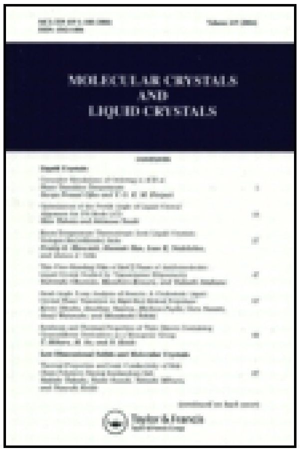

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FT-IR Studies of the Interfacial Alignment of the Liquid Crystal 4′-Cyano-4-biphenyl[4-(4-pentenyloxy)] benzoate Bonded to Silica

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The liquid crystal, 4′-cyano-4-biphenyl[4-(4-pentenyloxy)] benzoate (CBPB) has been chemically bonded to silica and the resulting material's interfacial properties examined by Fourier transform infrared spectroscopy. The spectral features of the nitrile stretching region for the chemically anchored system were significantly less complex than those obtained from samples of silica physically coated with CBPB. Further when CBPB was physically coated onto the chemically modified surface, its interactions with the substrate were reduced significantly.

INTRODUCTION

One of the important steps in fabricating liquid crystal displays (LCDs) is the surface coating process which typically involves the application of thin alignment layers to both the upper and lower glass substrates [1]. As such, the bulk orientation of mesogenic molecules is controlled by the anchoring forces of the alignment layers through molecule–molecule interactions [2, 3]. Many materials and processes have been examined as means of obtaining desired surface alignments for various display applications. A popular procedure is first to physically coat the substrate with either an

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inorganic or organic material followed by some form of mechanical treatment [4, 5]. However, display failure may still occur due to strong interactions between the mesogen and substrate which results in the degradation of interfacial alignment.

In an effort to minimize the above problem, more stable interfaces can be produced via chemical derivatization of the substrate. Several studies have been reported which have employed different types of silanes in order to control surface alignment [6–8]. Commonly used reagents are simple chlorosilanes and alkoxysilanes. A principal disadvantage of these reagents is that many of them do not produce the desired interfacial effects [9].

Potentially a better means of controlling the molecular orientation of liquid crystals is the preparation of substrates with directly bonded mesogens since the resulting surfaces will have a much greater influence on the bulk alignment than surfaces modified using standards silanes (e.g., alkylsilanes). Thus, the objective of the current work has been to develop a surface modification approach which uses a bonded liquid crystal to control the alignment of liquid crystals in contact with it.

Molecular orientation of surface alignment layers can be studied by various techniques [10–20]. Among them, Fourier transform infrared spectroscopy (FT-IR) is an effective tool for characterizing the interfacial behavior of liquid crystalline molecules [16–20]. Previously, the interfacial structure of a liquid crystal, 4′-cyano-4-biphenyl[4-(4-pentenyloxy)]benzoate (CBPB), in contact with silica has been examined by FT-IR [21, 22]. Complex infrared nitrile stretching bands were observed for the physically coated material, resulting from several distinctly different surface interactions. The bands were resolvable into three Lorentzian components via iterative curve fitting procedures that were centered at 2239 cm^{-1}, 2228 cm^{-1} and 2223 cm^{-1}. These components were assignable respectively to populations of molecules that either formed hydrogen-bonds with surface silanols, were randomized, or resembled the bulk crystalline state. The relative contribution of each of the components to the overall band shapes varied with the coating level. At lower surface coverages, CBPB molecules which formed hydrogen-bonds with the substrate were the dominant species, whereas, the population of molecules which resembled the bulk crystalline species increased with increasing coating level.

In the current study, infrared spectroscopy has been used to examine the interfacial properties of a chemically modified surface which contains directly bonded 4′-cyano-4-biphenyl[4-(4-pentenyloxy)]benzoate. Likewise, the ability of this material to orient bulk CBPB coated onto it also has been examined.

