Gas Chromatographic and Infrared Studies of 4'-Cyano-4-biphenyl 4-(4-Pentenyloxy)benzoate Coated on **Porous Silica**

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The physical properties and the solute-surface interactions of porous silica modified with either the liquid crystal 4'-cyano-4-biphenyl 4-(4-pentenyloxy)benzoate (CBPB) or the structurally similar compound 4-biphenyl 4-(4-pentenyloxy)benzoate (BPB) have been investigated by gas chromatography (GC) and Fourier transform infrared spectroscopy (FT-IR). The measured adsorption energies for various linear and aromatic solutes indicate a significant difference in interaction of the two types of materials. In the case of CBPB (i.e., 7% coverage), no mesogenic properties were observed by gas chromatography as reflected by the linearity and absence of any discontinuities in plots of $\ln V_g$ vs 1/T. Additionally, the nitrile stretch region for CBPB modified silica contained a complex infrared band made up of at least two or more components. These latter results as well as the chromatographically measured adsorption energies for selected hydrocarbons suggest the presence of at least two populations of CBPB molecules on silica, those which form hydrogen bonds with surface silanols and those which do not.

Liquid crystals have found widespread applications in many types of electronic displays where small amounts of the materials are coated onto flat optical cells.¹ Under these conditions the physical properties of the liquid crystal may be identical to those of the bulk or they may be altered substantially, depending on the nature of the substrate and the amount of material deposited on the support.²⁻⁴ In some instances, the mesogenic properties will disappear due to strong interactions with the substrate and degradation of alignment at the interface.5,6

Although many techniques have been developed to produce uniform molecular orientation, the physical mechanisms which control surface-induced alignment still are not understood clearly.⁷ The degree of orientational order of liquid crystalline molecules at the interface has been investigated by a variety of techniques such as X-ray diffraction measurements,8 nuclear magnetic resonance spectroscopy,9,10 scanning tunneling microscopy,^{11,12} gas chromatography,^{4,5} and Fourier transform

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infrared spectroscopy.¹³ These techniques have provided information about coating level, molecular alignment, phase transition temperatures, and interactions of interfacial mesogenic molecules with the substrate's surface. It has been found that the surface properties have a significant influence on the mesogenic orientation of the molecules in the first adsorption layer which in turn influences the orientation of additional layers and hence the properties of the bulk.

Gas chromatographic measurements have been used extensively in the past to investigate liquid crystal/substrate interactions on a variety of supports.¹⁴ For example, it has been observed that liquid crystals behave differently on Chromosorb supports which have been subjected to various pretreatment procedures.^{15,16} Because the observed retention characteristics of solutes are connected with the alignment of liquid crystalline molecules on the surface, this technique also has been used to study the interactions between the liquid crystal and the substrate.^{5,15} Data obtained by chromatography have demonstrated that the interaction of liquid crystalline molecules with an adsorbent's surface is the greatest in the layer directly adjacent to the surface and that no distinct phase transitions are observed when a small amount of mesogen is deposited on a chemically heterogeneous surface.¹⁵⁻¹⁷

Another commonly used technique to study the interfacial properties of surface materials is Fourier transform infrared spectrometry (FT-IR). The information derived from such studies provides additional insights about surface-ligand structure and interactions. For example, FT-IR has been used to elucidate the conformational features for silica immobilized n-alkyldimethyl,¹⁸ cyanoalkyl,¹⁹⁻²¹ and acetoacetamide²² ligands. This technique is especially suitable for studying mesogenic compounds which contain a nitrile group because the nitrile stretch band is isolated from interference bands arising from many commonly used matrix materials such as glass and silica.²³ Previously, infrared measurements have been used to examine the interaction of the liquid crystal

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N-(p-cyanobenzylidene)-p-(octyloxy)aniline (CBOA) with underivatized and alkyl-modified silica.^{24,25} In this work, various chemically derivatized as well as underivatized silicas were physically coated with varying amounts of the liquid crystal and FT-IR spectra were acquired from these samples. An extremely broad and asymmetrical band was observed for the nitrile stretch region (2190–2290 cm⁻¹), which could be deconvoluted into a doublet with overlapping higher and lower frequency components arising respectively from hydrogenbonded and non-hydrogen-bonded nitrile groups. These same experimental results also showed that the distribution of isolated and hydrogen-bonded groups varied with coating level and surface treatment.

