmethacrylate (PMMA) as host have been prepared by taking different concentrations of the guest and characterized by observing their electrical and optical behaviour. The prepared guest-host system has been found to have large band gap ~2.86 eV and transmission over visible range. Pure polymer (PMMA) was not found to show any observable electrical non-linearity whereas mixing of dye (guest) has shown remarkable effect on its non-linear electrical behaviour. Moreover, the model guest-host blend (4-hydroxy-4′-nitroazobenzene/PMMA) has been found to exhibit desired order of non-linearity by optimizing the concentration of guest, poling current and poling temperature.

Keywords: Polymethylmethacrylate films, Electrical properties, Optical studies, Molecular polarizability, Birefringence
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1 Introduction

In recent years, organic and polymeric materials instead of inorganic have emerged as promising candidates for advanced non-linear devices and system applications including planar waveguides1-4, optical fibers5 and electro-optic switches6-8. This interest has arisen from the promise of extraordinary optical, structural and mechanical properties of certain organic materials and from the fundamental success of molecular design performed to create new kinds of materials9. From optical standpoint, organic materials offer temporal responses ranging over fifteen orders of magnitude, including large non-resonant electronic non-linearities (fsec-psec), thermal and motional non-linearities (µsec-sec) and photochemical non-linearities (psec-sec). Usual criteria for preferring organics are: (i) Most polar organic materials have a large birefringence due to the anisotropic nature of molecular polarizability due to delocalized π-electron orbital. The electron clouds of these π-electron systems are readily influenced by the electric field of incident light giving rise to high polarizabilities10. (ii) Small changes in molecular structure can have large effect on crystal symmetry. Hence, addition of some chemical groups creates a high degree of asymmetry, creating donor/acceptor groups into the conjugated systems giving rise to high non-linearities11. (iii) The second order non-linear susceptibility coefficient $\chi^{(2)}$ for organic materials has been found to be one or two orders of magnitude greater than inorganic materials.

Additionally, organic and polymeric materials can exhibit high optical damage thresholds and broad transparency ranges. Structurally, materials can be made as thin or thick films; mechanically the materials can be strong and resistant to radiation, shock and heat. The collective properties of these extraordinary materials show great promise towards improving the performance of existing electro-optic and non-linear optical devices.

It is well-known that to create useful second order susceptibility $\chi^{(2)}$ as would be required for frequency doubling or electro-optic modulation, it is necessary to create a preferred direction in a medium. In the case of amorphous polymeric materials, no second order effects could be achieved (due to presence of inversion symmetry) without considering the poling process. Poling of organic polymeric materials can be accomplished by raising the temperature of the polymeric system to close to its glass transition temperature $T_g$, while simultaneously applying a large static electric field. After equilibrium is attained, the temperature is lowered slowly to room temperature while the field remained on. For the application of electric field, either the metal electrodes or the corona poling technique is used. Recently, it has been observed that corona poling12 is much more useful for
thin films since the lack of a lateral conduction path across the surface of the film prevents local defects from causing a macroscopic short circuit\textsuperscript{13-15}. The poling fields of the order of the dielectric strength of the polymer can be applied.

The starting point for the development of effective non-linear optical (NLO) polymers is the synthesis of NLO chromophore possessing large molecular hyperpolarizability. At the molecular level, the NLO chromophore must exhibit exited state close in energy with large dipole moment difference between these states. To fulfill these requirements, the NLO chromophore must possess electron donating group and electron withdrawing group connected by highly conjugated $\pi$-electronic system. After that these chromophores are incorporated into polymeric backbone either covalently or by guest-host systems\textsuperscript{16-17}. The simplicity in preparation of non-covalently bonded guest-host materials might be an attraction if suitable stability of polar alignment can be attained. Hydrogen bond associations are one such example, whereby stability of the alignment may be enhanced\textsuperscript{18-20}.

In the present study, we have synthesized 4-hydroxy-4$'$-nitroazobenzene containing -OH group as electron donating and $-\text{NO}_2$ group as electron withdrawing group connected by conjugated system. The guest-host samples were prepared with varying concentration of guest (4-hydroxy-4$'$-nitroazobenzene) in the host (PMMA) to study their optical and electrical properties.

2 Experimental Details

2.1 Synthesis of 4-hydroxy-4$'$-nitroazobenzene (guest)

0.5 g (5.4 mmol) of aniline was dissolved in a mixture of 1.5 ml of HCl and 1.5 ml of H$_2$O contained in a 25 ml conical flask. To this, a cold solution of 0.41 g (5.9 mmol) of sodium nitrite in 1 ml of H$_2$O was added slowly with constant stirring. The temperature of the solution was not allowed to rise above 2°C. Phenol of 0.51 g (5.4 mmol) was dissolved in 3 ml of ice cooled 10% NaOH. Diaziotized solution was added slowly to the phenol solution with vigorous stirring at 0-2°C. After the addition of diazonium salt solution, the reaction mixture was allowed to stand in an ice-bath for 30 min followed by addition of HCl to neutralize the solution. The solution was filtered, washed with water until free from acid and dried in vacuum. Fig. 1 shows the chemical reaction, which yielded 4-hydroxy-4$'$-nitroazobenzene used as guest.