EXPERIMENTAL SECTIONS

Materials

The dimethylchlorosilane and chloroplatinic acid used in the synthesis of the bonded liquid crystal phase were purchased respectively from HULS, Inc (Bristol, PA) and the Aldrich Chemical Company (Milwaukee, WI). The liquid crystal, 4′-cyano-4-biphenyl[4-(4-pentenyloxy)]benzoate (CBPB), was synthesized as previously reported [21]. It was chemically bonded onto LiChrospher 100 silica (mean particle size 0.008–0.011 mm and surface area 250 m^2/g) from E.M. Sciences (Cherry Hill, NJ). All of the other chemicals used in the current experiments were of Analytical Reagent Grade from Aldrich and were used as received.

Preparation of the Physically Modified Surfaces

Silica LiChrospher 100 was physically coated with CBPB at levels of 8.1%, 10.9%, 23.0% and 43.1% by weight. This was done by first dissolving a known amount of CBPB in chloroform and then adding appropriate amounts of silica. The resulting mixtures were allowed to equilibrate and the solvent was removed with a rotary evaporator at 40°C. The coated samples were dried in a vaccum oven at 40°C for 48 hrs and then stored in brown bottles in a desiccator. The exact coating levels were determined by elemental micro-combustion analysis, which was carried out by Huffman Laboratories (Golden, CO).

Preparation of the Chemically Modified Surface

The liquid crystal CBPB-silane that was chemically anchored to the silica was prepared using a method similar to that described by Subramaniam and Gilpin [23]. The reaction scheme for the chemical modification is illustrated in Figure 1: A mixture of the CBPB (4 g, 0.0106 mmol), dry toluene (10 ml), dimethylchlorosilane (2.4 ml, 21.56 mmol) and chloroplatinic acid (0.122 M THF solution, 5 drops) was heated under nitrogen at 60°C for 8 hrs. The reaction mixture was cooled and filtered through active carbon under nitrogen. The excess dimethylchlorosilane was removed by vaccum distillation and the remaining clear solution, which contains the CBPB-silane, was kept under nitrogen for the next step of the reaction.

Five grams of silica (i.e., LiChrospher 100 silica) were first slurried with deionized water and excess water was decanted away. The hydroxylated silica was then dried at 110°C for 2 hrs and transferred into a specially

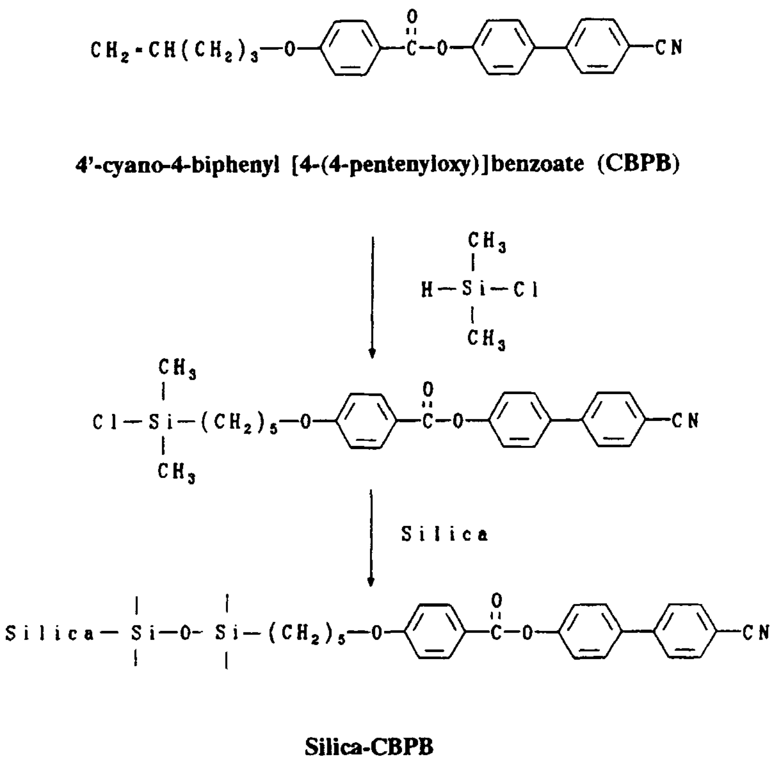

FIGURE 1 The reaction scheme for the preparation of the chemically modified surfaces.

