Photoinduced Gliding of the Surface Director in Azo-Dye Doped Nematic Liquid Crystals.

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ABSTRACT

We report, photoinduced surface director gliding with azo dye-doped nematic liquid crystals. This gliding has the same characteristics as that induced by an applied magnetic field. Fast and slow dynamic regimes are observed, the latter fitting to a stretched exponential. In addition, the gliding demonstrates a memory effect for sequential measurements.

1. Introduction

The interactions between nematic liquid crystals and polymer surfaces have been the subject of several recent studies. It has been demonstrated that when an external torque is applied to the liquid crystal via an electric or magnetic field, inducing a change in the director orientation in the bulk, the surface director also changes orientation[1]. Part of the surface director reorientation involves the gliding of the easy axis[2]. The easy axis is that axis in which the interfacial energy between the liquid crystal molecules and the polymer surface is minimized. Both azimuthal (in-plane) and zenithal (out-of plane) gliding have been observed in the presence of externally applied electric[1,2,3,4] or magnetic fields[5,6]. Various workers have suggested that gliding can be the result of adsorption and desorption of the liquid crystal on the polymer surface[7], of a mutual reorienting of the liquid crystal and polymer network[2,5,6], or of sub-layers with different physical properties near the polymer surface[7,8]. It has also been demonstrated that gliding is not restricted to polymers with weak anchoring energy, so-called "soft" polymers[3,4].

Gliding has been characterized by dynamics that do not follow the standard description of surface reorientation. Typically, two dynamic regimes are observed; a fast regime and a slow regime. Faetti, *et al.*[1] have shown that the fast regime is in good quantitative agreement with a classical description of director anchoring and surface viscosity. The slow regime, on the other hand, shows the surface director angle changing continuously without appearing to reach a stationary value. Most studies indicate that the slow dynamics associated with gliding can be characterized either by a stretched exponential[1,9] or a power law[5]. Another characteristic of gliding is that it is not only slow, but appears to be plastic; there is a memory effect[10]. Upon removal of the external

torque, the easy axis does not immediately return to its original orientation. Rather, that return can take hours or days and is the probably the result of the bulk liquid crystal molecules exerting a torque on the polymer bringing the easy axis back to its original orientation.

Evidence of photoinduced gliding with azo dye doped nematics has also been reported in the literature. In studies of bulk reorientation, we have found that interpretation of photo-induced reorientation required the inclusion of gliding on the rubbed polyimide surface[11,12]. A drift in baseline measurements between experiments, that could not be associated with thermal drift, has also been common. Francescangeli, *et al.*[13] have demonstrated gliding of the easy axis of a nematic doped with azo dye methyl red on an isotropic polyvinyl-cinnamate-fluoride surface. In this case, the surface has a weak anchoring energy. Measuring the modulus surface director reorientation angle versus time, they also observe two dynamic regimes; an initial sharp rise followed by a decay to zero, and then by a second slower rise. They interpret the first rise as coming from the photoinduced torque in the bulk, similar to an applied magnetic or electric field, and the second rise as coming from the formation of an easy axis parallel to the exciting field. They suggest that the mechanism responsible for this is the adsorption of phototransformed dye molecules[14]. This process is similar to that where azo dyes are incorporated into the polymer, by chemical attachment or simply by mixing, rather than in the bulk liquid crystal. In those cases, polarized light alters the orientation of the dye molecules, resulting in a change of the easy axis[14], or the establishment of an easy axis[15]. It appears to be evident that the formation of *cis* isomers upon photoexcitation is involved.

In this article, we report measurements of photoinduced azimuthal gliding on unrubbed PEMA. Although we do not observe the change in gliding direction indicated by the observations of Francescangeli, *et al.*[13], we do confirm that photoexcitation of azo dyes in nematics induces gliding on the polymer surfaces. We also find that this photoinduced gliding involves a memory effect we believe to be associated with the adsorption of dye onto the polymer surface. We have also characterized the time dependence of the gliding and show that it is also characterized by a stretched exponential. In section 2 we describe the experiment. In section 3 we present our experimental results. In a future paper we will present the results of gliding on polyimide coated surfaces.

