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SECOND ORDER OPTICAL NONLINEARITY OF POLYMERS INDUCED BY CHARGE INJECTION ASYMMETRY

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Abstract A new mechanism for inducing bulk asymmetry and second order optical nonlinearity in polymer-dye systems is described. An anisotropic distribution of charges is established inside the medium resulting from the application of high voltage via an asymmetric electrode structure. The nonlinearity induced via this mechanism is perpendicular to the externally applied electric field. It is proven that the nonlinearity induced by charge injection cannot arise from dipolar alignment of molecules, but rather results from the nonlinearity of charged dye dimers in a bulk charge gradient.

INTRODUCTION

A major field of current interest in nonlinear optics (NLO) is the search for cheap and easily processable materials for second order nonlinear optical applications. Such materials must lack a centre of symmetry. One possibility is to break the isotropic symmetry of a polymer containing nonlinearly hyperpolarizable dyes by the application of a strong DC electric field.[1,2]

It is usually assumed that the dominant symmetry breaking responsible for inducing second order NLO properties in such systems is dipolar alignment of the dye in the electric field, and so the strongest nonlinearity is induced *parallel* to the direction of the applied field.

However, recent research in our group[3-5] has shown that a different mechanism of symmetry breaking may be operative, and even dominant, when high voltage is applied to polymeric systems. If the voltage induces some current flow or charge injection, it is possible to set up an asymmetric distribution of charge in the polymer. We have used sample/electrode geometries in which thin electrodes are in the plane of the polymer film (see Figure 1). In such cases, application of voltage can cause charge injection into the polymer followed by diffusion away from the surface, and charge trapping on the dye. This sets up an asymmetric distribution of charged species along the direction perpendicular to that of the static DC field.

Consequently, this procedure breaks symmetry and induces nonlinearity simultaneously along two directions - parallel to the field (x-direction) due to the familiar dipole alignment, and *perpendicular* to the field (z-direction) due to the gradient of injected charges. Using a voltage of 2000 V in the geometry of Figure 1 can lead to a situation where the charge injection induced nonlinearity, $\chi^{(2)}_{zzz}$, along the direction perpendicular to the field is much stronger than the dipole induced nonlinearity parallel to the field, $\chi^{(2)}_{xxx}$. The magnitude of this nonlinearity, as determined by optical second harmonic generation (SHG) can be sufficiently large ($\chi^{(2)}_{zzz} \approx 10^{-8}$ esu) that this method may ultimately be useful in nonlinear optical device applications.

The magnitude of the nonlinearity induced by charge injection and its temporal stability after turning off the voltage depend on the charge injection, trapping and storage of the polymer-dye film. Thus there is tremendous importance in the electrical properties of the polymer host and the polymer/substrate and polymer/metal interfaces.

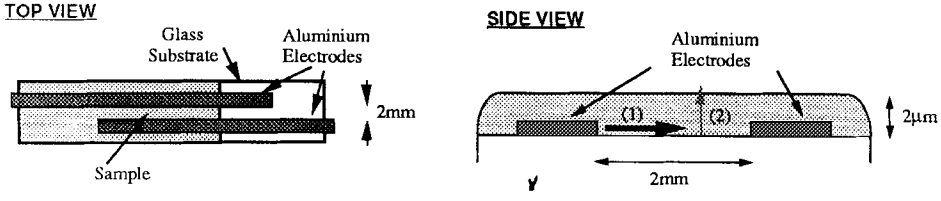

FIGURE 1. Geometry for 'in-plane' poling. Charge injection (1) during application of voltage across the electrodes sets up a charge gradient (2) along the direction perpendicular to the electric field. The strongest optical nonlinearity is measured along this direction.

EXPERIMENTAL

Our techniques for preparation of polymer films, application of voltage and measurement of SHG and nonlinearity both parallel and perpendicular to the field have been fully described in earlier papers.[3-5] Films are prepared using the geometry as shown in Figure 1, and activated for SHG by application of 2000 Volts at room temperature for 5-10 minutes. SHG is measured at the conclusion of the voltage application, and at subsequent times.

RESULTS AND DISCUSSION

We have observed[3-5] production of strong $\chi^{(2)}_{zzz}$ nonlinearity perpendicular to the applied field direction for various dye molecules (DANS = dimethylamino nitrostilbene, Disperse Red 1 and merocyanine) in several polymer hosts (polymethyl methacrylate, polyvinyl chloride, poly carbonate and poly sulfone). It has been observed for both polymer-dye blends and co-polymers, and in amorphous and liquid crystalline host polymers. Thus it can be a very general phenomenon.

However, for a given polymer-dye system (e.g. 2% DANS in PMMA) the magnitude of the perpendicular nonlinearity has been found to vary greatly depending on the current flow when the voltage is applied. In the geometry of Figure 1 (applying 2000V with the electrodes 2mm apart) we measured a current flow of about 10 μA and a nonlinear optical coefficient $\chi^{(2)}_{zzz} = 2\text{x}10^{-8}$ esu is obtained in the perpendicular direction. Variation of the substrate conductivity or the amount of charge injection by use of different metallic electrodes can lead[5] to significant enhancement or reduction of the nonlinearity, which is in direct correlation with the magnitude of current flowing during voltage application. Conversely, discharge of trapped charges upon removal of the high voltage is correlated with the loss of the nonlinearity.[3]

After removal of the high voltage, the decay of the nonlinearity is an indication of the charge retention (electret) properties of the polymer. For 2% blends of DANS in various polymers, we observed essentially a total loss of SHG within a few hours in PMMA host, whereas in poly sulfone and poly carbonate[5] the nonlinearity dropped only by about 50% after 1 week.

