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Anchoring strength coefficient of a monomer and its dimer at a polymer-coated interface

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The dialkoxyphenylbenzoate monomer '5005' ($C_5H_{11}OC_6H_4COOC_6H_4OC_5H_{11}$) and its dimer were aligned parallel to a buffed polyimide-coated glass substrate. A magnetically induced Freedericksz transition in both thick and thin cells was used in conjunction with a capacitance technique to determine the anchoring strength coefficient W as a function of temperature in the nematic phase. It was found that for both monomer and dimer, W increases with decreasing temperature. The anchoring coefficient for the dimer, however, was found to be an order of magnitude larger than for the monomer at comparable reduced temperatures. The splay elastic moduli were also determined for both species, and found to be of comparable magnitude, consistent with previous results.

Anchoring of liquid crystals at non-liquid crystal interfaces has been the subject of intense study from both an applied and basic scientific perspective [1]. To lowest order an additional surface term $F_s = \frac{1}{2}W(\theta - \theta_0)^2$ must be added to the free energy [2], where W is the quadratic anchoring strength coefficient, θ is the molecular tilt angle with respect to the interface, and θ_0 the undisturbed (pretilt) angle. Although higher order corrections have been investigated [3, 4], most workers to date have concentrated on this lowest order term. Thus, during the past decade numerous papers have appeared reporting values of W for various liquid crystals at a non-liquid-crystalline interface [3, 5–13]. These generally range between 10^{-11} and 10^{-9} J, although higher values have been obtained [14–18]. Nevertheless, despite the large number of experimental results, theoretical progress on understanding the interfacial behaviour of liquid crystals has been slow. Parsons, for example, examined the possibility of a surface phase transition whereby the equilibrium orientation is determined by competition between

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dipolar and quadrupolar interactions [19,20]. For sufficiently strong quadrupolar interactions, the liquid crystal director will lie at some non-zero angle relative to the interface normal. Okano and Murakami have given the dependence of the surface tension on the complex dielectric tensor [21]. The subject of wetting has also seen considerable theoretical treatment, both from a Landau perspective as well as from a more microscopic approach [22,-24]. The anchoring energy itself has also been studied theoretically, although to date the approach has been primarily phenomenological [12,25-27].

Given the importance of anchoring as it relates not only to fundamental surface science but to technology as well, it is important to have a systematic set of data from which a microscopic picture might emerge. Thus, to further illuminate the nature of liquid crystal anchoring we have investigated a rather interesting system composed of the liquid crystal monomer '5005' ($C_5H_{11}OC_6COOC_6H_4OC_5H_{11}$) and its dimer '5–10–5'. Although dimers of various spacer lengths have been synthesized and experimentally investigated [28], this particular dimer is just two monomers attached end-to-end, with two hydrogens removed. Although the dimer's spacer has been shown to be nearly completely flexible in the isotropic phase [29], X-ray, NMR, and Cotton–Mouton results indicate that the relative population of all-*trans* conformers is extremely high in the nematic phase [24, 30–32]. The spacer does show a small amount of flexibility in the nematic phase, however, as indicated by recent light scattering results [33]. Nevertheless, if we assume a fully extended conformation, the molecular lengths are $L_{\mathrm{monomer}} = 27{\cdot}6$ Å and $L_{\mathrm{dimer}} = 53{\cdot}7$ Å, and the diameter $d = 4{\cdot}6$ Å for both oligomers [34]. This monomer–dimer pair, then, represents a nearly ideal system for study: one species is simply two monomers attached almost rigidly end-to-end. (Alternative systems, such as the polyelectrolyte polybenzyl glutamate, are too dilute and possess very different sorts of surface interactions to be useful in understanding the interfacial behaviour of thermotropic liquid crystals.) Thus our system, unlike a homologous series of liquid crystals where only the terminal group lengths are varied, provides us with a unique opportunity to isolate the effects of molecular length on the anchoring energy at a liquid crystal–substrate interface.

