Available online at www.sciencedirect.com

ScienceDirect

Journal of Colloid and Interface Science 304 (2006) 459–473

Journal of
Colloid and
Interface Science

www.elsevier.com/locate/jcis

Influence of 4-cyano-4′-biphenylcarboxylic acid on the orientational ordering of cyanobiphenyl liquid crystals at chemically functionalized surfaces

Joon-Seo Park, Chang-Hyun Jang [1], Matthew L. Tingey, Aaron M. Lowe, Nicholas L. Abbott *

Department of Chemical and Biological Engineering, University of Wisconsin-Madison, 1415 Engineering Drive, Madison, WI 53706, USA

Received 29 May 2006; accepted 30 August 2006

Abstract

We report two methods that involve tailoring of the chemical composition of the nematic liquid crystal 4-cyano-4′-pentylbiphenyl to achieve control over the orientational ordering of the liquid crystal on chemically functionalized surfaces. The first method involves the direct addition of 4-cyano-4′-biphenylcarboxylic acid to 4-cyano-4′-pentylbiphenyl. The second method involves exposure of 4-cyano-4′-pentylbiphenyl to ultraviolet light and photochemical generation of a range of products, including 4-cyano-4′-biphenylcarboxylic acid. The addition of the acid or exposure to ultraviolet light accelerated the rate at which the liquid crystal exhibited an orientational transition from planar to perpendicular (homeotropic) alignment on surfaces presenting ammonium groups. The appearance of the homeotropic orientation of the UV-treated 4-cyano-4′-pentylbiphenyl on ammonium-terminated surfaces was dependent on the thickness of the film of liquid crystal (13–50 μm), consistent with a dipolar coupling between the liquid crystal and the electric field associated with an electrical double layer generated at the ammonium surface. Although the addition of 4-cyano-4′-biphenylcarboxylic acid or UV treatment of the liquid crystal also promoted homeotropic orientations on surfaces presenting hydroxyl groups, the orientations of the UV-treated liquid crystal on the hydroxyl-terminated surface did not change with thickness of the film of liquid crystal in the manner observed on the ammonium-terminated surfaces. The latter result indicates that the mechanism leading to homeotropic anchoring on hydroxyl-terminated surfaces is distinct from that on ammonium-terminated surfaces. Measurements performed using polarization modulation infrared reflection–absorption spectroscopy suggest that hydrogen bonding between the 4-cyano-4′-biphenylcarboxylic acid and the hydroxyl-terminated surface is responsible for the homeotropic anchoring on the surface. Finally, the orientation of the liquid crystal on methyl-terminated surfaces was not influenced by the addition of 4-cyano-4′-biphenylcarboxylic acid nor UV treatment. These results illustrate how the chemical composition of liquid crystals can be manipulated to achieve control over their ordering on surfaces that possess chemical functionality relevant to the development of liquid crystal-based sensors and diagnostic tools. We illustrate the utility of this approach by using the tailored liquid crystal to amplify and optically transduce the presence of proteins arrayed on ammonium-terminated surfaces.

Keywords: Liquid crystal; Chemically functionalized surface; Electrical double layers; Hydrogen bonding; Orientational ordering; Anchoring; Acid dopant; UV treatment

1. Introduction

Chemically functionalized surfaces provide access to a wide range of interfacial properties through the introduction of interactions that involve hydrogen bonding [1–5], electrical double layers [6–10], and metal ion coordination with ligands at the interfaces [11–13]. Organic monolayers presenting chemical functional groups have, therefore, been explored in the context of various technological applications and phenomena including biotechnologies [14–18], molecular electronics [19–21], and stabilization and immobilization of nanoparticles [22–24]. Recently, we have reported investigations of the use of chemically functionalized surfaces in the context of the orientational ordering of liquid crystals near interfaces and the potential use

---

* Corresponding author. Fax: +1 608 262 5434.
E-mail address: abbott@engr.wisc.edu (N.L. Abbott).

[1] Current address: Korea Electrotechnology Research Institute, South Korea.

0021-9797/$ – see front matter © 2006 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcis.2006.08.063

of this phenomenon for the creation of chemical and biological sensors based on liquid crystals [16,25–29]. Although it is well established that the ordering of liquid crystals is sensitive to the molecular-level structure of interfaces [30], the types of chemically functionalized surfaces and liquid crystals that are relevant to the creation of chemical and biological sensors differ from those typically studied in the past in the context of creating electro-optical technologies such as liquid crystal displays (e.g., surfaces prepared from polyimides). For example, the introduction of ionizable groups at surfaces as well as the addition of electrolytes to liquid crystals leads to useful ordering behaviors of liquid crystals when using the liquid crystals to amplify the presence of chemical and biological species at interfaces [10,31,32]. The study reported in this paper sought to advance our understanding of the ways in which the chemical functionality of liquid crystals and surfaces can be manipulated to control the ordering of liquid crystals at surfaces relevant to chemical and biological sensors.

