

Gliding of liquid crystals on soft polymer surfaces

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Magnetic field induced reorientation of nematic liquid crystals on polymer layers is studied near the glass transition temperature of the polymer. Kinetic curves for different field strengths and temperatures are presented. A model is developed, which takes into account the structural rearrangements in the polymer induced by its interaction with the anisotropic potential of the liquid crystal. Simulations based on the model are in good quantitative agreement with the experimental data.

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I. INTRODUCTION

The interaction between polymer surfaces and liquid crystals is an attractive subject for fundamental research and it also plays an essential role in the operation of many liquid crystal-based devices. This interaction determines the alignment properties of a liquid crystal at its interface with a polymer layer. A standard method consists of rubbing polyimide layers unidirectionally to produce anisotropy in the surface structure of the polymer; as result the liquid crystal director is aligned parallel to the rubbing direction. In this procedure the liquid crystal apparently plays a purely passive role; its orientation is fully determined by the previous treatment of the polymer. There are, however, other situations, when the influence of the liquid crystal on the surface structure of the polymer is also important. We suggest that, in general, a polymer-liquid crystal interface should be regarded as a coupled system, where the two components - the polymer and the liquid crystal - mutually effect each others structure. An example of such behavior was discussed

earlier, namely the influence of the presence of liquid crystal on photo-orientation of dye-doped polymers [1]. Here we apply our concept to the case of azimuthal director reorientation at polymer - liquid crystal interfaces (director gliding).

Director gliding has been demonstrated in the past by Vetter et al. [2] and Vorflusev et al.[3] on polyvinyl alcohol (PVA) coatings. They applied an in-plane electric field to reorient the liquid crystal on the PVA-coated plate and measured the back-relaxation of the nematic director after the field was switched off. Further studies were carried out on the same phenomenon by Faetti et al. [4] and Stoenescu et al. [5] on PVA layers and evaporated SiO_2 coatings. No systematic study was reported, however, on the role of the polymer structure on the temperature and field dependence of the kinetics of the gliding process.

In the present paper, we describe experiments on field-induced rotation of the nematic director on polymer surfaces in the vicinity of the glass transition temperature of the polymer. We demonstrate that gliding speeds up considerably when the temperature approaches the transition region from glass-like to rubber-like behavior. We show that the kinetics of the gliding process can be interpreted by taking into account the orienting action of the liquid crystal on the polymer chains. A simple phenomenological model is presented which describes quantitatively the observations.

II. EXPERIMENTAL

In the experiments we studied polyethyl-methacrylate (PEMA, $T_g = 56^\circ C$), polymethyl-methacrylate (PMMA, $T_g = 110^\circ C$) and an azo-dye functionalized PMMA. The last system will be discussed in a separate paper [6]. The liquid crystal (E49 from British Drug House, clearing point $100^\circ C$) was sandwiched between two polymer-coated plates; the cell thickness, L , was typically $60\mu m$. One plate was coated with polyimide (PI) and rubbed to ensure strong anchoring on it ("hard plate"). The other substrate was coated with PMMA or PEMA and was not treated mechanically ("soft plate"). After filling the cells, they were heated near or above T_g and subsequently cooled to room

temperature. This procedure resulted in good quality planar alignment. The sample was placed into an electromagnet with the field oriented perpendicularly to the rubbing direction. The director gliding was followed with a He-Ne laser beam, passing through the cell from the PI side and polarized parallel to the rubbing direction. As the cell thickness was much larger than the light wavelength, the polarization followed the director orientation adiabatically within the cell. Thus measuring the polarization direction behind the sample provided straightforwardly the director angle on the soft plate (gliding angle, φ_s).

III. RESULTS

In Fig.1a, the gliding angle is shown for PEMA as a function of time at different magnetic field strengths, at a fixed temperature ($27^\circ C$). As it can be seen from the figure, gliding of the director towards the magnetic field, took place on time-scales orders of magnitude higher than the bulk relaxation time of the director ($\approx 10sec$). Within the time of application of the magnetic field (1 hour), the gliding angle did not saturate. On log-log scale the curves show a linear increase in time (see figure inset). Also, the back-relaxation towards the rubbing direction after the field was switched off was not completed within reasonable times (Fig 1b). In order to remove the twist deformation entirely, the sample was heated to T_g and then cooled back to the measuring temperature.