In order to obtain the anchoring energy W, we performed magnetic Freedericksz measurements in the splay geometry for both very narrow (thickness $l_n \sim$ several μm) and wide samples (thickness $l_w \sim$ many tens of μm). For the case of rigid anchoring ($W \to \infty$), the magnetic Freedericksz threshold field $U(l)$ is given by

$$U(l) = (\pi/l)(K_{11}/\Delta\chi)^{1/2}, \tag{1}$$

where l is the sample thickness, K_{11} the splay elastic constant, and $\Delta\chi$ is the magnetic susceptibility anisotropy. On the other hand, for the case of finite W, Rapini and Papolar have shown [2] that the magnetic Freedericksz threshold field $H_{\mathrm{th}}(l, W) < U(l, W = \infty)$ is given by the equation

$$\cot(\pi H_{\mathrm{th}}/2U) = (\pi K_{11}/lW)(H_{\mathrm{th}}/U). \tag{2}$$

Equation (2) actually represents a pair of equations, one for the narrow sample and one for the wide sample, each involving the appropriate threshold field and U. Finally, since

$$U(l_n) = (l_w/l_n)U(l_w), \tag{3}$$

we obtain four equations in four unknowns. Thus, by measuring the threshold fields for two samples of different thickness, these equations can be solved to obtain W, $U(l_w)$, $U(l_n)$, and K_{11} as functions of temperature.

The monomer and dimer were synthesized according to procedures described elsewhere [35–37]. Four samples were prepared: a narrow and a wide cell for the monomer, and corresponding cells for the dimer. A square glass slide 10 cm on a side and coated with strips of indium tin oxide (ITO ~ 20 Ω square^{-1}) was treated with a polyimide coating to achieve homogeneous alignment of the liquid crystals. The polyimide coatings were prepared as follows: a mixture of one part polyimide (DuPont PI-2555) and one part thinner (DuPont T-9039) was placed on the ITO-coated glass surface and spun at 3000 rpm. The wet film was then fully cured for 1 h at 200°C. Finally, the coating was buffed unidirectionally using a nylon cloth (Yoshikawa Kako Ltd., grade Y_0-10-N and rubbing density of 200); the resulting polyimide coating was nominally of thickness 0·5 μm. Upon completion of the surface treatment, the ITO-coated glass was scored and broken into smaller slides from which sample cells were made. It is important to note that this coating technique represents a consistently reproducible surface treatment, especially since all the surfaces were treated simultaneously and uniformly from the same initial square. This is, of course, essential if data from different sample cells are to be compared. Samples cells were made from a pair of treated slides separated by mylar spacers and adjusted for optimum parallellism. The overlap area of the ITO was determined by an optical microscope to within 1 per cent, and was generally about 0·390 cm^2. Using an interferometric scheme [10], the spacings of the two narrow cells (between the polymer) at the centre of their ITO overlap areas were determined: $l_{\mathrm{n,monomer}} = 5{\cdot}55 \pm 0{\cdot}15\,\mu\mathrm{m}$ and $l_{\mathrm{n,dimer}} = 5{\cdot}08 \pm 0{\cdot}15\,\mu\mathrm{m}$. Likewise, the wide cells had spacings of $l_{\mathrm{w,monomer}} = 81{\cdot}3 \pm 0{\cdot}8\,\mu\mathrm{m}$ and $l_{\mathrm{w,dimer}} = 54{\cdot}9 \pm 0{\cdot}5\,\mu\mathrm{m}$. It should be noted that thickness variations of approximately ±0·75 μm were found over the overlap areas in all four cells. In an optical Freedericksz experiment such gradients are of minor importance since the laser spot could easily be reduced to under 100 μm. In a capacitance experiment (required by the geometry of our magnet), however, cell thickness variations tend to round the Freedericksz transition, as has been discussed previously [38]. This rounding gives rise to some uncertainty in H_{th}, which is fractionally larger in the narrow sample. This uncertainty in H_{th}, moreover, propagates to K_{11} and W, and constitutes the largest component in their error bars.

