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Backbone effects on the anchoring of side-chain polymer liquid crystals

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By comparing the anchoring behaviour of (end-on) side chain polymer liquid crystals with that of the corresponding low molecular mass liquid crystals, we have studied the effect of the backbone on the anchoring of side chain polymer liquid crystals. We can distinguish two different effects: the loss of rotational freedom of the side groups and the interaction of the polymer chain with the surface. In the case of free surfaces, we can formulate a general rule stating that compounds with side groups ending with an aliphatic chain (at least four carbon atoms long) exhibit a homeotropic anchoring, and compounds with side groups ending with a polar group exhibit a planar anchoring.

1. Introduction

The phenomenon of orientation, or anchoring, of liquid crystals by surfaces has been known for nearly as long as have liquid crystals themselves [1]. Intensive studies of this phenomenon have been performed using low molecular mass nematic liquid crystals [2]. The anchoring behaviour of their polymeric counterparts however has hardly been explored, despite the growing fundamental and technological interest in these materials [3].

The macroscopic orientation of polymer liquid crystals at surfaces can formally be described in the same way as that of low molecular mass liquid crystals: the director at the surface takes a certain preferred orientation with respect to the surface (although this preferred surface orientation might be difficult to achieve because of the high viscosity of these compounds) [4]. However, the fact that the mesogenic groups are attached to a polymer chain has an influence on their surface behaviour at a microscopic level, which in turn can affect the macroscopic anchoring. This influence has hardly been studied so far.

We investigate here the effect of the backbone of end-on side chain liquid crystalline polymers on their anchoring behaviour. These materials can be seen as a collection of conventional low molecular mass liquid crystalline molecules attached to a polymer chain by one of their ends. By comparing the anchoring behaviour of a side chain liquid crystalline polymer with that of the corresponding low molecular mass liquid crystal (in other words, that of the free side groups), we can deduce what is the effect of the backbone on anchoring. We have applied this method to the study of the macroscopic and microscopic anchoring of cyanobiphenylyl side groups attached to a polyacrylate backbone, both at the free surface and in the interface with quartz.

The microscopic anchoring conditions apply on the layer of mesogenic groups in direct contact and interaction with the substrate (the so-called surface layer). They are given by the orientational distribution of the liquid crystalline side groups in this surface layer (which is generally different from the uniaxial orientational distribution found in the bulk of a nematic liquid crystal). This surface orientational order evolves into the bulk orientational order as one moves away from the surface. One such evolution minimizes the interfacial energy between the substrate and the bulk liquid crystal. It corresponds to a particular orientation of the bulk with respect to the substrate, which is thus energetically favoured; this anchoring direction defines the macroscopic anchoring condition of the liquid crystal onto the substrate [2].

Our results, together with others already published in the literature, allow us to put forward two different effects of the backbone on the anchoring behaviour of side chain polymer liquid crystals: the loss of rotational freedom of the side groups, and the interaction of the polymer chain with the surface.

2. Experiments

We have used three compounds in our experiments (figure 1).

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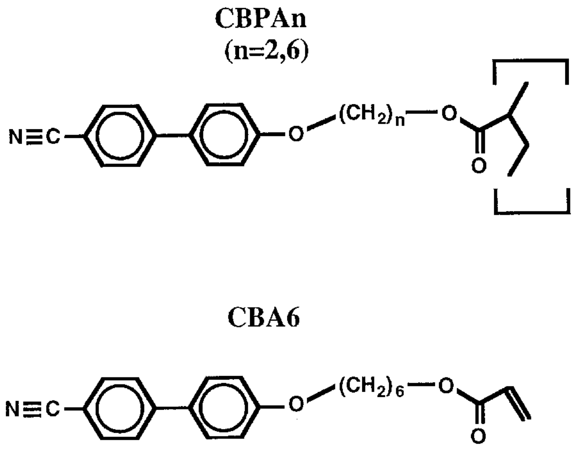


Figure 1. Chemical formulae of the compounds used in the present study.