In Fig. 2, the temperature dependence of the kinetics is shown at a fixed magnetic field. The gliding process speeded up considerably as T_g was approached. At sufficiently high temperatures the surface reorientation time became comparable with the transient time characteristic for the bulk deformation. We obtained qualitatively similar results with PMMA layers, but at about 20 degrees higher temperatures than with PEMA. In control cells, consisting of two hard plates, no director gliding was observed.

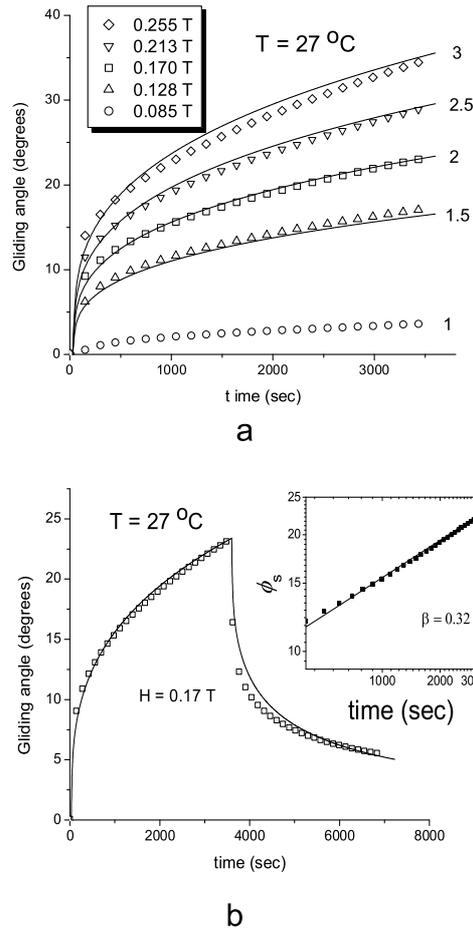


Figure 1: a; Gliding angle as a function of time on PEMA at different magnetic field strengths. Solid lines: simulations with $H_{Fr} = 0.085T$, $\tau_b = 12\text{ sec}$, $\xi = 0.5\mu\text{m}$, $Q_S^{eq} = 0.765$, $\beta = 0.31$, $\tau_0 = 14.6\text{ sec}$. The numbers at the end of the curves give the ratio H/H_{Fr} . b; Gliding angle for $H = 0.17T$ and relaxation after the field was switched off. Inset: gliding shown on log-log scale.

IV. INTERPRETATION

In order to interpret the results, the torques acting on the director at the interface should be considered [7]. A first torque is connected to the director stress tensor [8] and it is proportional to the twist deformation at the soft plate (surface twist torque). A second torque arises from the deviation of the director from the "easy axis" at the polymer i.e. from the axis along which the interaction energy between the polymer and the liquid crystal is minimal (anchoring torque). The director position at the inter-

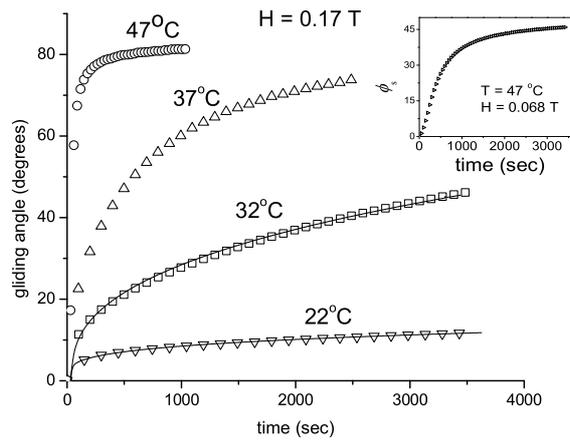


Figure 2: Temperature dependence of gliding on PEMA. Solid lines: simulations with $\beta = 0.255$, $\tau_0 = 70\text{sec}$, (22°C); $\beta = 0.38$, $\tau_0 = 5.8\text{sec}$, (32°C). Other parameters were the same as in Fig. 1. Inset: gliding below the Fredericksz transition ($H/H_{Fr} = 0.8$).

face is determined by the balance of these two torques. The balance is established in a very short time as compared to the characteristic time scales involved in the present experiments [9], hence we assume that the two torques are continuously equal during gliding.

One possible way to interpret the results would be to assume that the anchoring energy is small on the soft plate [3]. If the latter torque is small, the director should rotate by large angles away from the easy axis until the field-induced surface twist deformation is compensated by the anchoring torque. According to this model, however, gliding should saturate on a time scale comparable to the bulk relaxation time. In contrast to this expectation, in the experiments saturation was not observed even after times two orders of magnitude longer than the bulk transient time. A further difficulty of the model is that it does not give account of the origin of the anchoring energy on the soft plate - at least in our case.

