

SHG relaxation behaviour in m-nitroaniline doped PMMA guest-host system

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ABSTRACT

In present work, we have reported the second harmonic generation (SHG) property on the *Guest-Host* system based on optical grade poly(methyl methacrylate) (PMMA) and m-Nitroaniline (m-NA) for their use in optoelectronic devices. SHG signal of the m-NA doped PMMA freestanding films was determined using Nd:YAG laser by varying input energy from 6 mJ to 18 mJ. For evaluating SHG, films were poled at various temperatures to align the m-NA guest molecules in PMMA host matrix. Doped films were also characterized isothermally by thermogravimetric analysis (TGA) to get the information about loss of m-NA molecules at poling temperatures. It was found that there is no change in glass transition temperature. SHG intensity increases as the poling temperature increases. However, SHG signal intensity decreases as the decay time of poled films increases. After one week of poling more than half of the original SHG intensity is retained. The decay in SHG intensity might be attributed to the relaxation of m-NA molecules from thermodynamic unstable state to the equilibrium state. Copyright © 2010 VBRI press.

Keywords: Guest-host system, SHG, m-nitroaniline, PMMA, relaxation.



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Introduction

Polymeric guest-host systems have emerged as strong candidates for various futuristic optoelectronic devices in comparison to their inorganic counterparts due to their large optical non-linearity, lower dielectric constant, ultrafast and broadband electronic responses. They provide durability, environmental protection and packaging advantages that are not provided by inorganic nonlinear optical (NLO) materials. Moreover, they are easier to prepare and process than the inorganic counterpart such as LiNbO_3 .

High speed communication in the high technology computer fields is achieved via optical interconnections based on the application of a poled guest-host system in which a NLO guest molecule is incorporated into an

organic host polymer matrix. The guest-host system is basically an inter- and intra-molecular interactive system, which retain permanent dipole ordering with careful control of poling above glass transition temperature (T_g). Poling above the T_g alters the random orientation of the NLO molecules in the polymer film and develops a net alignment of molecules in the polymer film. The polymeric guest-host systems derive their NLO properties from the hyperpolarizability of chromophores [1-4]. Singer et al. reported the second order nonlinear coefficient (d_{33}) of azo dye disperse red (DR1) doped poly(methyl methacrylate) (PMMA) approximately five times that of potassium dihydrogen phosphate (KDP) [5]. Subsequently, they have studied the relaxation behaviour in SHG at various temperatures [6]. Having et al. reported the electrochromism of dye polymer mixtures consisting of a small amount of dye dissolved in PMMA and poled above the T_g of polymer [7]. The major problem of the guest-host system is the relaxation (decay) of the electro-optic activity with time. The relaxation behaviour of 2-methyl-4-nitroaniline (MNA) doped PMMA has been discussed [8].

The organic m-nitroaniline (m-NA) is well known for its nonlinear and electro-optic effects [9-13]. Therefore, recently we have investigated the thermal, structural and second harmonic generation (SHG) properties of m-NA doped PMMA films as a function of m-NA concentration [11]. The SHG is a NLO process that results in the conversion of an input coherent optical wave into an output coherent wave of twice the input frequency having same pulse width as that of input wave and optical intensity is proportional to the square of the input intensity. To the best of our knowledge, first time we report the effect of poling temperature on SHG intensity and relaxation of SHG intensity at room temperature with respect to time.

Experimental

Preparation of freestanding films

Optical grade PMMA was synthesized by the method reported in previous paper [11]. The inherent viscosity of PMMA determined by Ubblohde viscometer was 0.50 dl/g, which indicates the film forming property. Tough, transparent and flexible films of PMMA doped with 10, 20 and 30 wt% sublimed m-NA were prepared by solution cast method using toluene as solvent. The solvent was allowed to evaporate under ambient conditions until the film hardens. The film were then removed and placed in vacuum oven for 4-5 h at 100 °C to remove all residual solvent. After drying colored transparent films were obtained and subjected to optical and thermal studies. To align the NLO active m-NA molecule in the amorphous matrix a contact electrode poling of doped films was carried out. For this controlled and doped polymer films were heated from room temperature to 100, 120 and 140 °C. The sample was poled for 30 min at a given poling temperature with an applied dc electric field of 5 KV/cm. The samples were then cooled to room temperature and the poling field was subsequently removed, which results in a system where the dipole moment of m-NA guest molecule is aligned in the electric field direction within the PMMA host matrix.

