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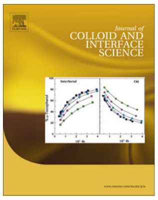

Effect of molecular structure and packing density of an azo self-assembled monolayer on liquid crystal alignment

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ABSTRACT

We studied the alignment of liquid crystals (LCs) on a photo-switchable azo-containing self-assembled monolayer (azo-SAM) with different packing densities and molecular structures. The packing density of the azo-SAM substrates was varied by changing the dipping time of the substrate in azosilane monomers solution (2 mM in toluene). The thickness of the monolayer on the silicon substrate increased as the dipping time was increased. The relative surface packing density on the glass substrates was estimated from the surface energies of the azo-SAM. The photo-induced dynamics of liquid crystal alignment on the azo-SAM significantly varied according to the packing density of the azo-SAM and the structure of the azo-SAM molecules. The azo-SAM from long octyloxy chain-terminated azosilane (azo-S1) possessed stable homeotropic alignment even after photobuffing, while the azo-SAM from short methyl group-terminated azosilane monomer (azo-S2) showed photo-switchable homeotropic and planar alignments. However, when the packing density was increased to an excessive degree, even the azo-SAM from azo-S2 exhibited stable homeotropic alignment regardless of photobuffing.

1. Introduction

Self-assembled monolayers (SAMs) are a facile pathway for creating well-defined organic surfaces on solid substrates using functionalized organic molecules [1]. Organosilanes are the materials typically used for surface modification through two-dimensional arrays over a wide range of solid substrates [2]. The molecular structure of an organosilane plays a vital role in imparting desirable properties in SAMs. A number of approaches have been developed for liquid crystal (LC) alignment, and the formation of SAMs on substrates is one method to which much research has been recently devoted [3–7]. SAM alignment layers can provide plenty of new features for LC sensor [8–11] and display applications [12,13].

Many types of SAMs have been utilized as active layers for LC alignment [12,14–19]. Among them, the azo-SAM is a unique system due to its wide accessibility [20]. The azo molecule has the ability to undergo photoisomerization from the *trans* to *cis* form upon UV irradiation and from *cis* to *trans* by visible light. The photo-induced geometry change in azo chromophore between *trans* and *cis* isomers results in a large change in both the geometry and the electric dipole moment of the molecule [21], which in turn gives rise to reversible switching of surface wettability through intermolecular interaction [20,22]. The azo-SAM aligns LCs in either a homeotropic or planar fashion depending on the wavelength of the exciting light [23–25]. In 1988, Ichimura reported that the long axis of *trans* molecules orients perpendicular to the substrate in the absence of exciting light, yielding homeotropic LC alignment. However, upon irradiation with UV light at 365 nm, the *trans* isomers converted to *cis* isomers and the LCs aligned parallel to the substrate (planar alignment) [22]. The *cis* isomer is then in a *meta* stable state and returns to the *trans* confirmation spontaneously or when illuminated with visible light at 440 nm [20]. Consequently, the LC alignment can be changed so as to be homeotropic. The azimuthal orientation of the alignment does not depends on polarization of the exciting light but rather on its wavelength, with the *trans* and *cis* isomers being absorptive in the UV and visible light regions, respectively [26].

Recently, Hoffmann et al. studied the wettability and photoisomerization of azosilane molecules with terminal alkoxy chains. The terminal alkoxy chain influenced the photoisomerization reaction of the azosilane molecule [27]. Schwartz et al. studied the homeotropic alignment of LCs using mixed alkyl silane SAMs. It was found that SAMs from long-chain alkylsilane possessed a low surface energy and the LC materials aligned homeotropically on the surface of the monolayer [12].

In SAMs, molecular coverage on the substrate is important for liquid crystal alignment. Recently, our group studied the alignment of liquid crystals using a molecular layer with a patterned molecular density [28]. In the present work, our aim is to study the influence of the molecular structure and relative surface molecular

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coverage of the SAM on the LC alignment of azo-SAM substrates. The substrates were prepared from two types of azosilane monomers with different structural features. The chemical synthesis of the azosilane monomers, including all intermediates, was characterized by nuclear magnetic resonance (NMR) and infrared (IR) spectral analysis. The photoisomerization of the azosilane monomers was also studied via UV–vis spectroscopy.