(i) A polyacrylate polymer (CBPA6) with cyanobiphenylyl side groups linked with a spacer of six carbon atoms [5] ($\bar{M}_n = 12\,000$, $\bar{M}_w/\bar{M}_n = 1{\cdot}44$). Its phase sequence is [6] (all temperatures are given in °C):

$$\mathrm{g}\,38\,\mathrm{N}_{\mathrm{re}} \approx 83\,\mathrm{SmA}_{\mathrm{d}}\,115\,\mathrm{N}\,123\,\mathrm{I}$$

(ii) A polyacrylate polymer (CBPA2) with cyanobiphenylyl side groups linked with a spacer of two carbon atoms [7] ($\bar{M}_n = 33\,058$, $\bar{M}_w/\bar{M}_n = 1{\cdot}44$). Its phase sequence is [8]:

$$\mathrm{g}\,84\,\text{quasi-N}\,113{\cdot}5\,\mathrm{I}$$

The phase referred to here as quasi-nematic does not spontaneously exhibit any birefringence (or a macroscopic anchoring) but it becomes birefringent under shear [8].

(iii) The monomer (CBA6) used to polymerize compound (i) [5]. This compound exhibits no liquid crystalline phases; its melting temperature is 69°C.

The macroscopic anchoring direction taken by a compound at a given surface was determined from the texture of macroscopically thick samples observed with a polarizing microscope. In the case of quartz surfaces, we used cells (thickness≈10 μm) made of two quartz plates separated by Mylar spacers. After melting the polymer in the cell, it was left to anneal in the nematic phase for approximately one day. For the case of free surfaces, we prepared free-standing films over a hole with sharp edges (diameter 5 mm) machined in a stainless steel plate, following the spreading procedure already used for low molecular mass smectic liquid crystals (see for instance [9]) and recently applied to polymer liquid crystals [10]. For CBPA6 the films were made using the nematic phase at around 120°C. Due to the high viscosity of the material, spreading had to be performed slowly to prevent breaking of the film; the resulting films were very thick (a few 100 μm). Once the films were formed, they could be thinned down to less than 1 μm by letting them drain vertically for approximately one day in the nematic phase.

The microscopic anchoring conditions in thin films were determined by optical second-harmonic generation. This technique is sensitive to polar ordering, since second-harmonic generation is forbidden in centrosymmetric media. It therefore allows determination of the surface orientational order of cyanobiphenylyl mesogenic groups which form a polar layer at the surface of polar substrates [11]. The films used for our measurements were deposited on float quartz plates by spin coating from a solution in chlorobenzene for CBPA6 and CBA6, and in cyclopentanone for CBPA2; the thickness, density and roughness of these films were characterized by X-ray reflectivity measurements. The thicknesses were in the range 15–50 Å. The second-harmonic signal from the samples was measured in reflection from the polymer film side using the 532 nm radiation from a frequency-doubled Q-switched Nd:YAG laser as source. The signal was detected by photon counting.

For all measurements, the samples were kept in a temperature-controlled cell under a flow of nitrogen to avoid thermal degradation.

3. Results

Both free-standing films and closed cells made with CBPA6 show schlieren textures in the high temperature nematic phase (figures 2(*a*) and 2(*d*)), with surface defects characteristic of an orientation parallel to the limiting surfaces (planar anchoring). When these samples are cooled down to the smectic A phase (figures 2(*b*) and 2(*e*)), the schlieren textures transform into fan-shaped textures, indicating that the smectic layers are perpendicular, and consequently the directors are parallel to the surfaces [12]. By cooling further into the re-entrant nematic phase, one recovers schlieren textures which still retain some features of the fan-shaped textures observed in the smectic phase (figures 2(*c*) and 2(*f*)). In the cells between quartz plates, the fan-shaped features dominate, probably due to pinning at the surfaces (figure 2(*f*)). In free-standing films, nearly pure schlieren textures can be obtained by letting the films relax for several hours (figure 2(*c*)).

