

# Orientation of azobenzene molecules in polymer films induced by all-optical poling

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A model of the alignment of azobenzene molecules in polymer film induced by all-optical poling is proposed and verified by experiment. We found that when the writing beams of frequencies  $\omega$  and  $2\omega$  are both linearly polarized with their polarization directions parallel to each other, azobenzene molecules tend to reorient to the direction perpendicular to the writing beams polarization. At the end of the writing process, more molecules orient to the direction perpendicular to the writing beams polarization than those which orient to the parallel direction. The alignment of molecules parallel or perpendicular to the polarization of the writing beams is characteristic of polarity or no polarity, respectively. The alignment of molecules along the polarization of writing beams results in the second order nonlinearity in the polymer film. According to the model, a new method to improve the optical poling efficiency is put forward.

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In the past decade, there has been intensive interest in second-order nonlinear optical polymers that are estimated to possess large optical nonlinearity. A key issue to provide second-order nonlinearity in polymer films is the achievement of non-centrosymmetric order. It is well known that the electric poling is frequently used to achieve the non-centrosymmetric order. However, a few years ago, experiments proved that it was possible to achieve non-centrosymmetric order by optical means<sup>[1,2]</sup>. Simultaneous irradiation on the film by the fundamental and the second harmonic (SH) lights can result in polar orientation and induce the second order nonlinearity,

which is called all-optical poling.

At present, the frequently used materials in optical poling are azobenzene-PMMA and azobenzene-Polyimide. The azobenzene molecules are characteristic of trans-cis isomerization. It will be easier for the molecules in cis state to freely rotate. Optical poling in this kind of material can be explained as follows: following the excitation, the azobenzene molecules undergo trans-cis isomerization, and then reorient to induce the polar alignment. If we consider the azobenzene molecule as a two-level molecule, the excitation probability  $P_{01}$  due to all-optical poling can be given by<sup>[3]</sup>

$$P_{01} \propto \frac{1}{4}(\mu_{10} \cdot E_{2\omega})(\mu_{10} \cdot E_{2\omega})^* + \frac{(\mu_{10} \cdot E_{\omega})(\Delta\mu_{10} \cdot E_{\omega})(\mu_{10} \cdot E_{\omega})^*(\Delta\mu \cdot E_{\omega})^*}{16(\hbar\omega)^2} + \frac{(\mu_{10} \cdot E_{2\omega})^*(\mu \cdot E_{\omega})(\Delta\mu \cdot E_{\omega}) + (\mu_{10} \cdot E_{2\omega})(\mu_{10} \cdot E_{\omega})^*(\Delta\mu \cdot E_{\omega})^*}{8\hbar\omega}, \quad (1)$$

where  $\mu_{10}$  is the transition dipole moment, and  $\Delta\mu$  is the difference between the dipole moments in the excited state and in the ground state ( $\Delta\mu = \mu_1 - \mu_0$ ). The first two terms of the Eq. (1) correspond to one- and two-photon absorption respectively, and lead to a selective axial excitation of the molecules. The last term is related to interference between a fundamental wave  $\omega$  and its SH wave  $2\omega$ , which leads to the presence of a polar field inside the medium.

However, the alignment of molecules induced by optical poling, especially the relation between the polar alignment of molecules and the polarization directions of the writing beams, has not been identified yet. In this paper, we present a model of the alignment of azobenzene molecules in optically poled polymer films, and then verify the model by experiment. A novel method to improve the optical poling efficiency is also put forward. We limit our discussion on the simple case of all-optical poling, namely the writing beams at fundamental and

SH frequency are both linearly polarized with the polarization direction parallel to each other.

Before analyzing the case of optical poling, let's consider a simple case. If irradiated by either of the writing beams (i.e. in the case of one- or two-photon absorption), the molecules perpendicular to the laser polarization direction will not be excited and keep their orientations, while those not perpendicular to the laser polarization direction will be excited and undergo many trans-cis-trans isomerization cycles until orient to the perpendicular direction<sup>[4]</sup>. Figure 1 shows the alignment of the molecules in this case. The trans-cis photochemical transition rate is proportional to  $\cos(\phi)$ , here  $\phi$  is the angle between the orientation of the molecule and the laser polarization direction. The lengths of arrows represent the molecule numbers oriented to the directions that the arrowheads point to. The increasing molecule number in the direction perpendicular to the polarization direction of the writing beams (abr. in perpendicular

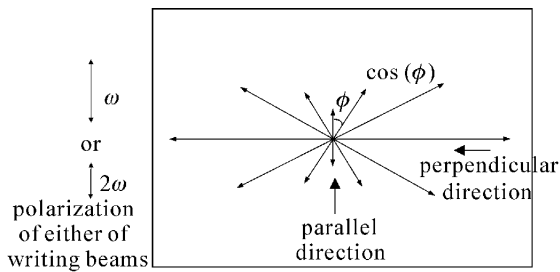


Fig. 1. The alignment of molecules induced by monochromatic irradiation.

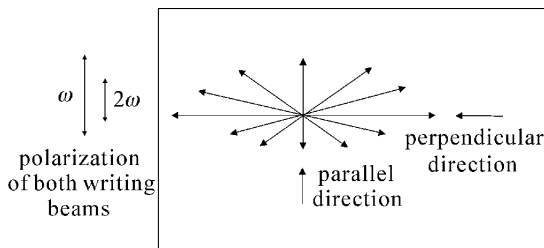


Fig. 2. The alignment of molecules induced by optical poling.

direction) and the decreasing number in the direction parallel to the polarization direction of writing beams (abr. in parallel direction) are both axial. They will not destroy the centrosymmetry, and have contribution not to the second order nonlinearity, but to birefringence and dichroism.