In this article, we describe a synthesis route for azosilane monomers where the silane anchor group undergoes a reaction with SiO_2 surfaces. These organosilanes facilitate the chemical modification of the SiO_2 with azobenzene containing monolayers in a one-step surface reaction. The surface wettability of the azo-SAMs is discussed using the results of contact angle measurements, while the relative surface packing density of the azo-SAMs is evaluated based on surface energy values. The thickness of the azo-SAMs was examined using ellipsometry analysis. In addition, the influence of the molecular structure and packing density of the azo-SAMs on the liquid crystal alignment is analyzed and discussed.

2. Experiments

2.1. Materials

4-Acetamidophenol, 1-bromooctane, 5-bromo-1-pentene, sodium nitrite, *n*-butylamine, *p*-toluidine, phenol, platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution (Pt(dvs)), potassium carbonate (K_2CO_3), potassium iodide (KI), hydrogen peroxide (H_2O_2), sodium hydroxide (NaOH), hydrochloric acid, and sulfuric acid were purchased from Sigma–Aldrich (Korea) Ltd. and used as received.

2.2. Synthesis of 4-octyloxy acetaniline (1)

Firstly, 5 g (0.0331 mol) of 4-acetamidophenol was dissolved in 30 mL of DMF, 6.9 g (0.0499 mol) of K_2CO_3 was subsequently added, and the mixture was then stirred for 30 min at 30 °C. Next, 7.67 g (0.0397 mol) of 1-bromooctane was added to the stirred mixture. The reaction mixture was stirred vigorously for 24 h at 100 °C. The resulting mixture was cooled to room temperature and poured into 500 g of crushed ice, and the resulting white precipitate was filtered off. The crude product was then dried and purified by recrystallization from ethanol to give compound 1 as a white solid. FT-IR (cm^{-1}): 3328, 2931, 2861, 1657, 1607, 1551, 1514, 1473, 1246. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.4 (d, 2H, Ar—H, *J* = 6 Hz), 7.05 (s, 1H, Ar—NH), 6.84 (d, 2H, Ar—H, *J* = 8 Hz), 3.93 (t, 2H, CH_2O, *J* = 6 Hz), 2.12 (s, 3H, $NHCOCH_3$), 1.78 (qn, 2H, $CH_2CH_2CH_2O$, *J* = 8 Hz), 1.42–1.46 (m, 10H, CH_2, *J* = 6 Hz), 0.89 (t, 3H, CH_3CH_2, *J* = 7 Hz) [29].

2.3. Synthesis of 4-octyloxyaniline (2)

To begin, 5 g (0.0189 mol) of compound 1 was dissolved in 140 mL of ethanol, and 30 mL of concentrated hydrochloric acid was added drop wise. The reaction solution was stirred for 24 h under reflux. The resulting claret-red mixture was cooled to ambient temperature and then poured over 500 g of ice, thereby generating a white precipitate. After the solution was neutralized to pH 7–8 with the addition of an NaOH solution, the precipitate was filtered off and washed with water. After drying in a vacuum oven, compound 2 was obtained as a pale yellow solid. Yield: 65.8% (6.73 g). FT-IR (cm^{-1}): 2928, 2844, 1637, 1514, 1479, 1233. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 6.6 (d, 2H, Ar—H, *J* = 7 Hz), 6.87 (d, 2H, Ar—H, *J* = 7 Hz), 3.94 (t, 2H, CH_2O, *J* = 7 Hz), 3.4(b, 2H, Ar—NH_2) 1.75 (qn, 2H, $CH_2CH_2CH_2O$, *J* = 7 Hz), 1.28–1.46 (m, 10H, CH_2, *J* = 7 Hz), 0.88 (t, 3H, CH_3CH_2, *J* = 8 Hz)[29].

2.4. Synthesis of 4-hydroxy-4′-octyloxyazobenzene (3)

First, 1.84 g (0.0267 mol) of sodium nitrite in a mixture of water (17 mL) and ice (15 mL) was added drop wise into a container with 5.5 g (0.0246 mol) of compound 2 dissolved in a mixture of concentrated hydrochloric acid (11 mL), ice (11 g), and acetone (55 mL). The reaction mixture was subsequently stirred for 30 min at −5 to 5 °C. To the cooled mixture, 2.4 g (0.025 mol) of phenol in a 2 mol/L sodium hydroxide solution was added. The reaction mixture was maintained at pH 9–10 and stirred for 2 h at room temperature. After neutralization with an HCl solution, the resulting mixture was filtered off and washed with water. The crude product was then dried and purified by recrystallization from ethanol to give compound 3 as a red-brown solid. Yield: 65.5% (6.50 g). FT-IR (cm^{-1}): 3469, 2924, 2859, 1604, 1589, 1504, 1472, 1244. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.9 (d, 2H, Ar—H, *J* = 10 Hz), 7.84 (d, 2H, Ar—H, *J* = 13 Hz), 7.02 (d, 2H, Ar—H, *J* = 10 Hz), 6.89 (d, 2H, Ar—H, *J* = 12 Hz), 4.01 (t, 2H, CH_2O, *J* = 7 Hz), 1.82–2.19 (qn, 2H, $CH_2CH_2CH_2O$, *J* = 7 Hz), 1.26–1.39 (m, 10H, CH_2, *J* = 6 Hz), 0.89 (t, 3H, CH_3CH_2, *J* = 7 Hz) [29].