To overcome the first difficulty, Vorflusev et al. introduced a "surface viscosity" term into the balance equation for surface torques, without justification. Vetter et al. [2] suggested that the anchoring on the soft plate is due to an adsorbed layer of the liquid crystal molecules on the polymer. According to their model, through desorption and

re-adsorption of the liquid crystal molecules, the easy axis can rotate. Similar ideas were put forward in [4, 5]. In this model, however, it is difficult to explain why is the magnitude and the kinetics of the gliding process correlated with the glass transition temperature of the polymer.

Our interpretation of the observations is based on the assumption that the polymer main-chains can undergo conformational transitions under the influence of the anisotropic potential of the liquid crystal. The induced structural changes in the polymer decrease the interfacial energy between the liquid crystal and the polymer, hence self-strengthening of the surface anchoring of the liquid crystal takes place. This mechanism can account for different kinds of alignment effects which occur on untreated polymer surfaces, like flow-induced alignment or surface memory effect [12]. Using this concept, we assert that the initial easy axis on the soft plate is created during the preparation of the cell by the nematic liquid crystal itself, through orienting the polymer chains to a certain extent. When no field is applied, the easy axis becomes parallel to the rubbing direction. The corresponding anchoring energy is not necessarily very weak, not even above T_g . The gliding process in magnetic field can be understood as follows. Above the magnetic Frederiks threshold, H_{Fr} , a surface twist torque appears, which rotates the director towards the magnetic field direction until it is balanced by the anchoring torque. The change of the director position at the surface initiates conformational changes in the polymer and as a result, the easy axis rotates towards the director. This latter rotation, in turn, decreases the anchoring torque, therefore the director can rotate further towards the magnetic field. The process ends when both surface torques become zero, i.e. the twist deformation is zero at the surface and the easy axis coincides with the director at the soft plate.

To make the above considerations quantitative we present a two-dimensional model. We take the x axis along the rubbing direction, y in the substrate plane perpendicular to x , and z along the sample normal. Consider a polymer chain unit oriented along the unit vector \mathbf{d} in the substrate plane. The interfacial energy between the polymer segment and the liquid crystal is taken in the usual Rapini - Popoular form [10], $w = w_0 - \frac{1}{2}w_a(\mathbf{d}\mathbf{n}_s)^2$, where $\mathbf{n}_s = \{\cos \varphi_s, \sin \varphi_s\}$ is the nematic director at the soft surface. Introducing an order parameter tensor [11] for the polymer chains with the definition $Q_{ij} = 2\langle d_i d_j \rangle - \delta_{ij}$, the

anisotropic part of the interfacial energy per unit area, W , can be expressed as $-\frac{1}{4}W_a\mathbf{n}_s\mathbf{Q}\mathbf{n}_s$ ($W_a = Nw_a$ where N is the number of chain units per unit area). The eigenvector of \mathbf{Q} defines the easy axis of the polymer, while its eigenvalue can be considered as the polymer scalar order parameter, Q_S , ranging from 0 (isotropic distribution of the chain orientation) to 1 (perfect orientational order). The anchoring torque is $-\partial W/\partial\varphi_s$; the twist torque is $K_2\varphi'_s$, where K_2 is the twist elastic constant and φ'_s is the derivative of φ_s along z at the soft plate. The balance of torques can be written as

$$\xi\varphi'_s = -\frac{1}{2}(Q_{xx}\sin 2\varphi_s - Q_{xy}\cos 2\varphi_s), \quad (1)$$

where $\xi = K_2/W_a$ is the extrapolation length.

To describe the kinetic curves one needs to establish dynamic equations for φ'_s and \mathbf{Q} , at fixed φ_s . The steady-state value of φ'_s , ($\varphi'_{s,eq}$), can be obtained from the balance equation for bulk magnetic and elastic torques [8]:

$$\frac{d^2\varphi}{dz^2} = -\frac{1}{2}\frac{\pi^2}{L^2}\left(\frac{H}{H_{Fr}}\right)^2\sin 2\varphi. \quad (2)$$

with the boundary conditions $\varphi(0) = 0$ and $\varphi(L) = \varphi_s$. To simplify mathematics, we use for φ'_s a simple relaxation equation

$$\frac{d\varphi'_s}{dt} = -\frac{\varphi'_s - \varphi'_{s,eq}}{\tau_b} \quad (3)$$

where τ_b is a characteristic bulk relaxation time in the order of $L^2\gamma/K_2$ (γ rotational viscosity of the nematic).