designed reaction vessel. The CBPB-silane obtained from the first step was added to the flask and the resulting mixture was refluxed overnight. In doing this, dry nitrogen was bubbled through the gas inlet during the reaction to stir the mixture and expel hydrogen chloride generated in the reaction. Solvent was then removed by applying a vacuum to the fritted glass tube. The resulting silica was washed four times with toluene, two times with methanol, and two times with diethyl ether. Subsequently, the material was washed further by first packing it into an HPLC column and passing chloroform through it overnight at a rate of 1.0 ml/min. The chemically modified silica was then dried in a vacuum oven at 40°C for 48 hrs and stored in brown bottles in a desiccator.

Spectrometry

Fourier transform infrared (FT-IR) spectra were collected in the conventional transmission mode by using a Bomem model DA-8-high-resolution

FT-IR spectrometer equipped with an MCT detector. The detailed sampling procedures for the modified silica samples were similar to those described previously [21, 22]. All of the spectral measurements were carried out at 50°C after having conditioned the samples at 110°C for at least 1 hr. The interferograms were collected at a resolution of 0.5 cm^{-1} under a nitrogen atmosphere and transformed by using a boxcar appodization. For all of the silica samples, 1024 scans were signal-averaged to obtain an acceptable signal-to-noise ratio. Expansions of spectra in the nitrile stretching region (2180–2280 cm^{-1}) were processed by using Jandel Scientific (San Rafael, CA) peakfit software to resolve and integrate each of the individual spectral components from the complex bands. All of the thermal results represent at least duplicated measurements.

RESULTS AND DISCUSSION

The liquid crystal, 4′-cyano-4-biphenyl[4-(4-pentenyloxy)]benzoate, which contains a terminal olefin group, was treated with dimethylchlorosilane under anti-Markownikoff conditions, the resulting product purified and then reacted with LiChrospher 100 silica (mean particle size 8–11 μm and surface area 250 m^2/g) under toluene reflux conditions. The resulting material was dynamically washed with chloroform to remove adsorbed CBPB molecules and infrared spectroscopy was utilized to confirm the success of the bonding reaction.

Shown in Figure 2 are infrared spectra for the starting material (i.e. CBPB and the silica substrate) and the chemically modified surface. The major peaks of the chemically modified surface in Figure 2c can be readily correlated to the structure of the CBPB shown in Figure 2a which indicates that CBPB was successfully bonded onto silica. Elemental analysis results indicate that the chemically modified surface contained 22.8% CBPB by weight.

Infrared studies were first carried out on samples of silica which were physically modified CBPB as a means of helping to characterise the interfacial properties of the surface anchored CBPB. In order to do this, physically modified materials were prepared by coating differing amounts of CBPB (i.e., 8.1%, 10.9%, 23.0% and 43.1%) onto LiChrospher 100 silica. Shown in Figure 3 are representative infrared spectra for the physically coated samples enlarged over the 2150–2300 cm^{-1} region and plotted in the absorbance mode. Broad, asymmetrical nitrile bands similar to those of CBPB coated onto Fractosil 500 silica [21, 22] were observed for all of the samples. The nitrile stretching bands for the samples at the lower coating