2. Experiment.

Dyed liquid crystal samples were prepared with a 0.5% by weight solution of disperse orange 3 (DO3) in nematic liquid crystal blend *E*7. Sample cells were prepared by spin-coating one glass slide with polyamic acid, which was heated to form polyimide and subsequently rubbed with velvet. The other glass slide was spin-coated with polyethyl methacrylate (PEMA), molecular weight M = 515,000 and a glass transition temperature $T_g = 63^{o}$C, which was also heated but not rubbed. Spacers were placed between the glass slides, giving a nominal cell thickness of 50 μm. Planar samples were prepared by filling the cells and checking the director orientation under a cross-polarized microscope.

The experimental set-up, shown in Fig. 1, is described in detail by Jánossy[16]. A pump beam from an argon ion laser was incident on the sample with a polarization at some angle φ to the director. The probe beam consisted of a white light source with an orange filter. A broadband probe, hence the white light source, is essential to avoid interference, and the orange filter prevents any dye excitation by the probe, as well as any spurious signal. The probe was polarized parallel to the rubbing direction and passed through the sample. Polarization direction of the exiting probe was determined by passing the signal through a Hinds photoelastic modulator (PEM) and then a polarizer oriented 45^{o} to the director. The second harmonic signal from the PEM is directly proportional to the polarization angle of the exiting beam, which is the direction of the surface director and therefore corresponds to the gliding angle. Calibration was done by rotating the PEM, in the absence of pump, by one degree and measuring the change in second harmonic signal.

3. Results.

Fig. 2 shows the gliding angle as a function of time for a pump polarization angle of 45^{o}. About halfway through the measurement, the pump laser is turned off, as indicated in the figure. This measurement was made at a fixed temperature of 30^{o}C. It is obvious that there is gliding of the easy axis, characterized by the long tail in the time dependence. Our measurements also show two dynamic regimes for photoinduced gliding. This gliding, however, differs from those of Francescangeli, *et al.*[13] in that we do not observe a change in the direction of the gliding angle upon transition from the fast to the slow regime.

Figs. 3 and 4 show how the gliding angle changes in time when the pump is on and after it is turned off, respectively. In this run the pump polarization is 60^{o} to the initial surface director orientation and the temperature is 40^{o}C. From Fig. 4, it can be seen that it takes a long time for the surface director to return to the initial angle. In fact, empirical fits the gliding angle described below, suggest that the surface director does not return to the initial angle. Rather, it returns to some angle on the order of 0.5^{o}. This is an order of magnitude less than that found when a magnetic field is applied. Over much longer periods of time, however, we find that the gliding angle after the pump has been removed continues to decrease. In our measurements, we try to account for this by considering only the change in surface director from the initial angle.

Empirical expressions for the change in the surface director from its initial direction include the fast regime fit to a simple exponential, and the slow regime fit to a stretched exponential, consistent with adsorption and desorption dynamics[1]. This change in surface director after the pump is turned on is then given by

$$\Delta\varphi_s^{on} = \Delta\varphi_{s,on}^{on}\left[1 - A\exp\left(\frac{t}{\tau_f^{on}}\right) - (1-A)\exp\left(\frac{t}{\tau_g^{on}}\right)^{\alpha}\right] \quad (1)$$

When the pump is turned off, the appropriate expression is

$$\Delta\varphi_s^{off} = \Delta\varphi_{s,\infty}^{off} + \left[A\exp\left(\frac{t}{\tau_f^{off}}\right) + B\exp\left(\frac{t}{\tau_g^{off}}\right)^{\alpha}\right] \quad (2)$$

where $\Delta\varphi_{s,\infty}{}^{on}$ and $\Delta\varphi_{s,\infty}{}^{off}$ are the differences between the apparent final surface director and the initial surface director, τ_f^{on} and τ_f^{off} are the fast relaxation times, and $\tau_g{}^{on}$ and $\tau_g{}^{off}$ are the gliding times, each when the pump is on and off, respectively. Ultimately, $\Delta\varphi_{s,\infty}{}^{off}$ goes to zero, but those long term dynamics are beyond the scope of this study.