The sample holders were filled with the appropriate liquid crystal and placed in a brass oven; the temperature was controlled to approximately 10 mK for the monomer and 50 mK for the higher temperature dimer. The entire assembly was placed into the bore of a superconducting magnet such that the orientation of the magnetic field **H** was perpendicular to the plane of the glass holders and thus normal to the liquid crystal director, which was aligned homogeneously by the polymer. The samples were connected, via a high temperature coaxial cable, to an Andeen Hagerling Model 2500A capacitance bridge operating at 0·0025 V (rms) and 1 kHz. This voltage was sufficiently small to prevent a measurable contribution to the Freedericksz torque from the electric field. Each sample was first brought deep into the nematic phase ($T_{\mathrm{NI}}-T \sim 16$°C, where T_{NI}, the nematic–isotropic transition temperature, was 80·97°C for the monomer and 149·69°C for the dimer). At a fixed temperature, the capacitance was recorded as the magnetic field was swept slowly upward. Typically, the sweep rate in the wide cells was 0·6 G s^{-1}, while for the narrow cells (with a response time which scales as l^{-2}) it was approximately 10 G s^{-1}. These ramp rates were sufficiently slow to maintain near equilibrium conditions.

Figure 1 shows a typical experimental trace of the effective dielectric constant $\varepsilon_{\mathrm{eff}}$ versus magnetic field, used to determine the Freedericksz threshold field H_{th}. H_{th} is somewhat ambiguous owing to the rounding of the data; this problem has been

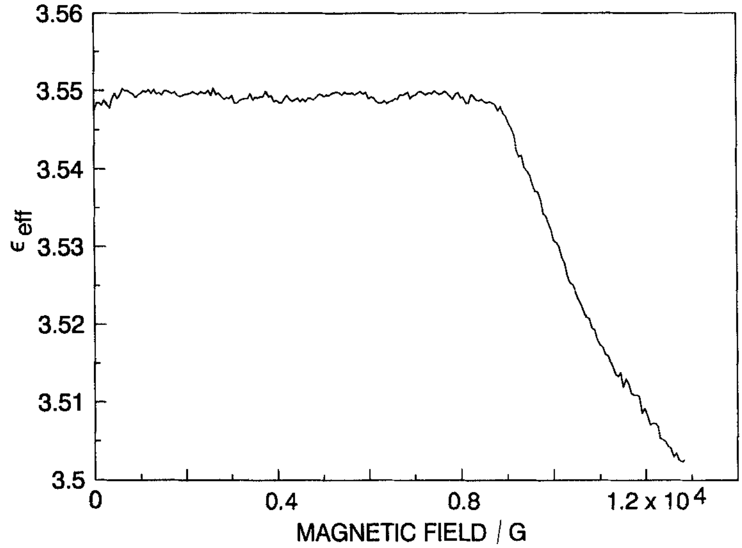

Figure 1. Typical dielectric data plotted versus magnetic field. Trace shown is for monomer in a narrow cell at $T-T_{NI}=-7{\cdot}06°C$.

discussed in detail elsewhere [38]. For these measurements, the rounding of the transition field is due partially to the non-ideal orientation of the sample with respect to **H** (i.e. **H** is not perfectly perpendicular to the liquid crystal director) but more importantly to the variations in cell thickness, probably due to variations in the polyimide coating, across the active region of the sample.

For each cell the threshold field H_{th} was determined as a function of temperature. For each species the data obtained for narrow and wide samples were fitted using equations (1)–(3). The magnetic susceptibility anisotropy $\Delta\chi$ plotted versus $T_{NI}-T$ was obtained from the literature [39]. Figures 2 and 3 show the measured threshold fields H_{th} and the calculated threshold fields U in the limiting case of $W\rightarrow\infty$, plotted versus $T_{NI}-T$ for narrow and wide samples. Error bars, approximately 3 per cent for the narrow samples and approximately 2 per cent for the wide samples, are due to uncertainty in determining H_{th}. Since it was necessary to know the threshold field H_{th} for both the narrow and wide samples at identical reduced temperatures, the data for the narrow samples represent interpolated values based upon measurements of $H_{th}(l_n)$ at nine points in both the monomer and dimer cases. Note that $U(l_w)$ is only slightly higher than $H_{th}(l_w)$ at each temperature, as expected for a wide sample, whereas $U(l_n)$ is considerably larger than $H_{th}(l_n)$ at each temperature.