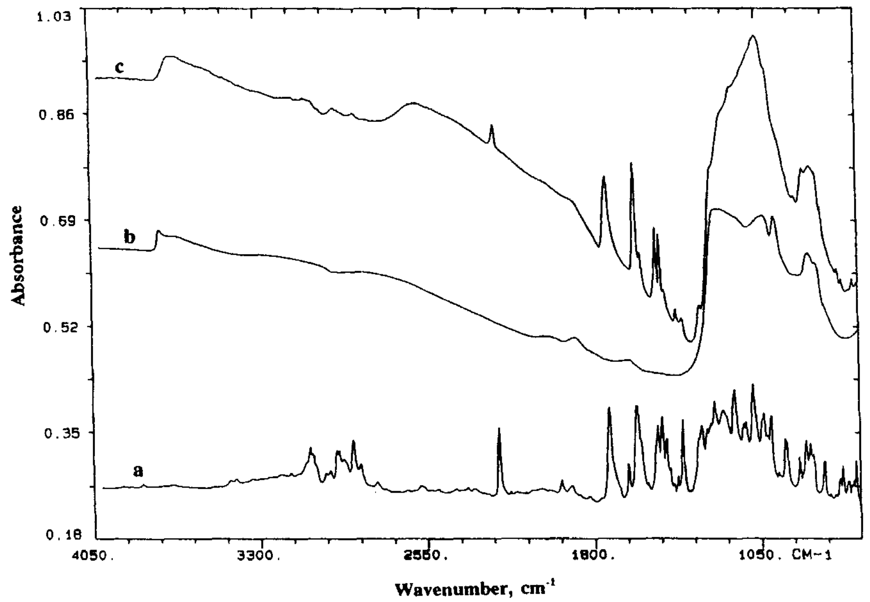

FIGURE 2 Infrared spectra for: (a) CBPB, (b) silica, and (c) chemically bonded CBPB.

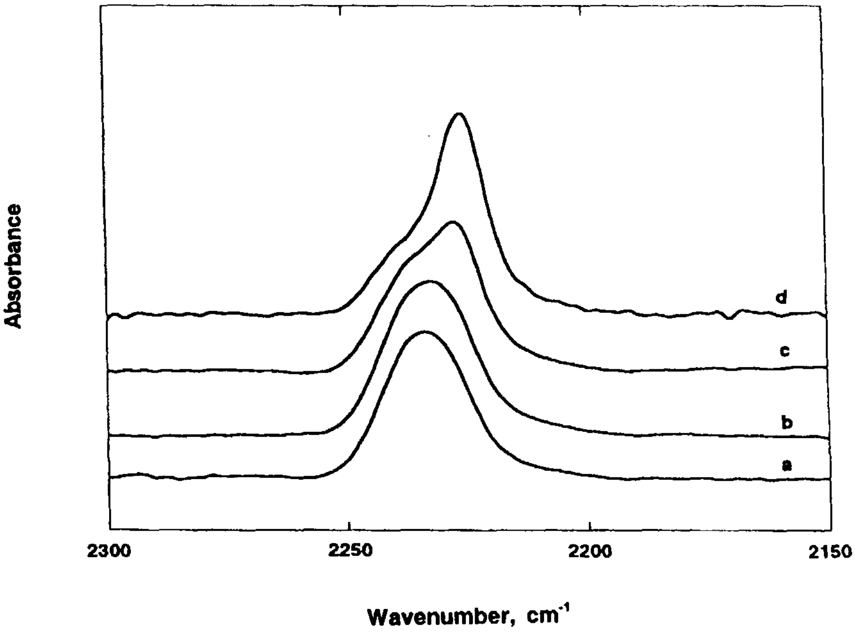

FIGURE 3 Nitrile stretching bands for CBPB physically coated on LiChrospher 100 silica with coverages of: (a) 8.1%, (b) 10.9%, (c) 23.0%, and (d) 43.1%.

levels (i.e., 8.5% and 10.9%) contained a spectral component that was shifted to higher wavenumber compared to that of pure CBPB. Further the band shapes were skewed to lower wavenumber as the coverage of CBPB was increased (Fig. 3).

Three Lorentzian components were resolved from these bands using an interactive curve fitting procedure [22]. The spectral component at the highest frequency (i.e., 2229 cm^{-1}) results from the interaction of the nitrile groups of CBPB with surface silanols (i.e., the hydrogen-bonded species) [22]. The component at lowest frequency (i.e., 2223 cm^{-1}) is at the same frequency as that observed for pure CBPB (i.e., the bulk crystalline species). The remaining component at 2228 cm^{-1} arises from the nitrile groups that neither hydrogen-bond nor have the same interactions of the bulk liquid crystal.

The relative contribution of each species to the overall shape of the nitrile band varies with the coating level of the liquid crystal as can be seen from the data summarized in Table I. At the lower coating levels (i.e., 8.5% and 10.9%), the dominant species are CBPB molecules that either hydrogen-bond with silica or are in a state which does not resemble the bulk CBPB (subsequently referred to as the noncrystalline state). When the coating level is increased, a bulk crystalline layer starts to form and increases with increasing coverage (Tab. I).