The gliding angle in Fig. 3 is fit to Eq. 1, and in Fig. 4 the gliding angle is fit to Eq. 2. As can be seen these are rather good fits. For all of our trials, regardless of pump polarization and temperature, we found the value of the exponent, α, to be between 0.35 and 0.6. However, the goodness of the fit, as determined by chi-squared, does not vary by much as α is varied. Figs. 3 and 4 are most typical with α equal to 0.44 when chi-squared is minimized. This is similar to the findings of Faetti, *et al.*[1] for gliding from an external electric field, and Faetti and Marianelli's determination of α equal to 0.362[9]. In comparing different sets of data, we used a value of α equal to 0.44, even when that value did not minimize chi-squared, since time constants can vary slightly with this exponent, and changes in chi-squared were not significant. For Figs. 3 and 4, the fast relaxation

times τ_f^{on} and τ_f^{off} are 2.7 ± 0.1 s and 3.3 ± 0.1 s, respectively. The gliding times, τ_g^{on} and τ_g^{off} are 310 ± 30s and 102 ± 2s, respectively. While gliding times do appear to vary from measurement to measurement, these values are typical of what we have observed. According to this fit, $\Delta\varphi_{s,\infty}^{on}$ is 3.7 ± 0.1°, which is an order of magnitude smaller than that found when a magnetic field is applied.

In spite of the fact that the initial surface director is compensated for, we still observe a "memory" effect, as shown in Fig. 5. This figure shows the gliding angle change at a temperature of 40°C and pump polarization of 60° for four runs. Run 2 was done approximately fifteen minutes after run 1, run 3 was done approximately one hour after run 2, and run 4 was done fifteen minutes after run 3. We see that for each subsequent measurement the gliding angle increases. Between runs 2 and 3, there was enough time for the system to relax nearly back to the run 2 state.

What is also interesting about this memory effect is that the first run of any day consistently demonstrates a longer gliding time. In Fig. 5, the gliding time for the first run is 1200 ± 200 s, whereas for runs 2 – 4, the gliding time ranged between 260 and 360 s. This effect is observed even when the pump polarization is reversed, as shown in Fig. 6. Here run 1 has a gliding time of 1400 ± 100 s while run 2 has a gliding time of 480 ± 20 s.

These latter results raised the question as to whether there was a photophysical/photochemical reaction, such as adsorption, between the dye and the polymer surface facilitating the gliding. To investigate this, we first induced reorientation of the surface director for a short time using a pump polarized by 45 degrees. We then irradiated the same spot with circularly polarized beam for 10-15

minutes. During this irradiation there was no reorientation of the surface director. Afterwards, however, we again irradiated the sample with 45 degree pump polarization, and found an increase in the reorientation effect by 6-7 times. Yet, we found no effect of irradiation on the magnetic field induced gliding. This is shown in Fig. 7. We also found no photoinduced gliding when anthroquinone dyes were used instead of azo dyes.

As a control, photoinduced gliding was compared with gliding from an external magnetic field, shown Fig. 8 These measurements show gliding from above the Freéderickz threshold, for the same sample, also at 30^{o}C. Clearly the photoinduced gliding is weaker than gliding resulting from an external field. One apparent difference between gliding from an external field and photoinduced gliding is the time lag when the magnetic field is initially applied. This time-lag is connected with the threshold character of the Freédericksz transition; the torque is initially (almost) zero and increases as the director rotates towards the magnetic field.

4. Discussion

We have measured photoinduced azimuthal gliding on unrubbed PEMA. Although we did not observe the change in gliding direction indicated by the observations of Francescangeli, *et al.*[13], we do confirm that photoexcitation of azo dyes in nematics induces gliding on "soft" polymer surfaces. We also find that this photoinduced gliding involves a memory effect. In particular, for a series of measurements, the amount of gliding increased with each subsequent measurement, and that illumination of the sample with circularly polarized light increased the amount of gliding by several times.

We have also demonstrated that the photo-induced surface director reorientation is characterized by a fast dynamic regime and a slow dynamic regime. Our results indicate the former is be described by director anchoring and surface viscosity. The latter, however, is described by a stretched exponential. Stretched exponentials are sometimes associated with adsorption and desorption processes.

While the detailed nature of the interactions is still unknown, it is clear that this photoinduced gliding is the result of photophysical/ photochemical interactions between the dye molecules, the liquid crystal molecules, and the surface polymer. Our results suggest that the dye is adsorbed onto the polymer surface upon irradiation. It is not clear whether that adsorption takes a preferred direction. It is possible that dye orientation upon adsorption is determined by a combination of the polarization of the pump beam and the director angle near the surface. However, our experiments involving circularly polarized light show that this is not necessary. In any case, dye molecules already adsorbed will reorient upon irradiation, as indicated by the results of Palffy-Muhoray, *et al.*[14] and Jánossy[15].

