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Double mechanism of electric field induced reorientation of dipoles in MNA/PMMA guest-host system

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The time, temperature and frequency dependent birefringence of MNA doped PMMA film in waveguide structure are investigated using ellipsometry. The relaxation of dye molecules in the polymer matrix is studied. It is shown that for a small molecule like MNA, by increasing the frequency of the applied voltage a single KWW function is not sufficient to describe the change in the signal, which is a measure of the relaxation dynamics, and we need two stretched exponential functions to fully describe the process.

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1. Introduction

Dye doped polymers have shown potentials for different applications expected in photonics devices [1]. Efficient high speed electro-optic effect is possible in this class of materials [2]. In most applications orientation of chromophores in polymer matrices is of great importance. This orientation may occur due to the application of external electric field during electric field poling to induce a non-centro symmetric structure necessary for second order nonlinear effects [3], or due to other processes which end with chromophore orientations such as orientation by cic-trans photo-isomerasion [4], photo assisted poling [5] and electro-optic effects [6]. In all cases it is important to study the orientational dynamics of the dye molecules in the polymer matrix [7].

Different theoretical models such as oriented gas model [8], a model including molecular fields [9], the Dissado-Hill many-body relaxation model [10], Kohlausch-Williams-Watts (KWW) model and empirical decay model [11], have been developed to describe the relaxation dynamics of dye in the polymer matrix.

In this article the relaxation of 2-methyl-4-nitroaniline (MNA) chromophore in polymer matrix after applying an external electric field in a waveguide configuration is studied. This study is based on ellipsometric technique by monitoring the refractive index variation of the thin polymeric film when the electric field is applied. It is shown that for a small molecule like MNA, by increasing the frequency of the applied voltage a single KWW function is not sufficient to describe the change in the signal, which is a measure of the relaxation dynamics, and we need two stretched exponential functions to fully describe the process.

2. Sample preparation

Thin film of poly (methyl metacrylate) (PMMA) doped with 2-methyl-4-nitroaniline (MNA) chromophore was used in form of a planar waveguide in the experiments. The structure of all materials used in this study is shown in Fig. 1. Wave guiding was achieved by help of layers of lower refractive index polymer on both sides of the doped polymer film as clad layers. Poly-vinyl alcohol (PVA), due to its solubility in water and also suitable refractive index (n=1.48) was chosen for clad layers. All the materials were from Aldrich. The bottom electrode was Indium Tin Oxide (ITO) which was already coated on glass substrate (from Diamond Coatings) and the top electrode was gold which was coated by sputtering. The coatings were performed after thoroughly cleaning the ITO coated substrate. After cleaning the substrate with solvents and ultrasonic bath, the first PVA layer with thickness of about 2 to 3 micrometers was coated by casting the filtered solution of PVA in cold water over the ITO coated substrate. The thickness of all layers was measured using Dektak 8000 thickness profiler after removing the excess solvent. After drying the PVA layer, the doped polymer layer was coated by dip coating from the solution of MNA-PMMA mixture in dichloromethane. The weight concentration of dye in the polymer was 20% and the concentration of the mixture in the solvent was 150mg/ml. The thickness of the doped polymer layer was about 3 micrometer and the refractive index was 1.52. Another PVA layer as top cladding layer was coated by casting the PVA solution to make a layer of 2 micrometer thick. After curing, a semi-transparent gold layer with thickness of 150 nm was sputtered as the top electrode.

As the last step to complete the sample, two right angle prisms with refractive index of 1.79 were pressed on sample for coupling the laser light into the waveguide. The structure of the complete cell is shown in Fig. 2.

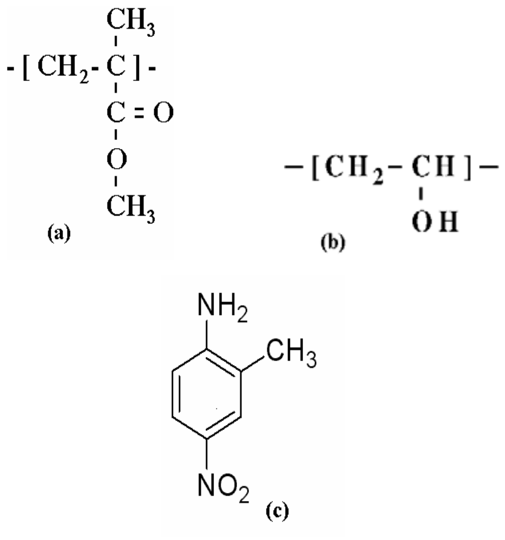

Fig. 1. Chemical structures of (a) PMMA, (b) PVA and (c) MNA.