A comparison of infrared spectra in the nitrile region for pure, physically coated, and chemically bonded CBPB samples indicates that the microenvironments of the nitrile groups of the chemically bonded CBPB are different from those of the physically coated or pure CBPB samples. As shown in Figures 4b and c, the nitrile stretching band for the chemically bonded CBPB was more symmetrical compared to the physically coated material with a similar surface coverage (i.e., the 23.0% sample). These results support the idea that the bonding process leads to a reduction in the nitrile-silanol interactions. Similarly, a significantly different central band frequency was observed between the bonded and pure CBPB samples (Figs. 4a and b) which suggests that the nitrile groups of the bonded CBPB

TABLE I Relative contributions of the individual components to the nitrile stretching band for the different coated samples

Moleculer Species	*Percent Integrated Intensities*			
	*8.1% CBPB**	*10.9% CBPB*	*23.0% CBPB*	*43.1% CBPB*
hydrogen-bonded	51.8% ± 3.7	46.7% ± 5.1	34.2% ± 4.2	17.2% ± 3.2
noncrystalline	48.2% ± 4.1	53.3% ± 6.4	51.3% ± 4.6	44.5% ± 4.3
crystalline	–	–	14.5% ± 5.2	38.3% ± 3.2

*surface coverage, weight percentage on LiChrospher 100 silica.

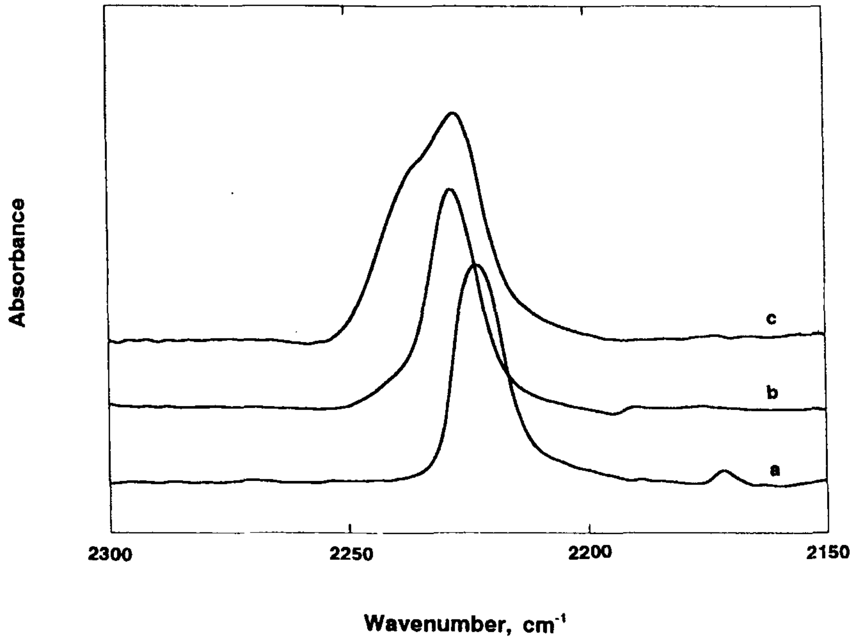

FIGURE 4 Comparison of the nitrile stretching bands for: (a) pure CBPB, (b) chemically bonded CBPB, and (c) 23.0% of CBPB physically coated on silica.

are in a different micro-environment compared to pure CBPB. The nitrile stretching band for the bonded CBPB could be fitted with a single Lorentzian component centered at 2228 cm^{-1}. This corresponds to the frequency of the nitrile groups which neither hydrogen-bond nor resemble those in bulk CBPB. Since one end of CBPB was chemically bonded to the surface, the above spectral features suggest that the bonded CBPB molecules are perpendicularly oriented on the surface.