Preliminary measurements also indicate that photoinduced gliding also occurs on the "hard" rubbed polyimide surface, although the dynamics differ from those on the PEMA surface. Those results will be presented in a future paper.

Figure Captions:

Fig. 1. Experimental setup: L – lens, P – polarizer, PEM – photoelastic modulator.

Fig. 2. Gliding angle as a function of time for a pump polarization angle of 45^{o}. Temperature is 30^{o}C.

Fig. 3. Gliding angle as a function of time while pump is applied. Pump polarization angle is 60^{o}. Temperature is 40^{o}C.

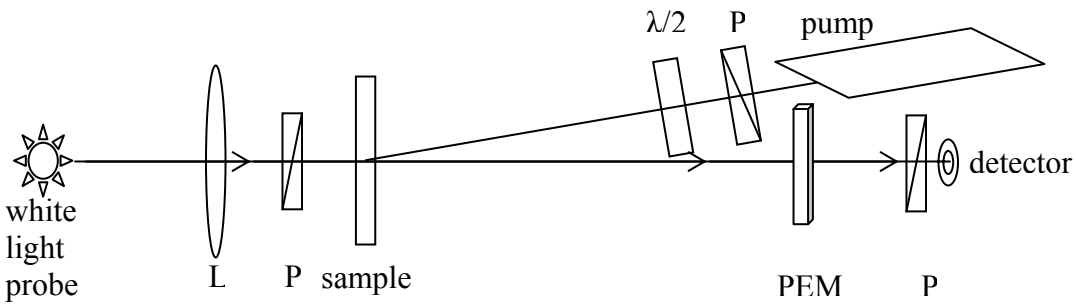
Fig. 4. Gliding angle as a function of time after pump is removed. Pump polarization angle is 60^{o}. Temperature is 40^{o}C.

Fig. 5. Gliding angle change for four sequential runs. Pump polarization is 60^{o}. Temperature is 40^{o}C.

Fig. 6. Gliding angle change for two sequential runs. Run 1: Pump polarization is -40^{o}. Run 2: Pump polarization is $+40^{o}$. Temperature is 30^{o}C.

Fig. 7. Gliding angle change before and after application of circularly polarized pump.

Fig. 8. Gliding angle as a function of time for an external magnetic field. Temperature is 30^{o}C.



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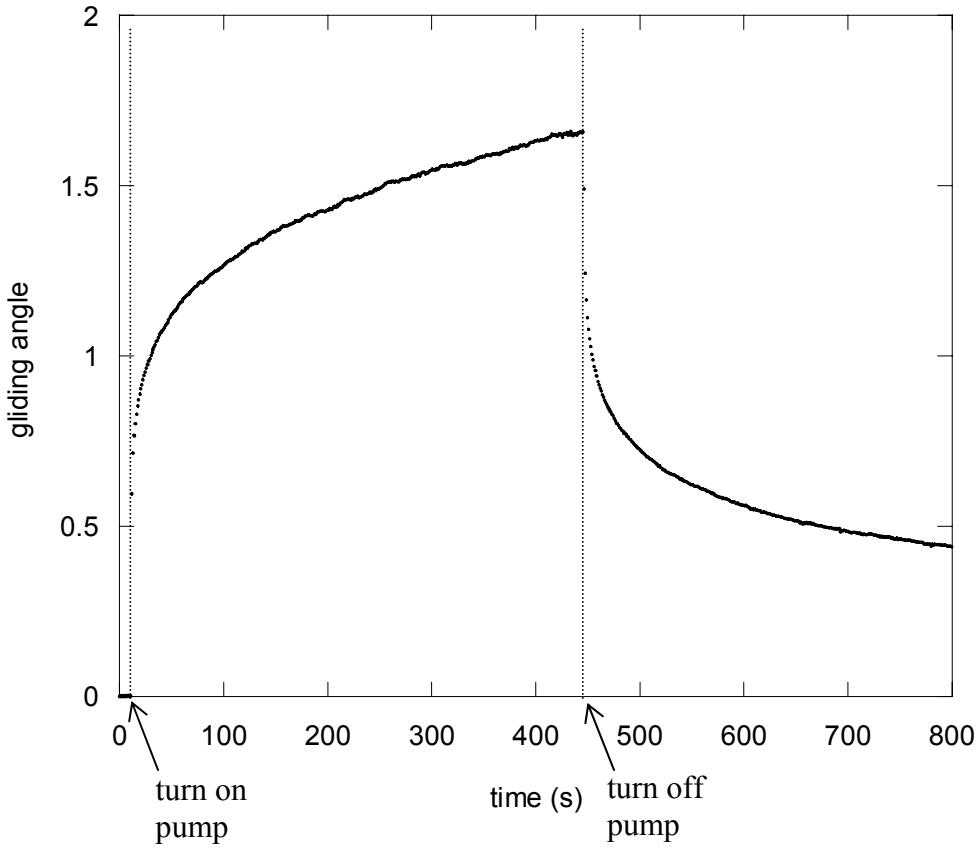