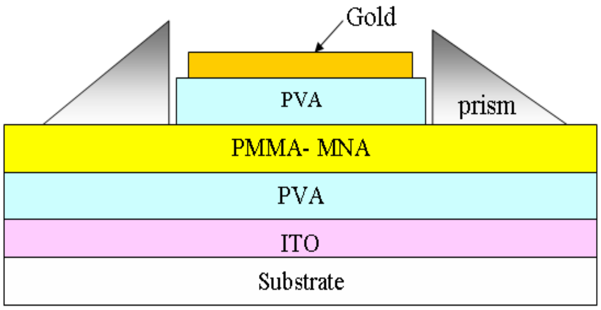

Fig. 2. Schematic structure of the waveguide including the coupling prisms.

3. Experiments

Fig. 3 shows the experimental setup. A He-Ne laser light at 632.8 nm and maximum power of 4.5 mw combined with a polarizer to insure linear polarization is used as laser source. The polarization angle of 45 degrees relative to the waveguide plane was chosen for the experiments. This provides equal s-polarized and p-polarized components. The sample was left on a stage in a temperature controlled oven with clear windows. After coupling the laser into the multimode waveguide by choosing the appropriate incidence angle, m-lines were clearly observable over the screen in front of the second coupling prism [12,13]. The brightest line was separated and after passing through a polarizer, was focused over the photo-detector by a lens. The output from the detector was monitored via a digital oscilloscope. A function generator was used to apply electric field across the waveguide at desired frequencies. The temperature was controlled with accuracy of 0.1 ^{o}C.

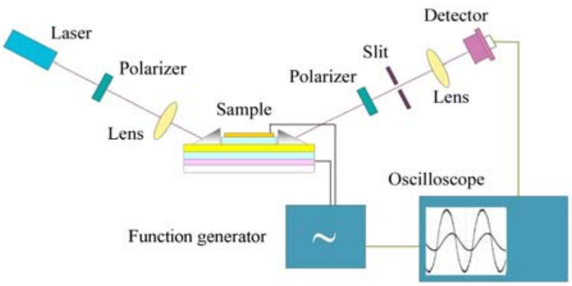

Fig. 3. The experimental set up.

In order to study the dynamic of MNA chromophore in the PMMA matrix, transient, thermal and frequency experiments were performed. In all experiments, the change in the refractive index was monitored by following the output signal from the photo detector in the computer after applying the external electric field. In the transient experiments the effect of switching the external field on and off at room temperature, in the thermal experiments the effect of the temperature on the relaxation behaviors and in the frequency experiments the response of the system to the periodic electric field were studied.

4. Results and discussion

4.1. Transient experiments

In the first set of experiments the effect of switching the external electric field on at room temperature at different applied voltages was studied. It is expected that applying the electric field for a long enough period of time ends with the alignment of the molecules which results in an induced birefringence and change in the refractive index of the doped polymer film in the direction of the applied field. Retardation in the 45 degrees linear polarized laser light occurs as it passes through the waveguide. The change in the polarization due to the retardation property of the waveguide is monitored by detecting the intensity of the output signal after passing through the second polarizer.

Fig. 4 shows how output signal varies with time after switching the external electric field on at different voltages. It is clear that by increasing the applied voltage and also by passing time, at the beginning, the output signal from the second polarizer increases. By increasing the change in the refractive index, the output signal follows few maximum and minimum cycles. The initial change in the signal is more rapid. Also it is evident that increasing the voltage affects both the slope and the strength of variations.

The fluctuating behavior of the output signal in time may be explained by adding the behavior of the signal as a function of change in the refractive index and the behavior of the change in the refractive index as a function of time. All three functions are shown in Fig. 5. Fig. 5a shows that at no applied voltage with no change in the refractive index, no light is detected from the crossed polarizer and by increasing the change in the refractive index, output light appears and reaches a maximum when the retardation is at amount of half a wavelength, following by a sinusoidal changes for further increase in the change in the refractive index. On the other hands Fig. 5b shows the time variation in the change in the refractive index after applying a fixed voltage. This shows an increase in the change in the refractive index to a maximum. Finally, the time variation of the output signal which is the sum of the other two functions, is shown in Fig. 5c which is very similar to the experimental data shown in Fig. 4. The difference is in the damping height of the signal in the experiments which is the result of randomness and thermal fluctuations which provides elliptically polarized output.