In the case of quartz surfaces, this planar orientation is identical to that of low molecular mass (LMM) cyanobiphenyl molecules; there is no difference between the macroscopic anchoring of the cyanobiphenyl side chains linked to a polymer backbone and that of free cyanobiphenyl molecules. This is not the case at the free surface; the anchoring of LMM cyanobiphenyl liquid

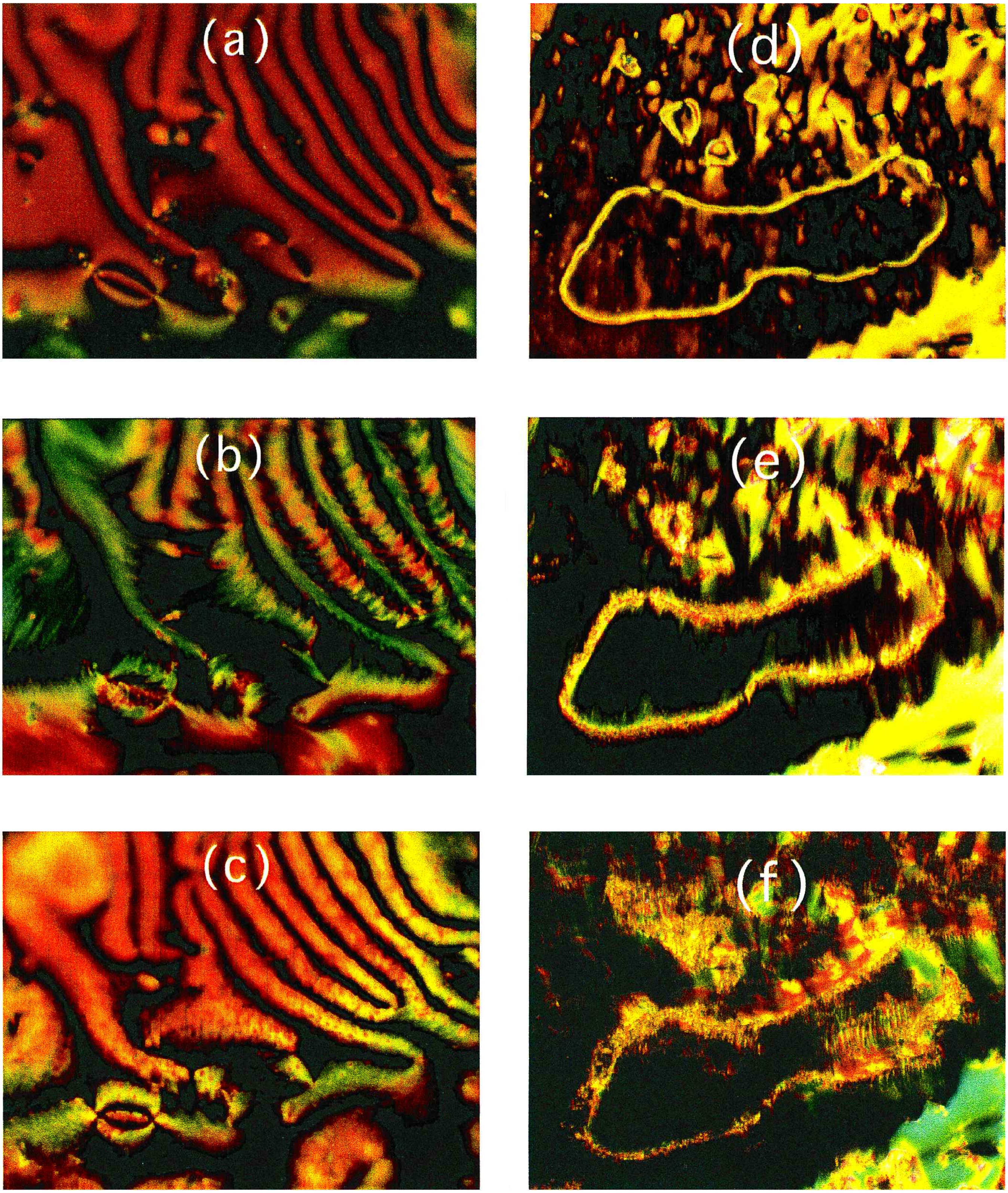


Figure 2. (*a*), (*b*), and (*c*) free-standing film of CBPA6 observed, respectively, in the nematic, smectic A and reentrant nematic phase using a polarizing microscope; the picture size corresponds to 500 × 375 μm^2. (*d*), (*e*) and (*f*) the same for a film between quartz plates; the picture size corresponds to 600 × 450 μm^2.