Fig. 2. Gliding angle as a function of time for a pump polarization angle of 45^{o}. Temperature is 30^{o}C.

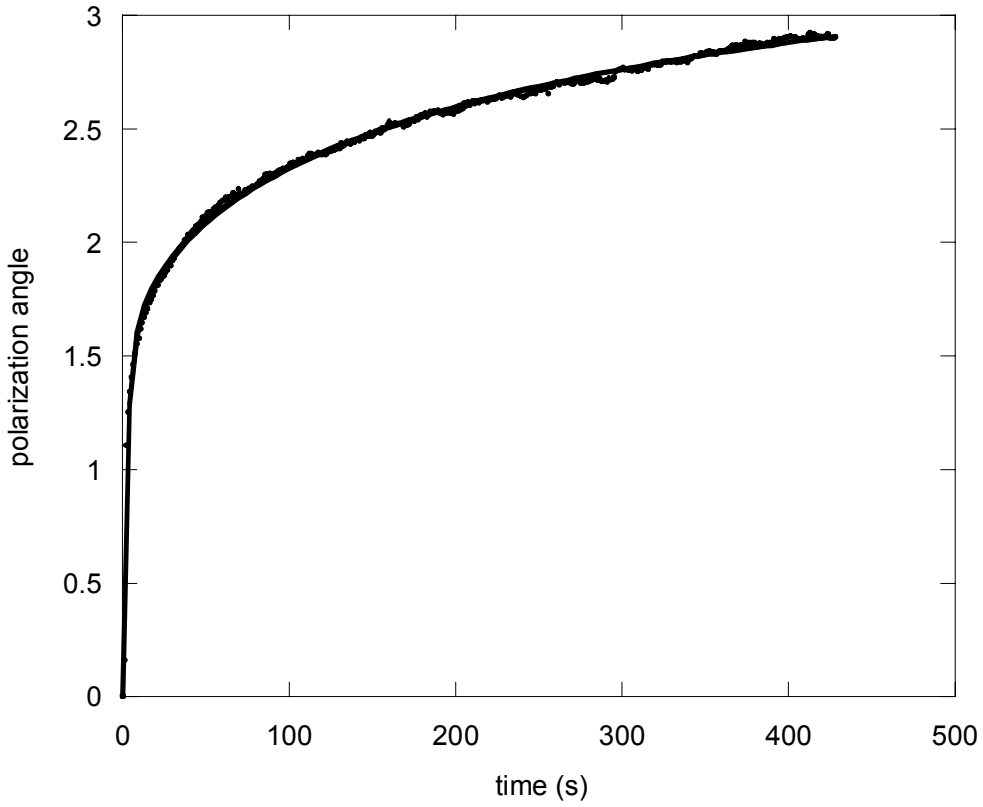

Fig. 3. Gliding angle as a function of time while pump is applied. Pump polarization angle is 60^{o}. Temperature is 40^{o}C.

