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Influence of the Molecular Weight of a Polymer on the Gliding of Nematic Liquid Crystals

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Gliding of the nematic liquid crystal director on polymethyl-methacrilate layers in a magnetic field is observed. It is found that the kinetics of the gliding process are strongly influenced by the molecular weight of the polymer chains. This fact supports the model of gliding based on the mutual orienting effect of the liquid crystal and polymer network.

Keywords: director gliding; polymer-liquid crystal interface; polymer molecular weight

The interaction between liquid crystals and solid substrates has been the subject of many investigations. One characteristic quantity of the interaction is the so-called easy axis *i.e.*, the direction of the liquid crystal molecules along which the interfacial energy is minimal. In a uniformly oriented liquid-crystalline layer, the easy axis and the liquid crystal director are parallel to each other. If an external torque is applied, which induces a director change along the normal axis of the interface, the surface director deviates by a certain angle from the easy axis; the magnitude of the deviation is determined by another characteristic quantity of the interaction, the anchoring energy.

It is a well-known fact that if the surface director and the easy axis are not parallel, the latter axis may reorient toward the former one (gliding effect). Gliding was first studied systematically by Vetter *et al.* [1] on polyvinyl alcohol coatings. Later further investigations

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were carried out both on in-plane (azimuthal) and out-of-plane (zenithal) gliding [2–7]. Most experiments were performed on polymer layers, although gliding was found to take place on inorganic substrates too.

Two mechanisms were proposed for the gliding process. In the models based on the first mechanism, it is supposed that the easy axis is determined by the orientation of the liquid-crystalline molecules adsorbed at the substrate. When a gradient of the director is created at the interface along the normal direction to the plane, the adsorbed molecules may change their orientation through desorption and re-adsorption processes to decrease the angle between the easy axis and the surface director. The second mechanism is specific for polymers. It relies on the assumption that under the influence of the anisotropic field of the liquid crystal, the structure of the polymer network may be modified. According to this model, the easy axis is determined by the orientational distribution of the polymer chain segments. If the easy axis is not parallel to the surface director, conformational transitions occur in the polymer chains, again in a way to shift the easy axis toward the director. The latter model is supported by the fact that the drift of the easy axis speeds up by orders of magnitudes when the temperature range of glass-like to rubber-like behavior of the polymer is approached.

The aim of the present article is to give further support to the second model by studying the influence of the molecular weight of the polymer on gliding. While the desorption–re-adsorption process is hardly affected by the molecular weight of the polymer chains, the probability of conformational transitions may be sensitive to this circumstance. In the experiments, we found a strong dependence of the kinetics of reorientation of the easy axis on the molecular weight, confirming the importance of the polymer structure in gliding.

In the experiments, we investigated polymethyl-methacrylate (PMMA), supplied by Aldrich. Three different molecular weights of PMMA were used: high ($M_w \approx 996,000$), medium ($M_w \approx 120,000$), and low ($M_w \approx 15,000$). The experimental technique was similar to the one described in [6]. The liquid crystal (E49 from British Drug House, clearing point 100°C) was sandwiched between two polymer-coated plates. One plate was coated with polyimide and rubbed to ensure strong anchoring on it. The other substrate was coated with PMMA and was not treated mechanically. After filling the cells, they were heated near the glass-transition temperature of PMMA ($T_g \approx 100^\circ\text{C}$) 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. Above the magnetic Freedericksz threshold, rotation of the

surface director on the PMMA side of the cell was detected. The surface director rotation was followed with a He-Ne laser beam, passing through the cell from the polyimide side and polarized parallel to the rubbing direction. Because the cell thickness was much larger than the wavelength of the light, the polarization followed the director orientation adiabatically within the liquid-crystalline layer. Thus, measuring the polarization direction behind the sample provided straightforwardly the director angle on the PMMA plate (gliding angle).

The results are shown in Figs. 1–3. The applied magnetic field was about twice the Freedericksz threshold. The bulk time constant of the deformation of the nematic layer was around 20 s. On a much longer timescale, the drift of the surface director was observed. At low temperatures, it was impossible to achieve saturation, and the director was increasing gradually, with a decreasing speed.

The drift of the surface director is connected with the reorientation of the easy axis (*i.e.*, with gliding) [6]. The twist deformation caused by the magnetic field initiates a surface torque, which rotates the director at the surface toward the magnetic field, until it is balanced by the anchoring torque. The easy axis rotates towards the surface director, and as a result the elastic and anchoring torques become out of balance. Therefore the director can rotate further toward the magnetic

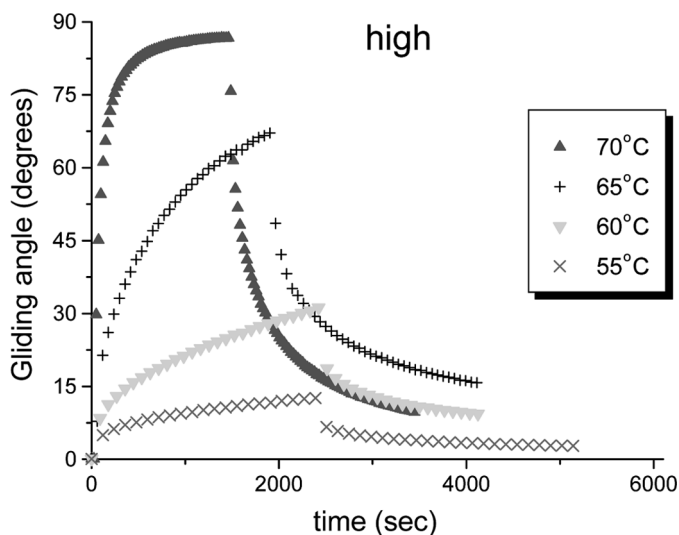


FIGURE 1 Gliding angle as a function of time at different temperatures. The magnetic field was about twice the Freedericksz threshold and switched off at the breaking points of the curves. High-molecular-weight PMMA.