2.2 Preparation of 4-hydroxy-4$'$-nitroazobenzene-PMMA guest-host matrix

The NLO guest-host systems were prepared by mixing 4-hydroxy-4$'$-nitroazobenzene and polymethylmethacrylate (PMMA). PMMA (host) of amount 1.0 g and 0.01 g of 4-hydroxy-4$'$-nitroazobenzene (guest) were separately dissolved in dichloromethane. These two solutions were then mixed and stirred for about 20 min. The homogeneous solution, thus, formed was evaporated to remove the solvent. The resulting concentrated sample was dried at room temperature for ~24 hr. This yielded 1% (by wt.) guest-host system. Similarly, 0.8, 0.6, 0.4, and 0.2% guest-host systems were prepared by this method.

2.3 Thin films and corona poling

Thin films of the guest-host systems, with different concentrations of guest were grown on the cleaned microscopic glass slides by vacuum deposition technique at a vacuum of 10$^{-6}$ mm/Hg in the vacuum coating unit (NIRVAT EU-300). The thickness of guest-host system (4-hydroxy-4$'$-nitroazobenzene-PMMA blend) was controlled by quartz film thickness monitor and was kept at about 1000Å. Thin films of guest and host materials alone were also prepared for comparison. These thin films were used for studying their optical absorption, structural and electrical properties. Optical UV-Vis spectra and electrical measurements of thin films were recorded with the help of UV 3400 Hitachi spectrophotometer and SMU-236 Keithley source measure unit. The IR spectra of the films were recorded on Paragon 1000PC FTIR spectrophotometer.

Since polymers lack crystalline alignment, the NLO moieties in the prepared films are randomly oriented, making their arrangement centrosymmetric, i.e., for the films to exhibit first order electro-optic effects or
second harmonic generation (SHG), the centrosymmetry has to be removed. This is conveniently done by applying high electric field, which serves to orient the chromophores with their dipole moments parallel to the applied field and eventually parallel to the light beam. This process is known as poling. In Fig. 2, we show our arrangement for corona poling. A high voltage was applied to a needle, positioned a short distance (1 cm) above the surface of the film. An electrode placed below the film was connected to earth. The corona discharge from the needle point results in the build-up of a large static charge on the surface of the film, which induces a strong electric field across the film and produces the desired orientation of the polar molecules within the film. It has been observed that appreciable polar order can be achieved when poling is carried out by heating the active material close to the glass transition temperature \( T_g \), so that the motion of the polymer chains is possible, under the application of a strong dc electric field across the sample. This field orients the highly polar non-linear optical molecules via the interaction with their permanent dipole moments. The temperature was then lowered back to well below \( T_g \), with the field still applied so that relaxation of the aligned molecules is restricted by the glassy nature of the polymer. To see the effect of poling, electrical behaviour of the blend was observed at different values of poling current and poling temperature and the effect of concentration of guest on electrical behaviour of the guest-host system has also been investigated.

3 Results and Discussion

3.1 IR studies

The IR spectrum of guest is shown in Fig. 3. The IR spectrum shows peak at 3415 cm\(^{-1}\) due to \(-\text{OH}\) group. The peaks observed at 1345 cm\(^{-1}\) and 1515 cm\(^{-1}\) are due to symmetric and asymmetric stretching vibrations of \(-\text{NO}_2\) group, respectively, supporting the structure of guest. IR spectra of the host (PMMA) and that of guest-host blend with KBr pellets are shown in Figs 4 and 5. The position of the IR peaks of host, 1732 cm\(^{-1}\) (C=O str.) and 1240 cm\(^{-1}\) (C-O str.) are retained after mixing with the guest (4-hydroxy-4′-nitroazobenzene) but the peaks observed in the IR spectrum of guest (4-hydroxy-4′-nitroazobenzene) at 3413 cm\(^{-1}\) (\(-\text{OH}\) group) and 1345 cm\(^{-1}\) as well as at 1515 cm\(^{-1}\) (NO\(_2\) group) are not retained in the IR spectrum of guest-host matrix due to very low concentration of guest in the composite.
3.2 Optical studies
UV/Vis absorbance spectra of the blend of 4-hydroxy-4′-nitroazobenzene/PMMA were recorded in the wavelength range 200-800 nm (Fig. 6) by dissolving it in dichloromethane (DCM). Absorption spectrum for pure host (PMMA) shows peaks at 238 and 274 nm (curve A). Peaks at 242, 371 and 478 nm (curve B) have been observed for guest (4-hydroxy-4′-nitroazobenzene) whereas for guest-host system, the peaks were observed at 241 and 372 nm (curve C). From the observed peaks, it can be inferred that the addition of guest (4-hydroxy-4′-nitroazobenzene) with the host (PMMA) has made a remarkable effect on absorption properties of the guest-host system. The pure guest has large absorption peak in the visible region (at 478 nm), while the guest-host system is almost transparent in the whole visible region, except small absorption over the blue wavelengths. The absorption spectra were also taken in the thin film form and no appreciable change was noticed.