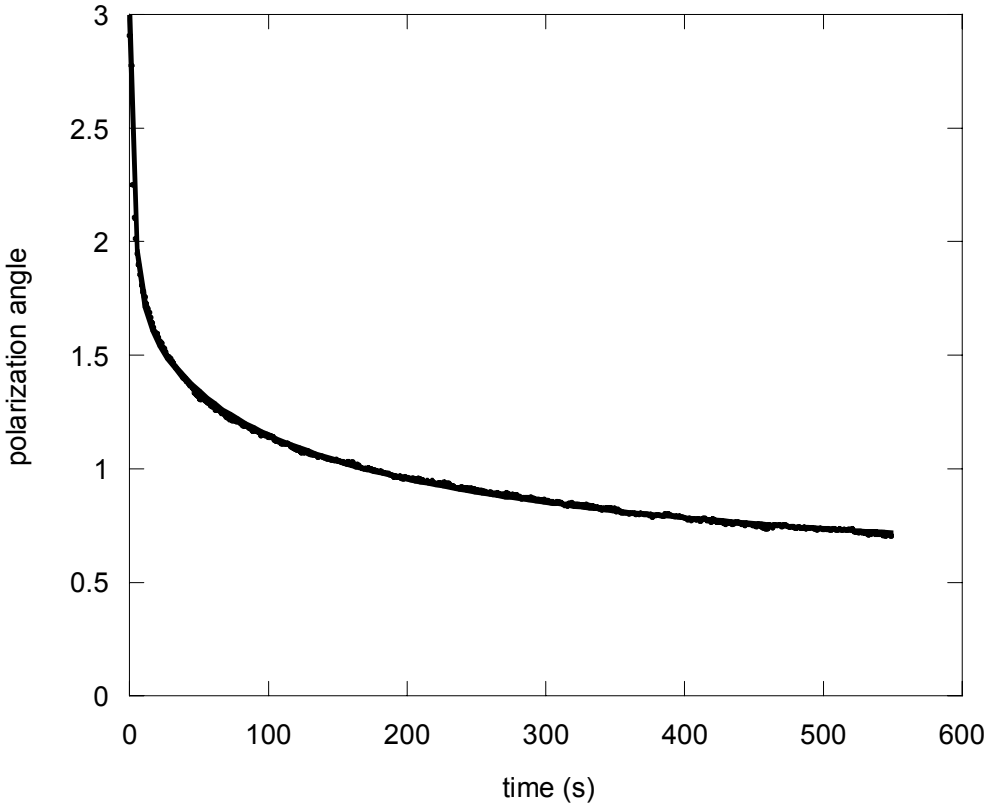

Fig. 4. Gliding angle as a function of time after pump is removed. Pump polarization angle is 60^{o}. Temperature is 40^{o}C.