It seems important from a practical point of view to study the properties of liquid crystals deposited on the silica because its surface chemistry is similar (i.e., silanol groups) to glass which is commonly used in display construction. In the current study the liquid crystal 4'-cyano-4-biphenyl 4-(4-pentenyloxy)benzoate (CBPB) and a structurally similar compound 4-biphenyl 4-(4-pentenyloxy)benzoate (BPB), which does not contain a nitrile head group, were physically coated onto porous silica and the interfacial properties of these materials were studied by gas chromatographic and FT-IR techniques. In doing this, two major points were of interest: (1) the characterization of the mesomorphic properties of the liquid crystal on the silica and (2) an estimation of the liquid crystalsurface interactions.

EXPERIMENTAL SECTION

Materials. 4-Cyano-4'-hydroxybiphenyl was purchased from TCI America (Portland, OR), and 4-hydroxybenzoic acid, 5-bromo-1-pentene, 4-phenylphenol, N,N'-dicyclohexylcarbodiimide, and 4-pyrrolidinopyridine were obtained from the Aldrich Chemical Co. (St. Louis, MO). The benzoate esters were physically coated onto Fractosil 500 silica (mean particle size 170-230 mesh ASTM and surface area 50 m²/g) from EM Science (Cherry Hill, NJ). All of the solutes used in the chromatographic measurements were of analyticalreagent grade from the Aldrich Chemical Co. and were used as received.

Synthetic Procedures. Preparation of 4-(Pentenyloxy)benzoic Acid. 4-(Pentenyloxy)benzoic acid was synthesized from 4-hydroxybenzoic acid and 5-bromo-1-pentene, as described by Ringsdorf.²⁶ Ethanol (200 mL) and potassium hydroxide (8.5 g) were added under nitrogen to a 500-mL two-neck round-bottom flask equipped with a reflux condenser. Next, 4-hydroxybenzoic acid (8 g, 0.058 mol) was added while stirring, followed by a small amount of potassium iodide and the dropwise addition of 5-bromo-1-pentene (10 g, 0.066 mol). The resulting solution was refluxed for 24 h and cooled, and 200 mL of water was added. Subsequently, the solution was acidified by the slow addition of 20% hydrochloric acid and the resulting precipitate was collected by vacuum filtration and recrystallized from ethanol. The yield of 4-(pentenyloxy)benzoic acid was 65% (7.7 g) with a melting point of 396 K.

Preparation of 4'-Cyano-4-biphenyl 4-(4-Pentenyloxy)benzoate (CBPB) and 4-Biphenyl 4-(4-Pentenyloxy)benzoate

(BPB). These two compounds were synthesized by the esterification of 4-(pentenyloxy)benzoic acid and different 4-substituted phenols. A mild esterification method^{27,28} was employed, in which N,N'-dicyclohexylcarbodiimide (DDC) was utilized as the dehydrating agent and 4-pyrrolidinopyridine (PPY) as the catalyst. Methylene chloride (40 mL) was placed in a 100-mL round-bottom flask followed by the addition of 4-(pentenyloxy)benzoic acid (4.7 g, 0.0225 mol), the 4-substituted phenol (0.0225 mol) (i.e., either 4-cyano-4'hydroxybiphenyl or 4-phenylphenol), and 0.2 g of PPY. DDC (4.6 g, 0.0225 mol) was added to this mixture and it was refluxed for 1 h. The resulting precipitate, which was dicyclohexylurea (DCU), a byproduct, was filtered from the hot reaction mixture and was washed with chloroform. The filtrate was first extracted with an equal volume of 3 M HCl and then with a 5% KOH solution. The organic layer was dried over anhydrous sodium sulfate and filtered through fluted filter paper. The organic solvent was removed via a rotary evaporator. The crude product was purified by recrystallizing it twice from a mixture of either chloroform-ethanol (1:1) for CBPB or acetone-ethanol for BPB. Yields of 93% (7.8 g) for CBPB and 96% (7.7 g) for BPB were obtained.