In order to see the stability of the guest-host system, we have taken the absorption spectra of the blend after 6 months. As shown in Fig. 7, the absorption peaks are almost at the similar positions, confirming the stability of the system. The pure guest has large absorption peak in the visible region (at 478 nm), while the guest-host system is almost transparent in the whole visible region, except small absorption over the blue wavelengths. The absorption spectra were also taken in the thin film form and no appreciable change was noticed.

In order to see the stability of the guest-host system, we have taken the absorption spectra of the blend after 6 months. As shown in Fig. 7, the absorption peaks are almost at the similar positions, confirming the stability of the system. The energy band gap of the polymer was determined by measuring the variation of optical absorption with the wavelength in the range 200-800 nm and using the relation \[ \alpha = (h\nu - E_g)^{1/2} \]
where \( \alpha \) is the absorption coefficient, \( h\nu \) the incident light energy and \( E_g \) is the energy band gap, which is equal to \( h\nu \) when \( \alpha \) is equal to zero. From Fig. 8, the energy band gap of guest-host system (4-hydroxy-4′-nitroazobenzene/PMMA) comes out to be 2.86 eV.

3.3 Electrical studies
The \( I-V \) characteristics of unpoled thin films of the pure host, guest and guest-host blend (0.6%) are shown in Fig. 9, which show non-linear behaviour. The \( I-V \) curve of guest-host blend is almost symmetric along the X-axis. Poling is done to remove the inherent centrosymmetry of the polymeric system. Various combinations of poling temperature and poling current were tried and the conditions and the parameters for poling were optimized. For this purpose, in Fig. 10, we show \( I-V \) measurements for the guest-host system (guest concentration 0.6%, poling current 60 \( \mu \)A) at different poling temperatures below \( T_g \). Curve A shows the electrical behaviour of
the thin film at room temperature. The curve indicates two peaks 7 V and –7 V, showing symmetrical behaviour for +ve and –ve fields. Curves B and C are for the sample poled at 60°C and 70°C, respectively, indicating the combination of even order of harmonics with distorted form at higher temperature. Curve D is showing non-linear behaviour of the blend poled at 80°C. At low voltage, no higher order of harmonics is generated but at high voltage the sample is found to exhibit the combination of even order of harmonics.

In order to see the effect of variation of corona poling current, keeping concentration of guest and poling temperature constant, the I-V characteristics of thin film of guest-host system (0.6% guest) are shown in Fig. 11 before and after the poling at room temperature. Curve A shows the electrical behaviour of the sample before poling. It is seen that there is non-linearity in I-V behaviour but no clear indication of higher order of harmonics. Poling of guest-host system at 40 µA (curve B) polarizes the chromophores thereby making the sample to exhibit the combination of even and odd orders of harmonics. Increasing poling current to 60 µA (curve C) gives rise to the presence of second order harmonics in the I-V curve. A further increase in corona poling current to 70 µA (curve D) helps the guest-host system to exhibit the combination of second and fourth harmonics, however, the magnitude of the various harmonics remains similar in all cases.

In Fig. 12, the effect of variation of guest concentration on I-V characteristics of the blend, keeping corona poling current 60 µA at room temperature is shown. The I-V characteristic of the polymer blend with guest concentration 0.2% is shown in curve A, indicating the presence of combination of even order of harmonics. The electrical behaviour of the polymer blends with guest concentrations 0.4, 0.6, 0.8 and 1.0% is shown in curves B, C, D, and E, respectively. The curves indicate the presence of combination of even and odd
order of harmonics with slight shifting of peak positions.

4 Conclusions
The electrical and optical studies have been used to gain information concerning the characterization of second order effects in model guest-host (4-hydroxy-4′-nitroazobenzene-PMMA) system. The prepared guest-host system was found to have amorphous structure with a large band gap (~2.86 eV) and a high optical transparency in the visible range, except over the blue wavelengths. The poled guest-host blend shows strong non-linearity and desired order of non-linearity can be achieved by optimizing the concentration of guest, poling current and temperature. Thus, vacuum deposited thin films of 4-hydroxy-4′-nitroazobenzene-PMMA matrix have tremendous potential to be used as non-linear optical material in photonics and optoelectronic devices.

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References