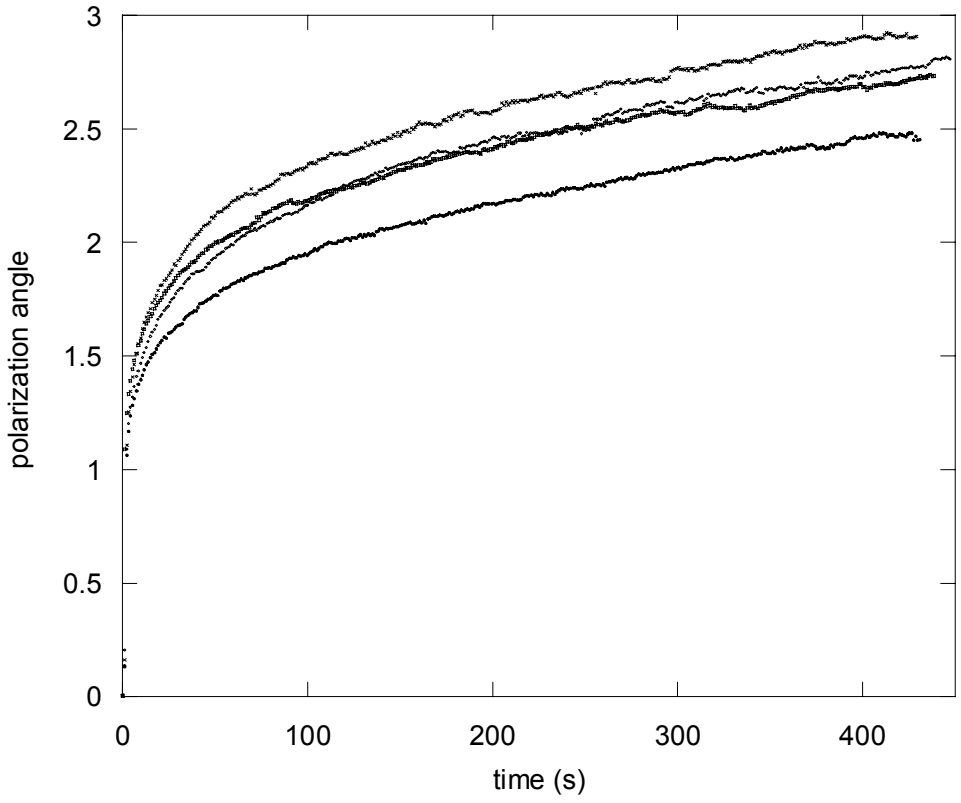

Fig. 5. Gliding angle change for four sequential runs. Pump polarization is 60^{o}. Temperature is 40^{o}C.

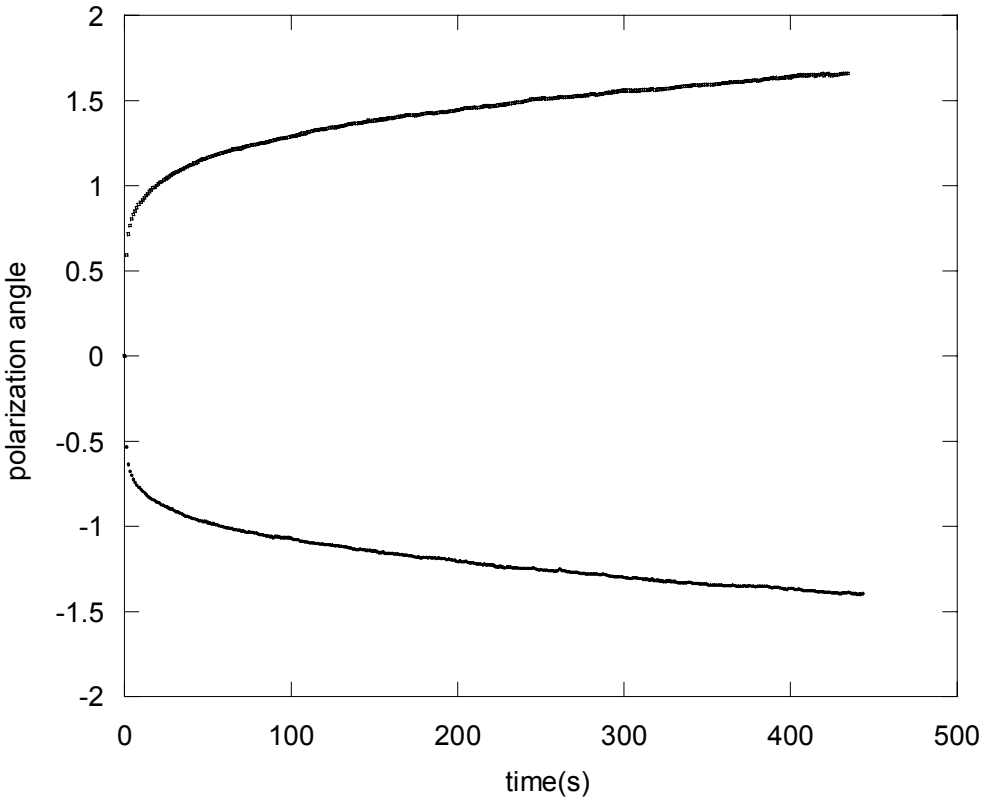

Fig. 6. Gliding angle change for two sequential runs. Run 1: Pump polarization is -40^{o}. Run 2: Pump gliding is +40^{o}. Temperature is 30^{o}C.