Results for the splay elastic constants, shown in figure 4, are in good agreement with our previous results [33, 34]. Note that we have recently discovered a small error in the thickness of the dimer cell used in [34]; this has been corrected and will be reported in the near future [33]. Overall, an uncertainty of approximately ±10 per cent is associated with the elastic constants due largely to systematic errors in the value for $\Delta\chi$ as well as the field rounding discussed earlier. Essentially, the splay elastic constants for both monomer and dimer, especially when scaled by the square of the nematic order parameter S [34], are quite similar, a result discussed in [33, 34].

Finally, the calculated values for W versus temperature are plotted in figure 5. Although both monomer and dimer show W increasing with decreasing temperature, it

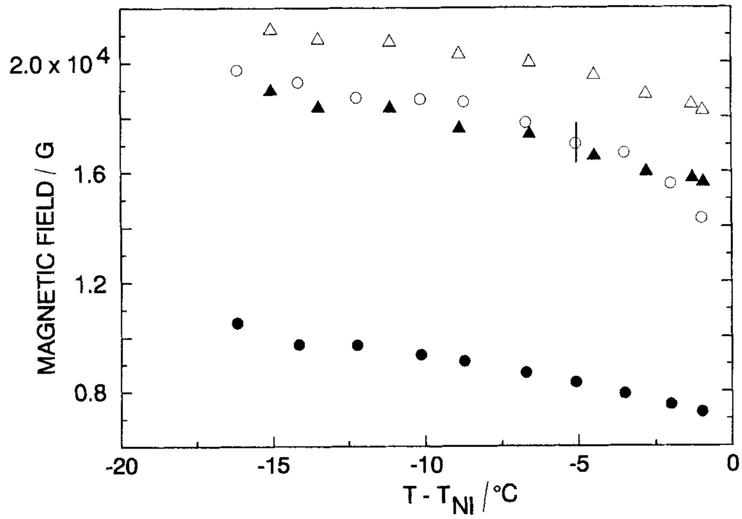

Figure 2. Narrow cell results for experimental threshold fields (H_{th}) and calculated fields (U), which assumes the anchoring strength is infinite. H_{th} for monomer (●) and for dimer (▲). U for monomer (○) and for dimer (△). Typical error bar is shown.

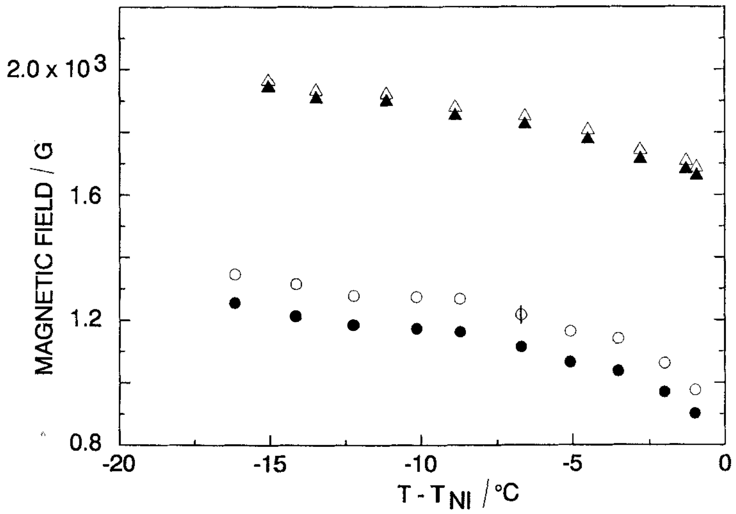

Figure 3. Wide cell results. H_{th} for monomer (●) and for dimer (▲). U for monomer (○) and for dimer (△). Typical error bar is shown.

is clear that W for the dimer is approximately ten times the monomer value. This is our central result. Note that the relative error is much higher for the monomer case, due mainly to the magnitude of W in this system. The error bars associated with W are dominated by the uncertainty in determining H_{th}: contributions from uncertainties in absolute sample thickness (as opposed to variations) and elastic constant were found to be insignificant.