Now let's see the case of optical poling. Because of the existence of polar field, the alignment of the molecules in parallel direction is not centrosymmetric, i.e. the molecule numbers in positive and negative directions are different. However, the variation of the orientation of the molecule from parallel direction to perpendicular direction under the effect of trans-cis isomerization is random, so the increasing number of the molecules in perpendicular direction is centrosymmetric. Therefore, the alignment of the molecules after poling can be modeled as shown in Fig. 2. The alignment in parallel direction is non-centrosymmetric, which contributes to the second order nonlinearity, while the alignment in perpendicular direction is centrosymmetric, which is independent of the second order nonlinearity. More molecules align in perpendicular direction than in parallel direction.

Experiments were performed to verify our model. A side-chain azobenzene polyimide (DR-19-polyimide) film was selected as a sample<sup>[5]</sup>. A similar experimental setup shown in Ref. [5] was used. Firstly, we verify that more molecules align in perpendicular direction than in parallel direction. Figure 3 shows the intensity of the green light in different directions after the absorption of the poled film. We note that the green light in parallel direction is more intensive (i.e. the absorption is lower here), which means that few molecules align in this direction, while the signal of the green light can be hardly detected in perpendicular direction. So it can be easily deduced that there are more molecules aligning in perpendicular direction than in parallel direction.

As we know, it is possible to erase the polarity of the poled film by monochromatic irradiation if the

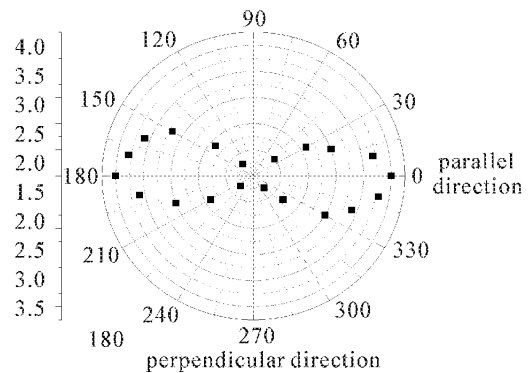


Fig. 3. The green light intensity detected by PMT.

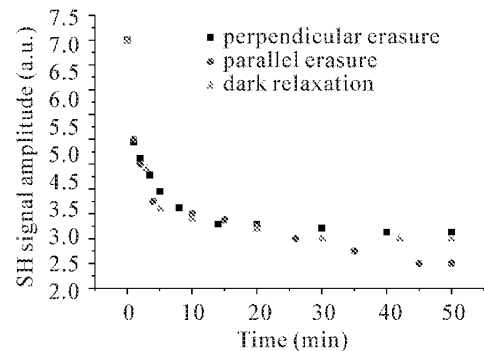


Fig. 4. The comparison of dark relaxation with perpendicular and parallel irradiation.

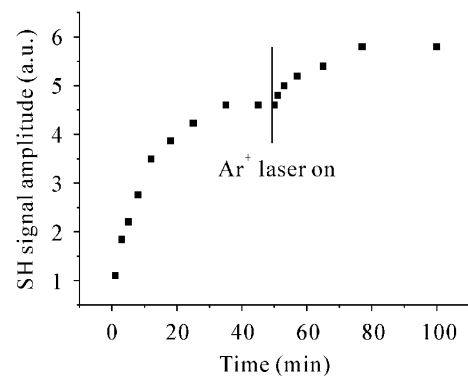


Fig. 5. The improvement of optical poling efficiency due to perpendicular irradiation.

polarization of the irradiating light is along the direction of the polarity<sup>[3]</sup>. So, light erasure experiments were performed to verify the direction of the polarity induced by optical poling in the polymer film.

Figure 4 gives the results. The perpendicular irradiation refers to irradiating the poled film by the light with polarization perpendicular to that of the writing beams, the parallel irradiation refers to irradiating the poled film by the light with the same polarization as that of the writing beams. The dark relaxation refers to decay of the polarity of the poled film when no light irradiates on the poled film. We can see that the result of perpendicular irradiation is similar to that of dark relaxation, and this means the perpendicular irradiation has little effect on the nonlinearity of the polymer, while the parallel irradiation is more efficient. Thus, we can conclude that

polarity in the poled film induced by optical poling is in the parallel direction but not in the perpendicular direction.

According to the model, the parallelly oriented molecules which contribute to second order nonlinearity are less than those of perpendicular orientation in an optically poled polymer film, and one may reasonably deduce that if the molecules which are perpendicularly oriented are excited to reorient in parallel orientation, then the poling efficiency may be increased. In Fig. 5, the 514-nm green light of an Ar<sup>+</sup> laser perpendicularly polarized to that of the poling beams was switched on to irradiate the poling saturated polymer film while the writing beams were still on. As we know, the effect of perpendicular irradiation on SH signal was the same as dark relaxation, however, the molecules which were perpendicularly oriented would be excited again and realigned to other directions, and finally stabilized in parallel direction. Since more parallelly orientated molecules were available for poling in this case, the poling efficiency was increased appreciably. The experiment not only provides a novel method to improve optical poling efficiency, but also reconfirm the model of the alignment of molecules induced by optical poling.

In this paper, we present a model to illustrate the alignment of molecules induced by optical poling, and verify

it by experiments. If the writing beams are linearly polarized with their polarization direction parallel to each other, the alignment of the molecules induced by optical poling can be identified as follows: the alignment in parallel direction is polar, while that in perpendicular direction is nonpolar, the former contributes to the second-order nonlinearity despite less molecules align in the direction. According to the model, a novel method was put forward to improve the optical poling efficiency.

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