By probing the SHG of these films with a focused laser beam, it is possible to monitor the spatial distribution of the perpendicular nonlinearity between the positive and negative electrodes. In Figure 2 we show the nonlinearity at various points between the electrodes (for a 2% DANS in PMMA sample) measured after applying 2000V for 10 seconds and 10 minutes. After 10 seconds, the nonlinearity near the positive electrode is more than two orders of magnitude stronger than that near the negative electrode (see Fig. 2a). However, after 10 minutes exposure to the high voltage the differences in the signals at various positions between the electrodes are much smaller (Fig. 2b). These results seem to indicate that hole migration, rather than electrons, is the dominant conduction mechanism in the polymer.

There is a large body of evidence which proves that the perpendicular nonlinearity cannot be explained by the conventional mechanism of dipolar alignment in an electric field.[3-5] The dominant electric field inside the polymer is of course parallel to the film plane, and yet the nonlinearity is strongest in the perpendicular direction. The spatial and

temporal distribution of the nonlinearity, as shown by the data of Figure 2, are clearly more consistent with a model in which the nonlinearity is connected with the distribution of trapped charges in the polymer. This is also evidenced by the dependence of the strength of the nonlinearity on the current flow during application of high voltage, and the correlation between the discharge current after removal of the high voltage and the decay of nonlinearity.

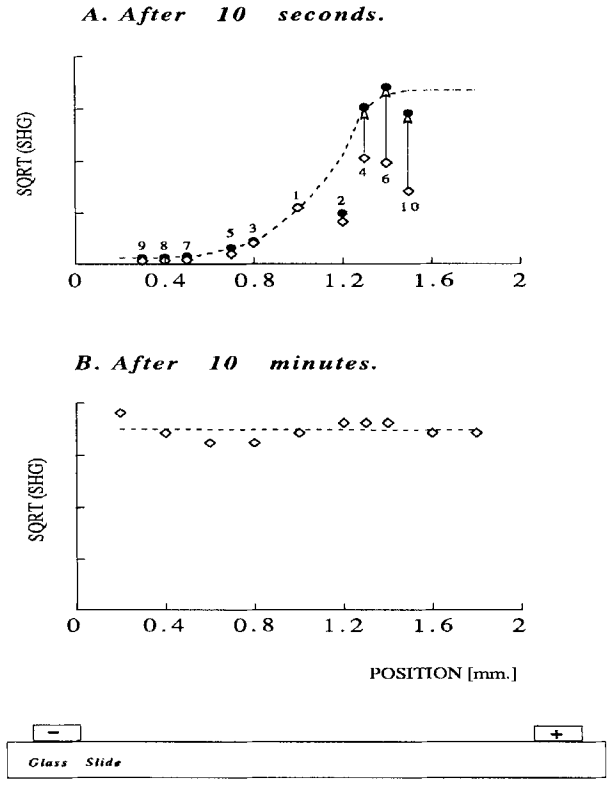

FIGURE 2. Measurement of the perpendicular nonlinearity $\chi^{(2)}_{zzz}$ using a focused laser beam passing through a 2% DANS in PMMA sample at various points between the electrodes. The top figure (a) shows the spatial distribution of nonlinearity as measured on a sample to which 2000 V is applied for 10 seconds. After turning off the voltage, SHG was measured at the points indicated in the order 1,2, .. 10. Since the SHG decays somewhat during the measurement, we also show how the measured data point (diamonds) should be corrected for this decay (circles). The extrapolation was performed according to the decay kinetics measured in a different experiment. Figure (b) shows the spatial distribution of nonlinearity in a sample exposed to 2000 V for 10 minutes. The dotted curves are for guidance only.

The trapped charges set up a charge gradient perpendicular to the field due to diffusion (see Figure 1), which is of course equivalent to an electric field component along the perpendicular direction. However, experiments in liquid crystalline polymers[4] prove that this field, E_z, is much less than the static parallel electric field, E_x. The important feature is the field *gradient* $\frac{d}{dz}E_z$. Interaction with the dye species in the polymer, and in particular dye aggregates leads to the bulk nonlinearity along the perpendicular direction. There will be an anisotropic distribution of charged dimers, which are non-symmetrical, unlike their neutral counterparts. Neutral dimers could however also contribute to the nonlinearity via a quadrupolar like interaction with the electric field gradient. A quantitative analysis of the nonlinearity on a molecular level is still incomplete, in particular with respect to the relative importance of these two contributions. Theoretical calculations, which are not yet available, could shed light on this issue.

These results clearly show that asymmetric charge injection into polymeric films can produce a substantial nonlinearity, which is of both fundamental and applied interest. Related phenomena, whereby charge injection leads to symmetry breaking and SHG, have been reported for glass[6] and fused silica.[7] In these cases, the nonlinearity has been attributed to setting up of an internal field leading to SHG via a $\chi^{(3)}$ mechanism. However, such a mechanism cannot be the reason for the nonlinearity in our polymers.[4]

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