Figures 4 and 5 immediately suggest an interesting dichotomy between the monomer and dimer systems. When considering the bulk sample, we find the splay elastic constants for both species to be similar. We have suggested [33] that these results, in conjunction with measurements of the viscosity coefficients, indicate that the small amount of flexibility associated with the dimer's spacer is sufficient to nullify the theoretical results for rigid rods which predict a strong dependence of K_{11} on the molecular aspect ratio [40–44]. On the other hand, we find a substantial difference in W between monomer and dimer. One possible explanation may lie with the orientational order parameter in the vicinity of the surface, as discussed by Yokoyama *et al.* [12] and by Pikin and Terentjev [26]. Based upon a van der Waals model of the liquid crystal interface, Poniewierski and Sluckin predict [23, 24] a degradation in S at a grooved interface [27] which is used to induce parallel alignment. This behaviour is consistent with the anchoring results near T_{NI} obtained by Faetti *et al.* [13] and by Yokoyama *et al.* [12] for an obliquely evaporated SiO substrate, and may even explain the homeotropic results of [10] as well. The surface reduction of the order parameter is also supported by birefringence [45–47] and contact angle measurements [48, 49]. Based

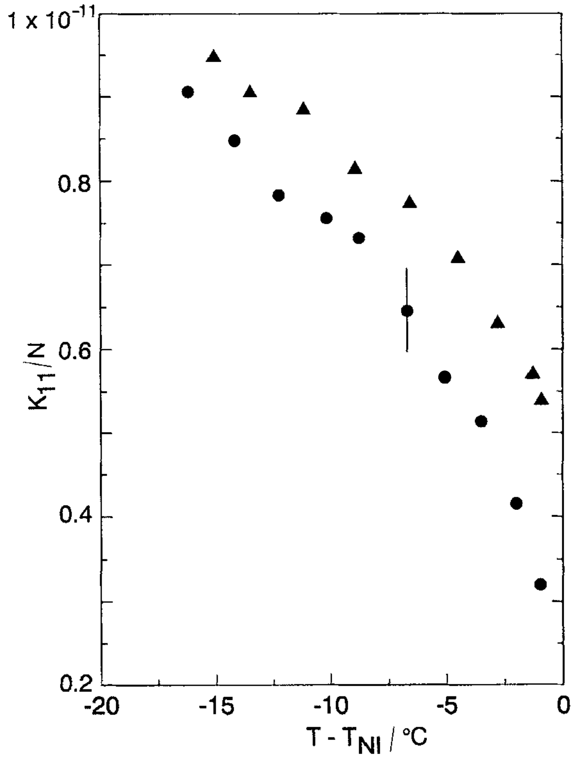

Figure 4. Splay elastic constant plotted versus reduced temperature for monomer (●) and dimer (▲). Typical error bar is shown.