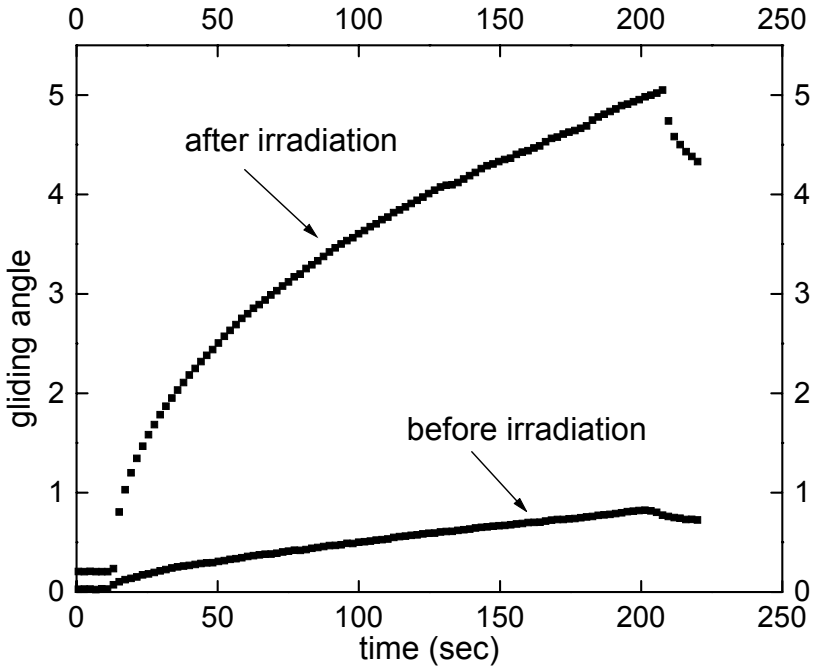

Fig. 7. Gliding angle change before and after application of circularly polarized pump.

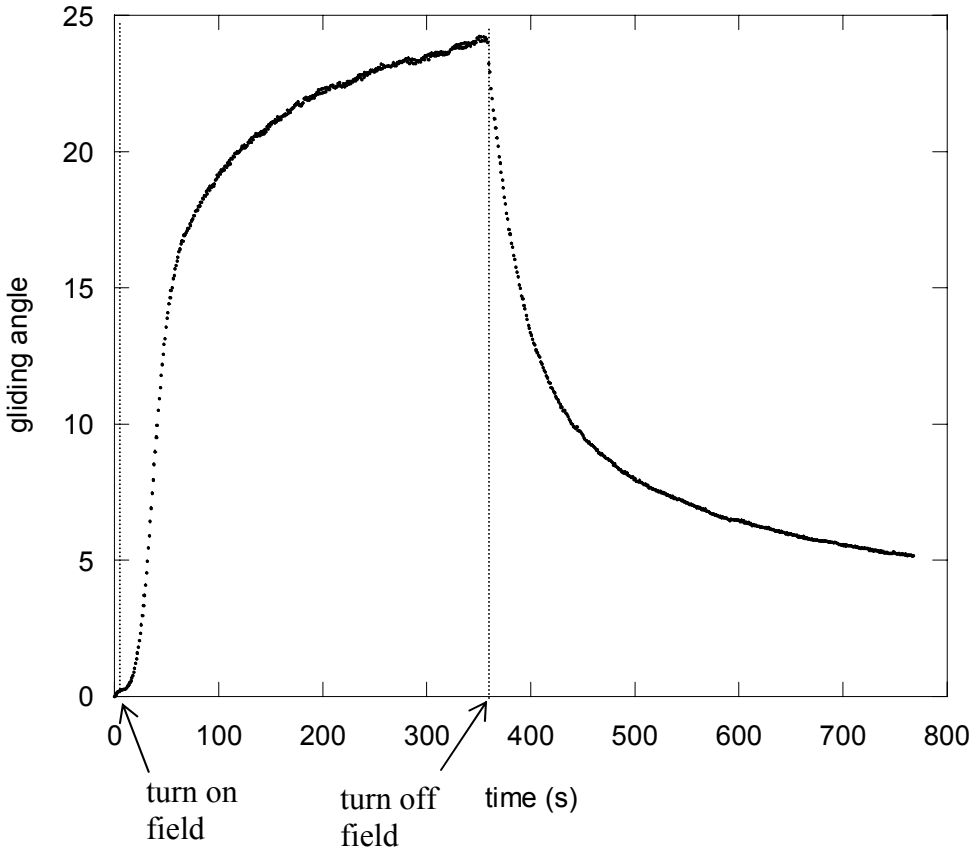

Fig. 8. Gliding angle as a function of time for an external magnetic field. Temperature is 30^{o}C.

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