crystals is homeotropic (perpendicular to the surface) while that of the corresponding side chains of the polymer liquid crystal is planar. Such a planar anchoring at the free surface has also been observed for polymers with cyanobiphenylyl side groups linked to a polymethylsiloxane backbone [10] and polymers with other side groups carrying a polar head-group [13].

Although the macroscopic anchoring of CBPA6 is the same as that of LMM cyanobiphenyl molecules at the interface with quartz, the microscopic anchoring from which it arises is different. Cyanobiphenyl molecules are known to orient with their cyano head-groups towards the quartz substrate with an angle of approximately 20 degrees with respect to the surface, as deduced from second-harmonic generation measurements [14].

In the case of CBPA6, we have observed that the side groups located at the interface with the substrate generate no second-harmonic signal. This means that they have a centrosymmetric ordering, which can only be achieved if these groups are oriented parallel to the substrate. The same result was obtained with CBPA2 and the monomer CBA6.

4. Discussion

From the above observations and other results already reported in the literature, we can deduce two general effects of the polymer backbone of side chain polymer liquid crystals on the orientational order of these materials at surfaces. The first one arises from the fact that the side groups are not free to move and orient independently from the backbone. The second effect is due to the interaction of the backbone itself with the surface.

These effects of the backbone are in competition with the orienting effects of the surface on the side groups. The anchoring behaviour of side chain polymer liquid crystals arises from the balance between these different factors. General rules can be drawn about the anchoring of side chain polymer liquid crystals according to their structures.

4.1. *Loss of orientational freedom*

Since the side groups are attached by one end to a polymer backbone, they lose the ability to orient independently of each other and of the backbone; in particular, they might not be able to adopt the surface orientation they would have if they were free. This effect can lead to a change in macroscopic anchoring direction with respect to that of the free mesogens, as we have observed at the free surface of CBPA6. Further evidence of this effect can be obtained by comparing the anchoring direction at the free surface of different side chain polymer liquid crystals with that of their low molecular mass counterparts (see the table).

Low molecular mass liquid crystalline compounds carrying a polar head orient perpendicularly to their free surface: their polar head prefers to point towards the more polar medium, which is away from the surface (figure 3 (*a*)). This leads to a homeotropic anchoring. This anchoring is observed with all polar compounds for which the anchoring at the free surface is known, which includes different kinds of cyano compounds (compound **A** in the table [13, 15]), and compounds with NCS [16] and NO_2 [17] head-groups.

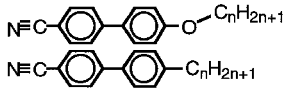
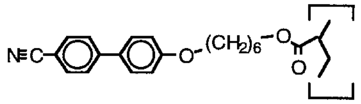
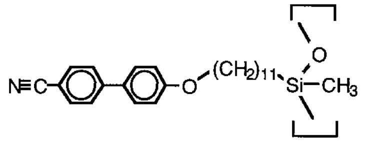
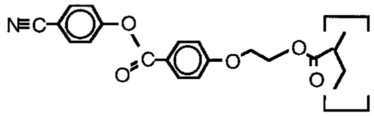
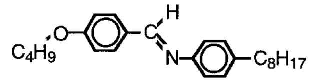
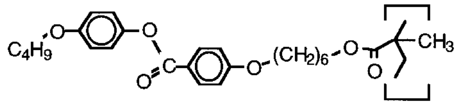
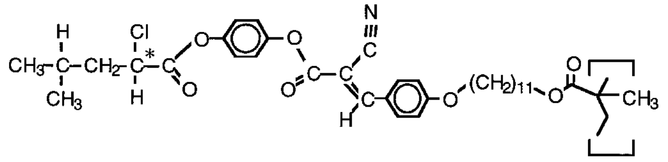
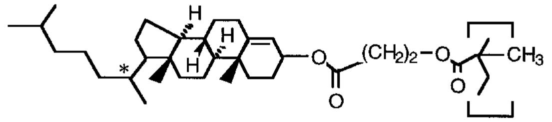
In a side chain polymer liquid crystal with polar side groups, having these side groups pointing away from the surface would require that the surface polymer molecules have their main chain confined at the surface and all their side groups pointing in the same direction (figure 3 (*b*)). This is sterically impossible because the width of the side groups is significantly larger than the extent of the monomer unit forming the backbone. The only configuration which does not introduce any distortion of the preferred local anti-parallel ordering of the side groups is the orientation of these side groups parallel to the surface, which leads to the observed planar anchoring (compounds **B**–**D** in the table).