In order to examine how the chemically anchored LC-substrate influences the alignment of bulk liquid crystal in contact with it, two physically modified surfaces were prepared by coating 11.2% and 23.1% of CBPB onto the chemically modified silica. Shown in Figure 5 are expanded infrared spectra of the nitrile stretching region for these two samples (b and c) along with a spectrum for the chemically modified substrate (a). The complex bands for the physically coated samples were resolved into their individual spectral components using the curve fitting procedures discussed earlier. The resulting data reveal that the ratio of molecules which form the bulk layer (i.e., crystalline species) to those that do not (i.e., the noncrystalline and hydrogen-bonding species) increases with increasing with increasing amounts of physically coated CBPB (Tab. II).

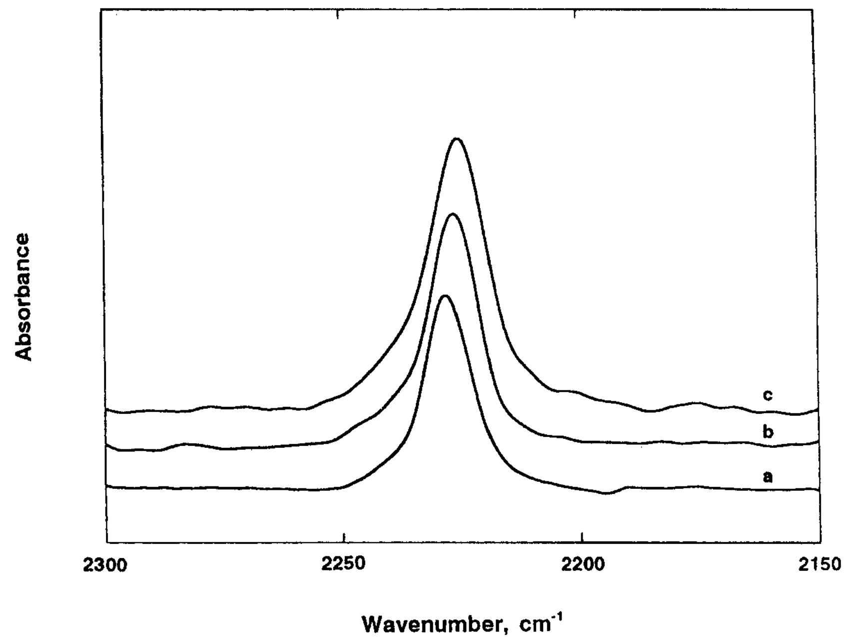

FIGURE 5 Comparison of the nitrile stretching bands for: (a) chemically bonded CBPB, (b) 11.2% of CBPB coated on the chemically modified surface, and (c) 23.1% of CBPB coated on the chemically modified surface.

TABLE II Relative contributions of the individual components to the nitrile stretching band for the CBPB coated on the chemical modification surface

Moleculer Species	*Percent Integrated Intensities*	
	11.2% CBPB	*23.1% CBPB*
hydrogen-bonded	5.6% ± 6.4	10.8% ± 5.4
noncrystalline	63.8% ± 5.8	40.9% ± 4.5
crystalline	30.1% ± 4.4	48.3% ± 4.5

*surface coverage, weight percentage on the chemically bonded surface.

Further, the chemically anchored CBPB molecules sterically hinder the interactions of the physically coated CBPB molecules with the surface silanols. Compared to the samples where similar amounts of CBPB were directly coated on the bare silica (Tab. I), on a relative basis, the hydrogen-bonding interactions of CBPB with the substrate surface were greatly reduced on the chemically modified surface. The dominant species for the sample at the lower coating level are the intermediate species that neither hydrogen-bond nor resemble pure CBPB, part of which are due to the chemically bonded molecules themselves. However, at the higher coating level more of CBPB are in the bulk crystalline state due to the surface chemical modification (Tab. II).

CONCLUSION

The micro-environments of the chemically bonded liquid crystal CBPB are different from those of either pure CBPB and samples of bare silica which have been physically coated with CBPB. The interactions of the liquid crystal, CBPB, with silica which has been chemically modified with CBPB were greatly reduced. This results in a larger population of the coated liquid crystal in the bulk state. Experiments are now in progress with using the other techniques (i.e., TGA and DSC) to study the thermotropic properties of the chemically bonded liquid crystals.

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