To obtain a dynamical equation for \mathbf{Q} , we first consider again the steady state at fixed gliding angle. According to our considerations, liquid-crystal induced structural changes rotate the easy axis of the polymer parallel to the director, \mathbf{n}_s . The scalar order parameter converges to a saturation value, Q_S^{eq} , determined by the interaction strength, w_a . The corresponding steady state order parameter tensor, \mathbf{Q}_{eq} , can be written as $Q_{eq,ij} = Q_S^{eq}(2n_{s,i}n_{s,j} - \delta_{ij})$.

In a simple dynamic equation one could describe the relaxation of the actual \mathbf{Q} tensor towards \mathbf{Q}_{eq} with a single relaxation time:

$$d\mathbf{Q}/dt = -(\mathbf{Q} - \mathbf{Q}_{eq})/\tau.$$

That approach, although gives a reasonable qualitative description of the phenomenon, fails to describe the significant slowing down of the gliding process, seen in the experiments. To obtain quantitative agreement with the observations, we have to suppose a wide distribution of relaxation times. Such an assumption is natural for an amorphous system near the transition zone from the glass-like to rubber-like behavior [13], where small environmental changes can cause large changes in the chain mobility. We assume that different microscopic parts of the polymer network relax with different relaxation times towards the same orientational distribution. Let $g(\tau)d\tau$ denote the fraction of chains or chain segments, which relax with a time constant between τ and $\tau + d\tau$, and let the corresponding order parameter tensor of these chains be $\mathbf{q}(\tau)$. The dynamical equation for $\mathbf{q}(\tau)$ is

$$\frac{d\mathbf{q}(\tau)}{dt} = -\frac{\mathbf{q}(\tau) - \mathbf{Q}_{eq}}{\tau} \quad (4)$$

and the order parameter of the polymer as a whole is

$$\mathbf{Q} = \int g(\tau)\mathbf{q}(\tau)d\tau. \quad (5)$$

In order to carry out simulations, the distribution function $g(\tau)$ has to be specified. The experimental results suggest that $g(\tau)$ should have a power-law form, starting from a relaxation time τ_0

$$g(\tau) = A/\tau^{1+\beta} \text{ for } \tau > \tau_0 \quad (6)$$

where A is a normalizing factor and β should be close to the observed exponent. We note that for kinetic processes in amorphous systems power-law type behavior is not unusual; similar relation was found in transient photocurrent measurements [14].

Eqs. /1-6/ provide a complete set of relations for the calculation of the gliding process. In Fig. 1, the solid lines correspond to simulations based on the above model. H_{Fr} and τ_b were determined from measurement on a control PI-PI cell, where no gliding was observed. β was chosen 0.31, which is close to the observed exponent. Regarding the further parameters, we found that it is impossible to determine ξ , Q_S^{eq} and τ_0 separately from the curves; for a wide range of meaningful values of ξ and Q_S^{eq} it is always possible to choose τ_0 to get a good agreement between the measured and calculated curves. In the simulation we choose ξ and Q_S^{eq} arbitrarily and adjusted τ_0 in a way to get the best fit for $H/H_{Fr} = 2$. As it can be seen from the figure, with the same set of parameters we obtained also good fit for other magnetic field

values and for the relaxation curves of the gliding process. This agreement gives a strong support of the idea behind the model. Fitted curves at fixed H and different temperatures show that β is increasing and - if ξ and Q_{eq} is kept constant - τ_0 is decreasing with increasing temperatures (Fig. 2). This fact can be attributed to the strong increase of the polymer chain mobility in the transition region from glass-like to rubber-like behavior of the polymer.

Experiments show that gliding takes place also at and below the Freedericksz threshold (Figs. 1a and 2). To simulate the kinetics for this situation, a small initial deviation of the magnetic field from the y direction has to be assumed. As a simple consideration shows, the model predicts that gliding can occur above half of the Freedericksz threshold. This problem will be discussed in a future paper.

In conclusion, we have shown that director reorientation on polymer surfaces can be attributed to structural changes in the polymer, induced by the liquid crystal. According to our model, the "surface viscosity" for gliding is determined by the rate of rearrangement of the polymer chains, rather by the surface friction of the liquid crystal. The study of the kinetics of gliding can thus provide useful information about the chain mobility. Finally we note that the concept proposed in this paper may work also in the case of zenithal gliding, i.e. field-induced change of the tilt angle of the director at the polymer surface [15].

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