This conflict between surface-induced mesogen orientation and internal molecular order does not arise in side chain polymer liquid crystals whose side groups are terminated by an aliphatic chain (figures 3 (*c*) and 3 (*d*)). This aliphatic chain can orient towards the vapour phase like the aliphatic chain of both polar and non-polar low molecular weight compounds (compounds **A** and **E** in the table); the side groups orient perpendicular to the surface and the anchoring is homeotropic (compounds **F**–**H**).

From the table, one can deduce a general rule about the anchoring of side chain polymer liquid crystals at their free surface according to the structure of their side groups: if the side groups terminate in a polar group, the anchoring is planar, and if the side groups terminate in an aliphatic chain, the anchoring is homeotropic. To our knowledge, there are no exceptions to this rule [18].

We should however note that in the case of groups with terminal aliphatic chains, this rule is probably valid only for sufficiently long chains (with, as a lower limit, three or four carbon atoms). This limit can be inferred from the anchoring behaviour of non-polar low molecular mass liquid crystals at the free surface. Liquid crystalline molecules carrying two long aliphatic chains (with at least four carbon atoms) orient perpendicular to the free surface [19]. There is one example of a molecule terminated by two methyl groups (PAA), and it orients parallel to its free surface [20, 21]. Other molecules have one long aliphatic chain and one short one: MBBA and EBBA carry one C_4 chain and, respectively, a methyl

Table 1. Macroscopic anchoring at the free surface of different side chain polymer liquid crystals and their low molecular mass counterparts. The anchoring relates to that in the nematic phase (and in the smectic A phase for compounds exhibiting both phases), except for the chiral compounds **G** and **H**, for which it corresponds to the anchoring at the surface of the smectic A phase.

Compound	Structure	Anchoring at free surface	References
A		homeotropic	[27–29]
B		planar	this work
C		planar	[10]
D		planar	[30]
E		homeotropic	[19]
F		homeotropic	[31,32]
G		homeotropic	[33]
H		homeotropic	[34]

and an ethyl group, I52 carries a C_5 and a C_2 chain. Their anchoring at the free surface is conical, with a tilt angle which varies with temperature (eventually leading to a homeotropic anchoring) [22–24]. Therefore one can conclude that the anchoring behaviour of molecules (and side groups) with short aliphatic chains (C_1 or C_2) is different from that of molecules carrying only long aliphatic chains (C_4 or longer).

4.2. *Interaction of the backbone with surfaces*

We have observed that in CBPA6, CBPA2 and CBA6 at the surface of quartz, the cyanobiphenyl side groups orient parallel to the substrate. This is in contrast with the tilted microscopic orientation of low molecular mass cyanobiphenyl molecules *at the surface* of quartz. This tilt has been explained by the combination of three factors: the attraction of the polar cyano group by the surface, the dipole–dipole interaction between polar heads, and the steric interaction of the biphenyl core with the substrate (figure 4(*a*)). The first factor leads to the orientation of the head towards the surface; the dipole–dipole interactions favour a core orientation parallel to the surface so that the dipoles can be essentially anti-parallel to each other, but the steric inter-