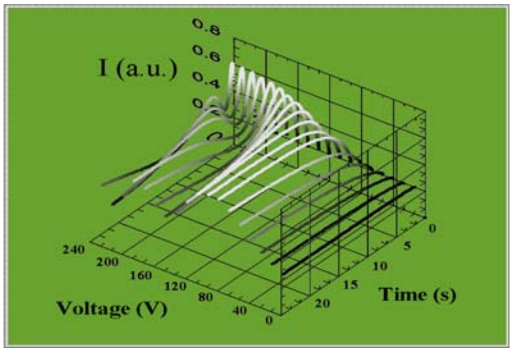

Fig. 4. output signal versus time at different applied voltages.

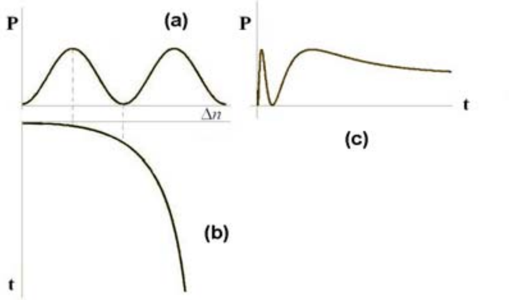

Fig. 5. (a) output signal versus Δn , (b) Δn versus time and (c) output signal versus time.

Fig. 6 shows the experimental data for the drop in the induced birefringence after switching the applied external field off (T=30 C, applied voltage=80v).

Stretched exponential function of KWW model (Equation 1) shows a poor fitting on the experimental data.

$$y = y_0 \times \exp[-(t/\tau)^{\beta}] + y_1 \qquad (1)$$

Instead, two separate stretched exponential functions as in Equation 2 shows a better fit.

$$y = y_0 \times \exp[-(t/\tau_1)^{\beta_1}] + y_1 \times \exp[-(t/\tau_2)^{\beta_2}] + y_2 \qquad (2)$$

In these equations, β is the temperature-dependent stretching and τ is characteristic relaxation time. The fits in Figs. 6a and 6b shows clearly that two separate stretched exponential functions of equation 2, is the best fit to the experimental data. These two parts are related to the slow and fast parts of the relaxations [9].

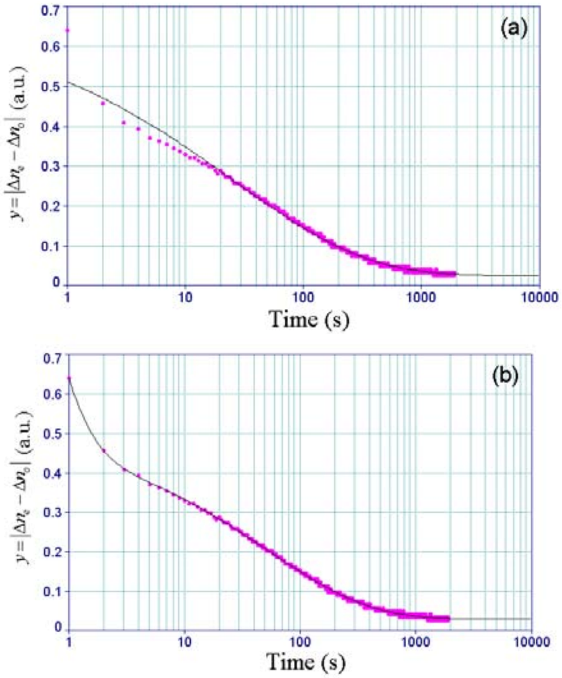

Fig. 6. Induced birefringence versus time after switching the voltage off and KWW fits with (a) one stretched exponential functions, that $y_0 = 0.65, \tau = 25.71s, \beta = 0.38, y_1 = 0.02$ and (b) two stretched exponential functions, that $y_0 = 0.47$, $\tau_1 = 52.3s$, $\beta_1 = 0.49$, $y_1 = 5.6$, $\tau_2 = 0.12s$, $\beta_2 = 0.56$, $y_2 = 0.03$.

4.2. Thermal experiments

Fig. 7 shows the effect of temperature on the relaxation of the chromophores after switching a fixed voltage off. The experiments were performed under similar conditions by varying the temperature and monitoring the output signal from the second polarizer versus time. This recorded intensity is a measure of the change in the induced birefringence and therefore a measure of thermal relaxation of the molecules to random directions, as a function of time after switching the external field off. The chosen voltage was small enough to insure a single period of variation in the detected intensity. It is clear that the slope of the changes in the response during the switching off time increases by increasing the temperature. This behavior is expectable due to the increase in the mobility of the polymer chain at higher temperatures.