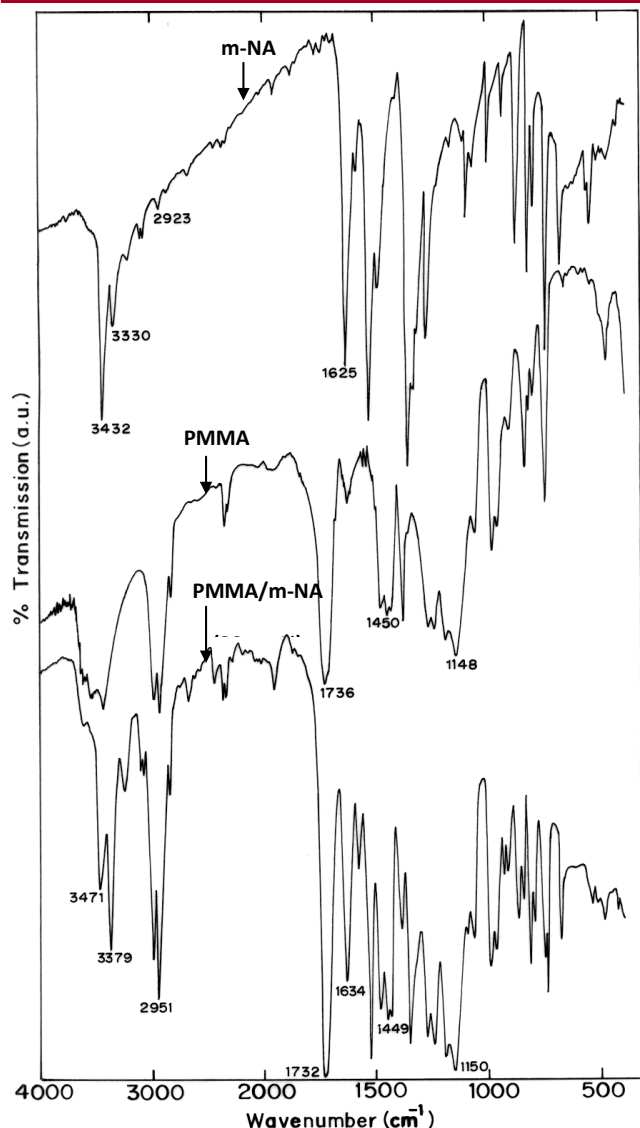


Fig. 1. FTIR spectra of m-NA, PMMA and m-NA doped PMMA freestanding films.

Characterization of doped films

The FTIR spectra of m-NA, PMMA and 20 wt% m-NA doped PMMA films were recorded on Perkin-Elmer FTIR spectrometer (SPECTRUM 2000). The scanning range is from 4000 to 400 cm^{-1} . This was carried out to find out the type of interactions between the m-NA and PMMA molecules. The isothermal thermogravimetric analysis (TGA) of the samples was conducted on a Mettler-Toledo 851^o at 120 and 140 $^{\circ}\text{C}$ for 60 minutes in air atmosphere. This was carried out to check the thermal stability of the m-NA doped PMMA films at poling temperature and time. The effect of m-NA doping on glass transition temperature (T_g) of PMMA was studied on DuPont Instruments 910 DSC. The samples placed in an aluminum pan were heated from 30 $^{\circ}\text{C}$ to 300 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ in nitrogen atmosphere. For evaluating SHG intensity, poled m-NA doped PMMA films were illuminated with a Q-switched Nd: YAG laser (wavelength 1064 nm, pulse width 40 ns and 1pps) beam. The generated SHG signal at 532 nm was separated from the fundamental wave by using

filters. SHG signal was measured relative to urea. SHG signal of the poled films was measured as a function of laser input energy and poling temperatures using the experimental set-up as reported elsewhere [14].

Results and discussion

The FTIR spectra of m-NA, PMMA and doped freestanding films are shown in **Fig. 1**. Characteristic absorption bands of m-NA are obtained at 3432, 3330 ($-\text{NH}_2-$), 2923 ($-\text{NH}-$), 1625 ($-\text{NH}_2-$), 1523 and 1349 cm^{-1} . FTIR peaks at 3330 and 3432 cm^{-1} is corresponding to symmetric and asymmetric stretching modes of free NH_2 group, respectively. The peak at 2923 cm^{-1} is due to N-H stretching mode. NO_2 stretching modes are observed at 1524 and 1349 cm^{-1} . Absorption bands of PMMA at 1148, 1450, 1736 and 2953 are due to ether band, C-H bending of CH_2 group, carbonyl group and C-H stretching, respectively. As shown in **Fig. 1**, there is significant shift in the carbonyl band from 1736 to 1717 cm^{-1} of PMMA. Symmetric stretching of NH_2 is shifted from 3330 to 3379 cm^{-1} . Asymmetric stretching of NH_2 group shifted from 3432 to 3471 cm^{-1} . The significant shifting of these bands suggests a hydrogen bonding formation between the amino group of m-NA and the carbonyl group of PMMA. The m-NA doped PMMA films also show additional bands in the region of 3220 to 3250 cm^{-1} . This may be due to hydrogen bonding between m-NA and PMMA. It is also noted that the N-H stretching mode at 2923 cm^{-1} is disappeared [11].