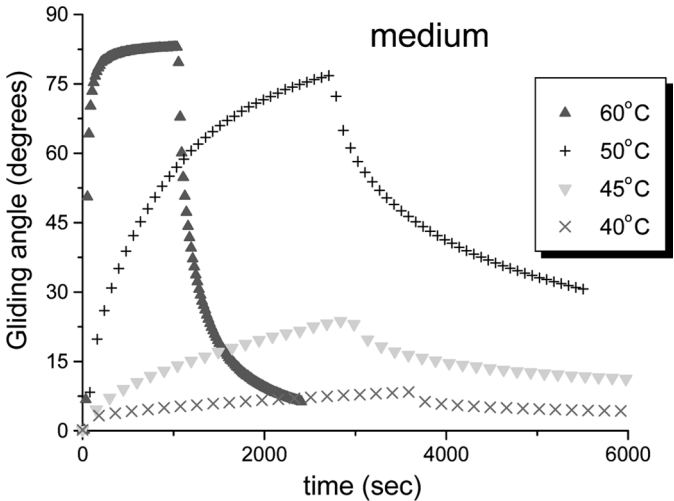


FIGURE 2 Same as in Fig. 1, for the medium-molecular-weight PMMA.

field. The process ends when the twist torque is zero at the PMMA interface (*i.e.*, the surface director is at that plate parallel to the applied magnetic field).

Similar to the data reported in Ref. 6, the gliding curves were found to be extremely temperature dependent. Changing the temperature by

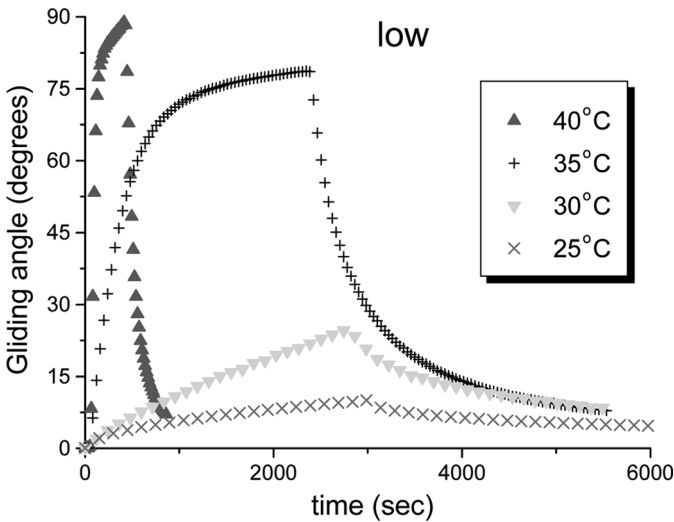


FIGURE 3 Same as in Fig. 1, for the low-molecular-weight PMMA.

approximately 15 degrees changed the character of the curves from slow, gradual gliding to an almost free rotation of the director at the surface. The temperature range, however, where the transition from slow to fast gliding takes place increased significantly with increasing molecular weight of the PMMA. For low molecular weight, it was 25–40°C, whereas for the high molecular weight, it shifted to 55–70°C.

As already pointed out, the strong dependence of the kinetics of gliding on the average molecular weight of the polymer cannot be explained within the framework of adsorption phenomenon. The liquid-crystalline molecules are much smaller than the polymer chains; therefore their adsorption properties cannot depend on how long the chain is to which they are bound. On the other hand, the model based on the mutual orienting effect of the nematic liquid crystal and the polymer network seems to be compatible with the observations. The orienting of the polymer network by the liquid crystal involves conformational transitions of the chains, which is a thermally activated process. The probability of a conformational transition caused by the liquid-crystalline molecular field is $\exp(-U/kT)$, where U is the energy barrier of the transition. As conformational transitions are not localized to a certain chain segment, but involve the chain as a whole, the parameter U can be sensitive to the number of monomer units in the chain. Our result suggests that U increases, so the probability of the rearrangement of a chain decreases with increasing chain length. Thus, with high chain length, a higher temperature is needed to achieve the same gliding speed than with the low one.

We note that the assumption that the probability of conformational transitions depends on the chain length also may provide an explanation of the wide distribution of gliding times, described in Ref. 6. The distribution of gliding times according to this assumption reflects the distribution of the chain lengths. The fast part of gliding originates from chains that are shorter, the slow part from chains that are longer than the average length.

In conclusion, we showed that the kinetics of gliding is significantly influenced by the molecular weight of the polymer. This observation supports the model based on the assumption that the drift of the easy axis is due to the rearrangement of the polymer under the influence of the liquid crystal.

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