Of particular relevance to the study described in this paper is the report by Luk and coworkers in which the azimuthal orientations of liquid crystals on carboxylic acid-terminated surfaces were shown to be influenced by the character of hydrogen bond acceptors in the liquid crystal [31]. The study demonstrated that the azimuthal orientations of liquid crystals were influenced by the relative strength of hydrogen bonding between the mesogens and the surfaces, which in turn could be tailored by changing the chemical functionality of the liquid crystal. In a second relevant study, Kuschel and Demus have reported on the influence of various carboxylic acid dopants on the molecular alignment of liquid crystals [30,33]. These investigators reported that doping of a nematic liquid crystal with various carboxylic acid derivatives induces homeotropic (perpendicular) alignment of the liquid crystal on SnO_2/In_2O_3 surfaces [30,33]. The authors proposed that the homeotropic alignment of the liquid crystals arose from the interaction between the SnOH groups exposed at the surfaces and the carboxylic groups of the dopants.

In this paper, we build from the above studies to report two methods which can be employed to tailor the orientational behavior of 4-cyano-4′-pentylbiphenyl (5CB) on various chemically functionalized surfaces: (1) the addition of 4-cyano-4′-biphenylcarboxylic acid to 5CB; (2) UV irradiation of 5CB, which leads to the generation of a range of products, including 4-cyano-4′-biphenylcarboxylic acid. We explore the influence of 4-cyano-4′-biphenylcarboxylic acid on the orientational behavior of 5CB using three different chemically functionalized surfaces: (1) ammonium-terminated surfaces, (2) hydroxyl-terminated surfaces, and (3) methyl-terminated surfaces. We find that the addition of the acid dopant or the UV treatment of 5CB leads to orientational behaviors of 5CB on these three surfaces that reflect different mechanisms of interaction between the modified liquid crystals and the surfaces. We also illustrate the utility of these methods by using UV-treated liquid crystal to enhance differences in the orientational ordering of the liquid crystals induced by proteins printed on surfaces.

2. Experimental

2.1. Materials

The liquid crystal 4-cyano-4′-pentylbiphenyl (5CB) was purchased from EM Industries (Hawthorne, NY). The acid dopant, 4-cyano-4′-biphenylcarboxylic acid, was purchased from Oakwood Products (West Columbia, SC). 2-Aminoethanethiol hydrochloride, 11-mercaptoundecanol, hexadecanethiol, and octyltrichlorosilane (OTS) were purchased from Aldrich (Milwaukee, WI) and used as received. Anti-biotin antibody (IgG) was purchased from Sigma (St. Louis, MO). Titanium (99.999%) and gold (99.999%) were purchased from International Advanced Materials (New York, NJ). The glass microscope slides were obtained from Fisher Scientific (Pittsburgh, PA) and the silicon wafers were obtained from Silicon Sense (Nashua, NH). The poly(dimethylsiloxane) (PDMS) stamps were prepared from Sylgard 184 (Dow Corning, Midland, MI).

2.2. Preparation of octyltrichlorosilane (OTS)-coated glass slides

The microscope slides were cleaned in piranha solution (70% H_2SO_4, 30% H_2O_2) at 80 °C for 30 min using nitrogen to provide agitation, and then thoroughly rinsed with deionized water. *Warning: Piranha solution should be handled with extreme caution; in some circumstances, most probably when it has been mixed with significant quantities of an oxidizable organic material, it has detonated unexpectedly*. The slides were then cleaned in base solutions (70% KOH, 30% H_2O_2) at 80 °C for 30 min, and thoroughly rinsed with deionized water, ethanol, and then methanol. After drying under a stream of ultrapure nitrogen, the clean slides were stored overnight in an oven at 110 °C. The slides were immersed in 10 mM solution of octyltrichlorosilane (OTS) in normal heptane at room temperature for 30 min. The slides were then rinsed with methylene chloride, and dried under a stream of nitrogen.

2.3. Preparation of gold films deposited at oblique angle of incidence

The microscope slides were cleaned in piranha and base solutions as described above and then mounted in an electron beam evaporator (VES-3000-C, Tek-Vac Industries, Brentwood, NY). The pressure in the evaporator was maintained at ca. 1×10^{-7} Torr during deposition. The slides were coated with 80 Å of titanium at a rate of $\sim$0.2 Å/s to promote the adhesion between the glass microscope slides and gold. A film of gold (thickness $\sim$200 Å; semi-transparent) was then deposited onto the stationary glass slides at a fixed angle of incidence of 30° (measured from the surface normal) at a rate of $\sim$0.2 Å/s.

2.4. Preparation of gold films deposited using a rotating planetary

Gold films used in the surface IR experiments described below were prepared on silicon wafers mounted on a rotating planetary in the electron beam evaporator described in the