Fig. 2 shows loss of weight at poling temperatures as a function of time (seconds) for pure m-NA and 20 wt% m-NA doped PMMA films. Since for poling, m-NA doped PMMA films were heated at 100, 120, and 140 $^{\circ}\text{C}$ for 30 minutes under applied constant electric field. Therefore, thermal stability of the m-NA and m-NA doped films were determined at these poling temperatures to know the loss of m-NA during poling. As shown in **Fig. 2**, the weight loss of m-NA run at 120 $^{\circ}\text{C}$ for 30 minutes is about 16 % whereas loss of m-NA run at 140 $^{\circ}\text{C}$ for 30 minutes is about 20 %. The weight loss may be attributed to the sublimation of m-NA molecules. The weight loss for 20 wt% m-NA doped PMMA film run at 120 $^{\circ}\text{C}$ for 30 minutes is only about 2.2 %. This shows substantial improvement in thermal stability of the doped films compared to that of pure m-NA crystals.

As shown in **Fig. 3**, pure PMMA has T_g at 123.7 $^{\circ}\text{C}$ and T_g of doped PMMA films did not change significantly. This is in contrast to 4-(N,N-dimethylamino)-4'-nitrostilbene (DANS) doped polycarbonate films, which shows decrease in T_g with increasing DANS content [15]. This may be due to the two contradictory mechanisms. First, formation of hydrogen bonding between m-NA and PMMA may lead to increase in T_g . Secondly; presence of m-NA probably decreases the bonding between the PMMA molecules which might be the reason of decreasing T_g . The resultant of these two factors probably gives no change in T_g in present work. Moreover, absence of endothermic peak of m-NA shows that there is no phase separation of m-NA in PMMA host up to 30 wt% n-NA. This was also confirmed from X-ray diffraction as reported elsewhere [11].

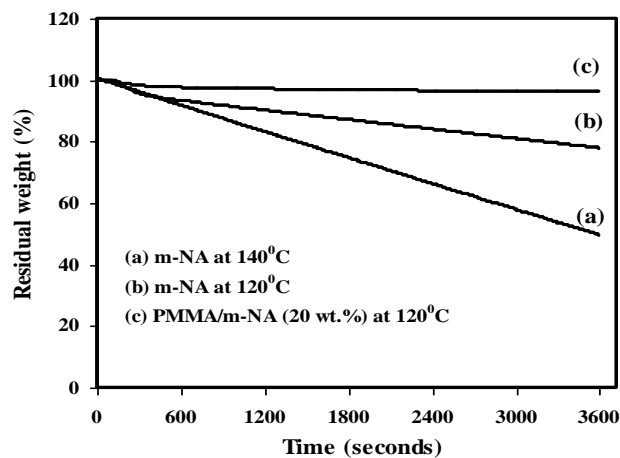


Fig. 2. Isothermal TGA run of pure m-NA (a and b) and 20 wt. % m-NA doped PMMA film (c) in air atmosphere.

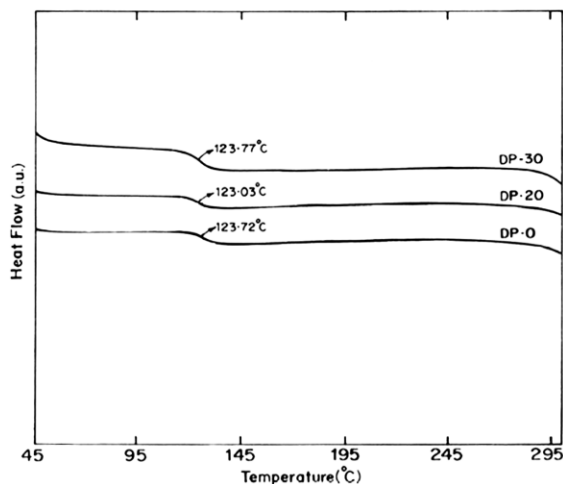


Fig. 3. DSC heating curves for pure PMMA (DP-0), 20 wt% m-NA (DP-20) and 30 wt% m-NA (DP-30) doped PMMA films.

Figs. 4 and 5 shows the SHG intensity of 10 wt% and 30 wt% m-NA doped PMMA films after poling at three temperatures, i.e., 100, 120, and 140 °C, respectively. As the input energy increases from 6 to 18 mJ, the SHG intensity increases. It can be seen that films poled at 100 and 120 °C did not show significant differences in SHG signal intensity because both the poled temperatures were lower than T_g . The film poled above T_g , i.e., 140 °C, showed highest SHG intensity among the films poled at various temperatures. This is attributed to the increased mobility of m-NA molecules as the temperature is increased and thus, higher number of molecules is aligned in the PMMA matrix.