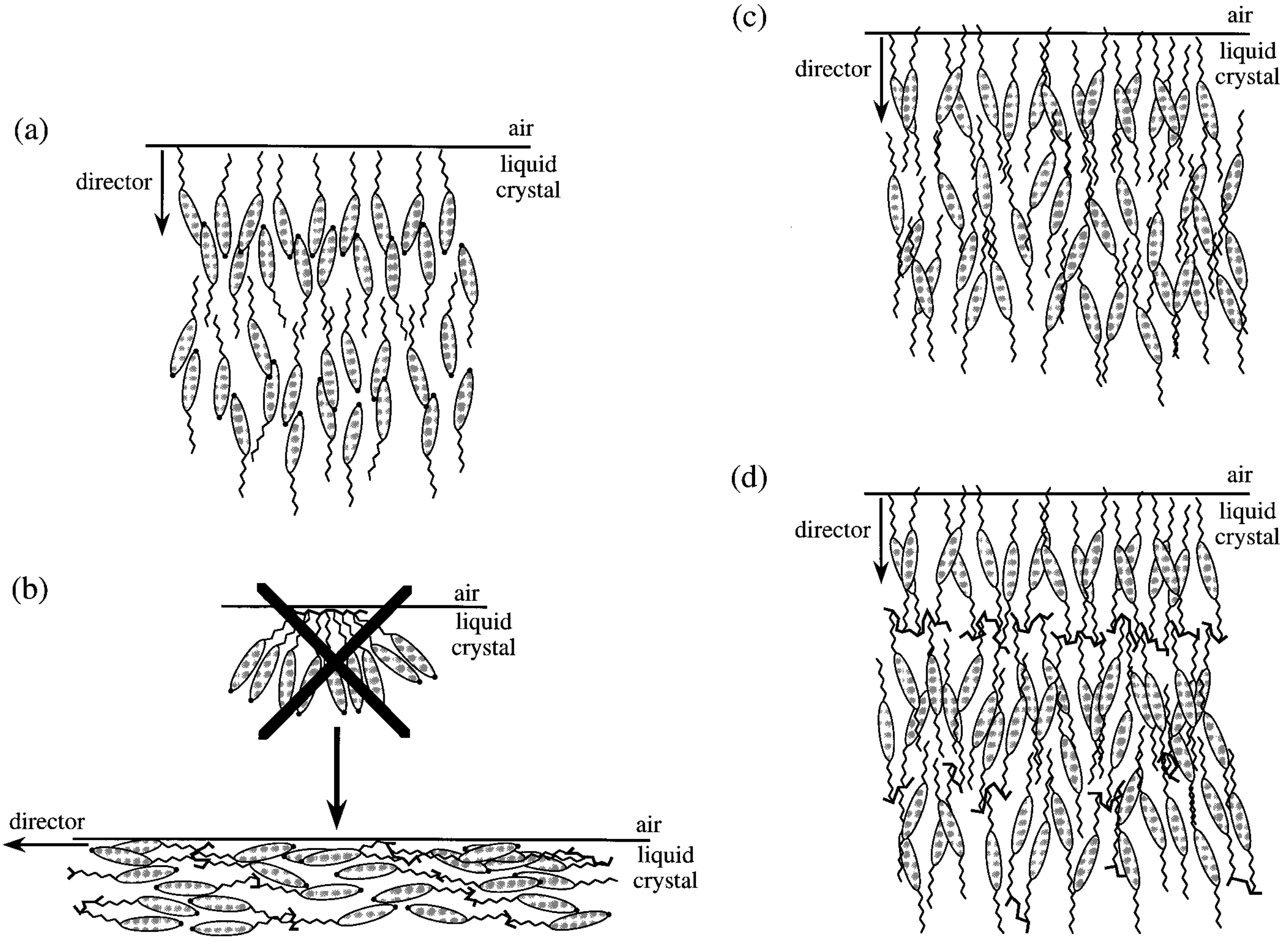


Figure 3. Anchoring at the free surface: (*a*) low molecular mass and (*b*) side chain polymer liquid crystal with polar terminal groups; (*c*) and (*d*) the same for non-polar mesogens and side chains.

actions prevent this orientation from being achieved because of the large size of the phenyl rings with respect to that of the cyano head-groups [25, 26].