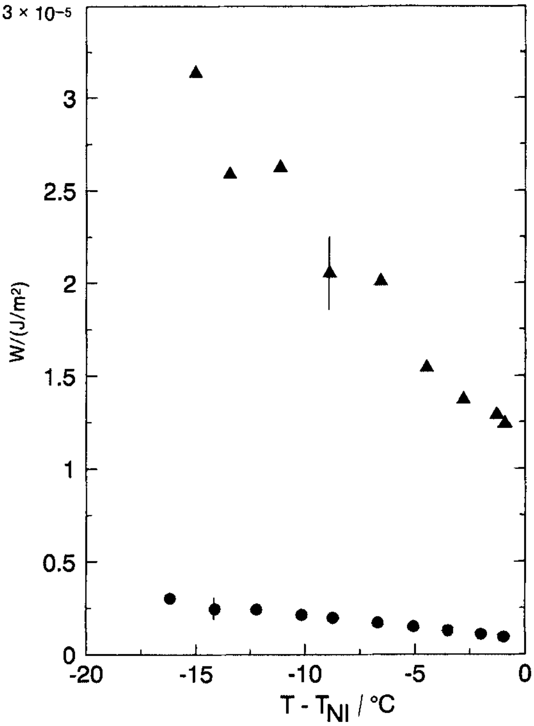

Figure 5. Anchoring strength coefficient W plotted versus reduced temperature for monomer (●) and dimer (▲). Typical error bars are shown.

on the grooved surface model of Berreman [27], W scales as the elastic moduli at the interface; a reduction in S would therefore result in a concommitant decrease in both the elasticity and the surface anchoring strength. Despite the superficial appeal of this mechanism, however, there are a number of problems. First, in order to explain our results it would be necessary that the nematic order parameter for the monomer at the interface be substantially less than that of the dimer over the entire nematic range, even though the bulk values of S differ by no more than 20 per cent at comparable $T - T_{NI}$ [39]. We do not know whether this is, indeed, the case. More critical, however, is the very nature of the alignment process. Geary *et al.* suggested that liquid crystal alignment can grow epitaxially on a buffed, linear-polymer-coated substrate [50]. Although their birefringence measurements overlooked the possibility of shape birefringence [51] at a grooved surface, their conjecture has nevertheless been verified by Chen *et al.* using second haromonic generation [52]. In their experiment they showed that the highly polar liquid crystal octyl cyanobiphenyl (8CB) aligns at a rubbed (and thus oriented) polyimide surface by means of short range molecular interactions, as opposed to grooves. Moreover, the order at the surface was found to be enhanced relative the bulk, with alignment observed near the surface even well into the isotropic phase. Although it is not clear whether the same mechanism would apply for the relatively non-polar liquid crystal molecules reported herein, it must be considered as a reasonable alternative to the groove theory, which tends to apply to thermosetting, as opposed to thermoplastic polymers. Thus, if the epitaxial alignment mechanism proposed by Geary *et al.* is indeed operative here, we would expect an increase in S at the surface for both species, and for the dimer in particular. In this light the dimer would be expected to exhibit a larger anchoring strength coefficient *W*, which was indeed observed.

In addition to the considerations noted above, Yokoyama *et al.* pointed out [12] that the anchoring strength may also be affected by higher order orientational order parameters (such as $\langle P_4(\cos\theta)\rangle$), biaxiality, incipient smectic order, adsorbtion, and the microstructure of the polyimide surface. Moreover, If *S* is indeed a function of position, then equation (2) may not be entirely correct, inasmuch as it involves an elastic modulus which is position dependent near the interface. (We nevertheless expect that our results for *W* are qualitatively quite reasonable.) In a sense then, the entire concept of anchoring strength may go beyond the microscopic nature of the interface, and include a host of macroscopic phenomena [12]. Despite these considerations, however, it is important not to lose sight of the central result of this work: the apparent anchoring strength of the dimer is much greater than that of the monomer, a result which likely arises from the dimer's spacer group behaving as a nearly rigid unit. This result is qualitatively quite different from the elastic moduli data [33, 34].

To summarize, the splay elastic constants as a function of reduced temperature for a monomeric liquid crystal and its dimer have been compared and found to be similar. These results agree with previous measurements. The anchoring strength coefficients *W* for these two systems were also determined as a function of reduced temperature. Although both the monomer and dimer anchoring energies behave qualitatively the same, it was found that the dimer values are approximately ten times the values measured for the monomer. It is beyond the scope of this paper to offer a unified model for this phenomenon, although factors such as the nematic order parameter at the surface may be important. Nevertheless, it is our hope that these (and future) measurements on oligomers will generate activity in the theoretical community.

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