The isothermal decay or relaxation in SHG intensity as a function of time (in hours) for a series of laser input energy for 20 wt% m-NA doped PMMA film poled at 120 °C for 30 minutes is shown in Fig. 6. It can be seen that SHG intensity decreases as the decay time is increased. The rate of decay is fast up to 50 h, thereafter, the decay rate is decreased. This is similar to the trends of DR-1 doped PMMA films [6]. The decrease in SHG intensity with time may be attributed to the relaxation of m-NA molecules

from thermodynamically unstable (poled) state to the thermodynamically equilibrium state. In other words m-NA molecules try to come from preferential oriented direction to random directions. Hence, SHG intensity decreases with time. However, the retained SHG intensity is more than 50 % of its original intensity after one week, which is comparable to that of DR-1 doped PMMA guest-host system [6].

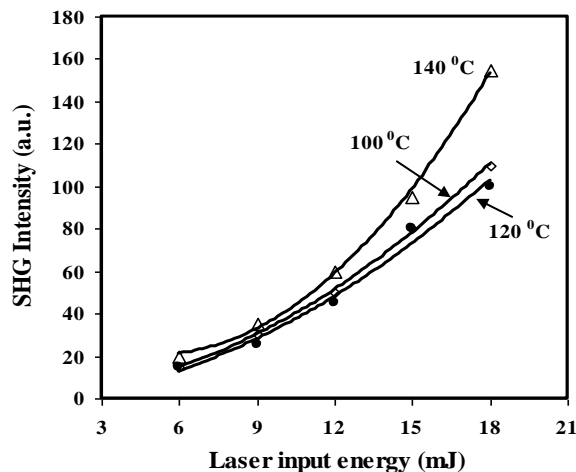


Fig. 4. SHG intensity as a function of laser input energy for 10 wt% m-NA doped PMMA film after poling at 100, 120, and 140 °C for 30 min.

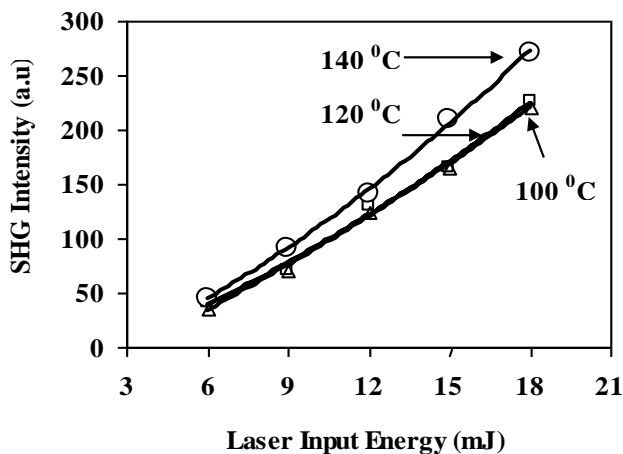


Fig. 5. SHG intensity as a function of laser input energy for 30 wt% m-NA doped PMMA film after poling at 100, 120, and 140 °C for 30 min.

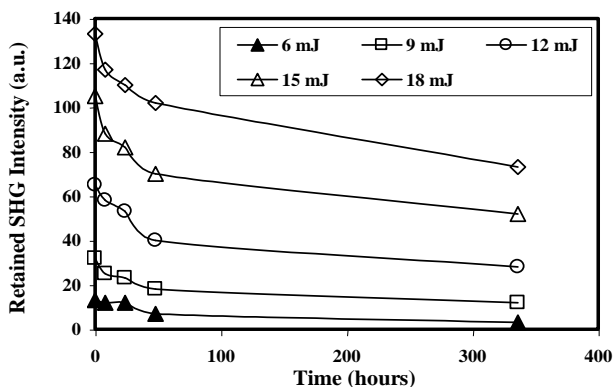


Fig. 6. Isothermal relaxation in SHG intensity with time (hours) at various laser input energy for 20 wt% m-NA doped PMMA film poled at 120 °C for 30 min.

Conclusion

Freestanding films of m-NA doped PMMA guest-host system were prepared successfully. The isothermal thermal stability of m-NA doped PMMA film was improved significantly as compared to m-NA guest. SHG signal intensity of films poled at 140 °C is higher than that of films poled at 100 and 120 °C for 30 minutes. For the poled films, SHG intensity decreases with relaxation time due to the relaxation of m-NA molecules from unstable thermodynamic state to equilibrium state. The SHG intensity of 20 wt. % m-NA doped PMMA film remained about 50 % of its original intensity after one week.

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