When cyanobiphenyl molecules are attached to a polyacrylate backbone, there is obviously another orienting effect which makes them orient parallel to the surface. The fact that this orientation is also observed in the monomer CBA6 is an indication that this orientation is not due to the connection of the side groups to a polymer backbone but to the addition of the acrylic group at the end of the aliphatic chain. Because this acrylic group contains a polar ester group (C=O), it is attracted towards the quartz surface. This drives the end of the aliphatic chain towards the substrate, leading to an orientation of the side groups parallel to the surface (figure 4(*b*)). This effect is observed for both short (C_2) and long (C_6) spacers between the acrylic group and the biphenyl core.

This is an example of how the adsorption of the polymer backbone at the surface can influence the anchoring behaviour of a side chain polymer liquid crystal. Similar effects can be expected with polysiloxane polymers because of their polar oxy groups. For other surface/backbone combinations, the polymer backbone might be repelled by the surface, which would also affect the microscopic anchoring conditions.

In the case of the polyacrylates studied here, the difference in the microscopic anchoring conditions at the interface with quartz between free cyanobiphenyl molecules and the cyanobiphenyl side groups of the polymer does not give rise to a change of the *macroscopic* anchoring conditions observed in these two materials, since both *microscopic* anchorings induce a planar *macroscopic* anchoring. In other polymers, the change in microscopic anchoring conditions due to surface/backbone interactions might induce a change in macroscopic anchoring.

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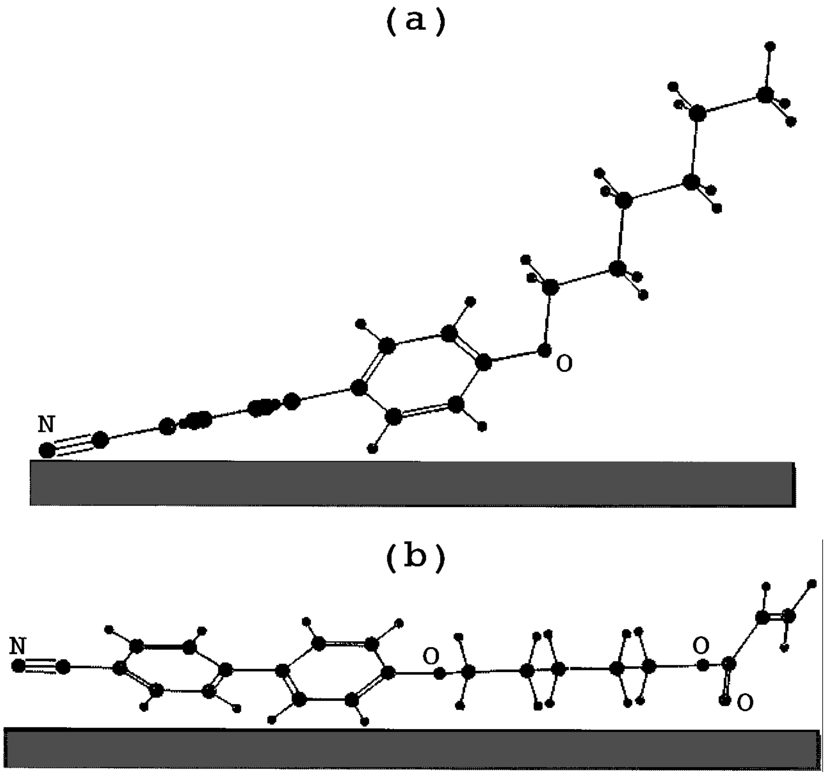

Figure 4. Orientation of (*a*) 6OCB and (*b*) CBA6 molecules at the interface with a quartz substrate.

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