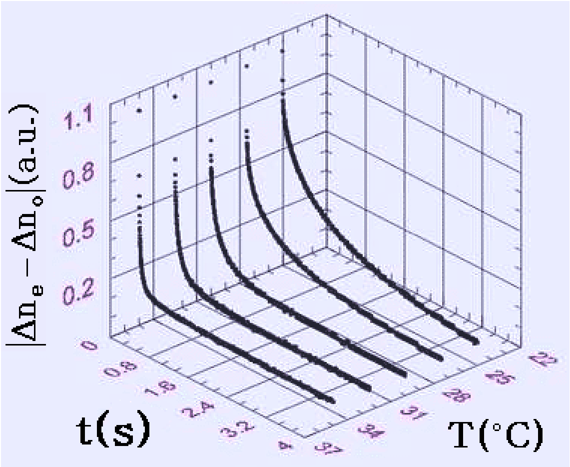

Fig. 7. Induced birefringence versus time at different temperatures after switching the 110V voltage off.

4.3. Frequency experiments

In this set of experiments an oscillating voltage, at different frequencies, from a function generator is applied across the sample to observe the relaxation behavior of the MNA molecules in the polymer matrix. It is expected that at low frequencies or by applying the voltage for long enough period of time, the alignment of the molecules reaches an equilibrium and maximum amplitude output signal may be observed. By increasing the frequency of the applied voltage, time for molecular orientation and relaxation will be reduced and therefore affects the intensity of the output signal. Fig. 8 shows the output signal versus frequency of the applied voltage on a semi logarithmic scale at room temperature. The amplitudes of AC and DC component of the applied voltage are 20 V and 42 V respectively. By increasing the frequency, a drop in the output signal is observed. At frequencies around 1 kHz another drop or change in the variation is observed. The V_{DC} as offset voltage is chosen such that the output signal remains in the linear part of the sinusoidal variations and hence the detector shows the induced birefringence.

The nonlinear chromophores embedded in a viscoelastic polymer matrix and the system are in a thermodynamic equilibrium. At very low frequencies, the change of electric field is very slow and the dipoles are able to move and follow the changes of electric field by moving the main chains and side chains of polymer. After the first drop in the signal by increasing the frequency, the reorientation of the dipoles decreases due to the rapid changes of electric field. Main body of the chromophores is slowed down at this stage because of low mobility of main chains, but there is still mobility for the side chains. The second change in the signal occurs by increasing the frequency (at about 1 kHz) because the side chains also become more restricted and can not follow the high frequency.

This also explains why a single stretched exponential function of KWW model shows a poor fitting on the experimental data (Fig. 6a), and the two separate stretched exponential function shows a better fit (Fig. 6b).

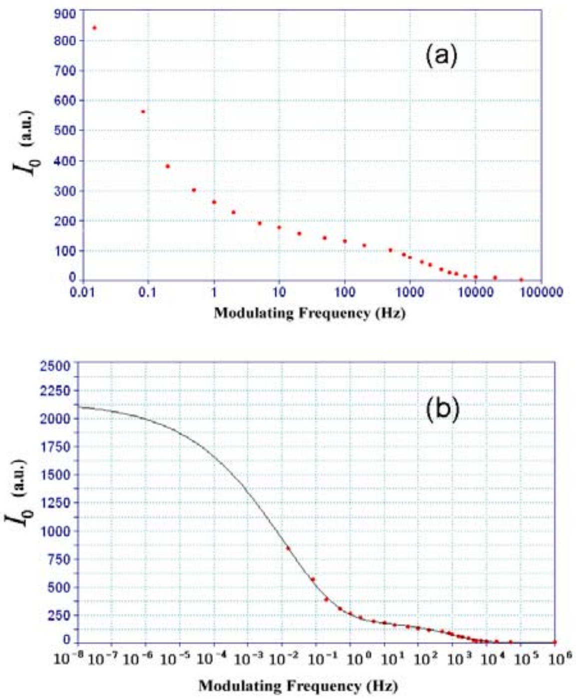

Fig. 8. The output signal versus frequency of the applied voltage at room temperature on a semi logarithmic scale (a) without fitting (b) with fitting.

When the electric field is switched off, relaxation of the chromophores affect the side chains of the polymer, causing a fast decay within a short period of time (β relaxation). Further relaxation can only happen after thermal equilibrium of the main chains, which is slow (α relaxation). Therefore, the first drop in the output signal after increasing the frequency of the applied voltage is due to the relaxation of the chromophores and their effects on polymer side chains and the next drop may be related to the further effects of the chromophore relaxations on the polymer main chain.

5. Conclusions

It is clear from the experimental relaxation data that after turning the applied electric field off, the change in the refractive index versus time may be fitted by two separate stretched exponential functions of KWW model. One of these functions has small relaxation time and the other has longer relaxation time which is related to the mobility of the main chain and side chain of the polymer respectively.

MNA is a nearly spherical molecule therefore its orientation movement is easier than elongated molecules.

Therefore the rotation of MNA molecule is important in the polymer systems.

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