2.5. Synthesis of 4-4′(octyloxy)phenylazo-phenoxy-)pentene (4)

To begin, 4 g (0.0331 mol) of compound 3 was dissolved in 40 mL of DMF, and 2.54 g (0.0499 mol) of K_2CO_3 was then added. The mixture was subsequently stirred for 30 min at 30 °C. Next, 2.18 g (0.0397 mol) of 5-bromo-1-pentene and 0.2 g of KI were added to stirred mixture. The reaction mixture was stirred vigorously for 24 h at 100 °C. The resulting mixture was cooled to room temperature and poured into 400 g of crushed ice, and the white precipitate that formed was filtered off. The crude product was dried and purified by recrystallization from ethanol to give compound 4 as a red-brown solid. Then, the crude product was dried and purified by recrystallization from methanol to give compound 4 as a red-brown solid. Yield: 89.0% (5.4 g). FT-IR (cm^{-1}): 3313, 2924, 2855, 1607, 1588, 1496, 1472, 1246. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.92 (d, 2H, Ar—H, *J* = 7 Hz), 7.82(d, 2H, Ar—H, *J* = 7 Hz), 7.03 (d, 2H, Ar—H, *J* = 9 Hz), 6.89 (d, 2H, Ar—H, *J* = 8 Hz), 5.8–5.91(m, 1H, —CH=CH_2, *J* = 7 Hz), 5.01–5.10 (m, 2H, —CH=CH_2, *J* = 6 Hz) 4.03 (t, 4H, ArOCH_2, *J* = 6 Hz), 1.96–2.2 (m, 2H, —CH_2-—CH=CH_2, *J* = 7 Hz), 1.82 (qn, 4H, ArOCH_2CH_2, *J* = 7 Hz), 1.25–1.39 (m, 10H, CH_2, *J* = 7 Hz), 0.89 (t, 3H, CH_2CH_3, *J* = 7 Hz).

2.6. 4-Phenylazo-(4′-(5-trimethoxysilanyl)pentyloxy) benzene (5)

First, 2.0 g (0.00506 mol) of compound 4 was dissolved in 20 mL of dry toluene, and 10 μL of Pt(dvs) catalyst was added. The mixture was stirred for 30 min in a nitrogen atmosphere at room temperature (27–29 °C) and then 5.0 g (0.0409 mol) of trimethoxysilane was added. The reaction mixture was refluxed in a nitrogen atmosphere for 24 h. The excess silane was removed under reduced pressure. The crude product was purified through column chromatography (dichloromethane and *n*-hexane (1:1) as an eluent) to give a red-brown semisolid. Yield: 91.0%. FT-IR (cm^{-1}): 2924, 2844, 1600, 1502, 1244, 1083. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.8(d, 2H, Ar—H, *J* = 7 Hz), 7.7(d, 2H, Ar—H, *J* = 7 Hz), 6.92 (d, 2H, Ar—H, *J* = 7 Hz), 6.9 (d, 2H, Ar—H, *J* = 6 Hz), 3.9 (t, 4H, ArOCH_2, *J* = 7 Hz), 3.5 (s, 9H, —Si—OCH_3), 1.82 (qn, 4H, ArOCH_2CH_2, *J* = 7 Hz), 1.25–1.39 (m, 14H, CH_2, *J* = 7 Hz), 0.89 (t, 3H, CH_2CH_3, *J* = 6 Hz), 0.62–0.77(m, —CH_2—Si, *J* = 7 Hz).

2.7. Synthesis of 4-hydroxy-4′-methylazobenzene (6)

To begin, 28 mL of water and 28 g of an ice solution with 5.02 g (0.0746 mol) sodium nitrite were slowly added drop wise to a mixture of 8 g (0.0746 mol) *p*-toluidine dissolved in concentrated