The identity of the compound CBPB was confirmed by using DSC, FT-IR, NMR, and elemental analysis. The results obtained are as follows: mp 381 K to nematic, 540 K to isotropic; IR 2223, 1725, 1605, 1511, 1492, 1396, 1265, 1202, 1166, 1073, 1045, 1005, 929, 884, 848 cm⁻¹; ¹H NMR (CDCl₃) δ 8.17–6.95 (m, 12H, aromatic), δ 5.93–5.81 (m, 1H, -CH=), δ 5.04 (m, 2H, CH₂=), δ 4.02 (t, 2H, -OCH₂), δ 2.25, 1.92 (m, 4H, -CH₂-CH₂-). Anal. Calcd for C₂₅H₂₁NO₃: C, 78.3; H, 5.5; N, 3.7; O, 12.6. Found: C, 78.4; H, 5.6; N, 3.7; O, 12.3.

Preparation of Physically Coated Silica. The silicas were physically coated by first dissolving a known weight of CBPB or BPB in chloroform and then adding appropriate amounts of silica. The mixture was allowed to equilibrate and the solvent was removed with a rotary evaporator at 313 K. The coated samples were dried in a vacuum oven at 313 K for 48 h and then stored in brown bottles in a desiccator. The weight percentages of the liquid phase on the packings (i.e., the liquid phase loading) were determined by using a TA Instruments, Inc. (New Castle, DE) model TGA 2950 high-resolution thermogravimetric analyzer as well as by elemental microanalysis (Huffman Laboratories, Golden, CO). The two samples studied by GC and FT-IR both had a loadings of 7%. In addition, a third sample with the 20% CBPB coating was prepared for FT-IR verification work.

Chromatographic Measurements. The seven nonmesomorphic solutes chosen as test adsorbates exhibit a range of sizes, shapes, and flexibilities. These included a homologous series of normal alkanes and monoalkylbenzenes. All gas chromatographic measurements were carried out using a Hewlett-Packard (Avondale, PA) model 5890 gas chromatograph equipped with a flame ionization detector and glass columns (100-cm \times 3.5-mm i.d.). The columns were packed with samples of either the unmodified silica with a surface area of about 50 m²/g or one of two different modified silicas and then conditioned with a gentle flow of carrier gas (nitrogen)

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Figure 1. Chemical structures of (a) 4'-cyano-4-biphenyl 4-(4-pentenyloxy)benzoate (CBPB) and (b) 4-biphenyl 4-(4-pentenyloxy)-benzoate (BPB).

b) BPB

for 24 h at 383 K. Retention times, which represent at least duplicate determinations, were measured from 353 to 403 K using a Hewlett-Packard model 3393A integrator.

Infrared Measurements. Infrared spectra were recorded in the absorbance mode by using a Bomem (Quebec City, Quebec, Canada) model DA-8 high-resolution FT-IR spectrometer equipped with an MCT detector. Ratios of 3200 sample scans vs 100 nitrogen-atmosphere background scans were taken. In order to assure that the liquid crystalline molecules were uniformly distributed on the surface of silica, the silica coated with the CBPB was placed between two KBr windows, preheated just above its crystal to nematic phase transition temperature, and then cooled to room temperature before carrying out any of the spectral measurements. The temperature of the sample was controlled to within 0.1 K by using a calibrated Eurotherm Corp. (Reston, VA) Model 808 hot-stage apparatus. Interferograms were collected from 323 to 403K at a resolution of 0.5 cm⁻¹ and transformed by using a boxcar appodization. The spectral data in the nitrile stretch region (2178-2278 cm⁻¹) were manipulated with using the instrument's integration software. The precisions of the area measurements for a given sample of both the pure liquid crystal and 7% coated CBPB materials as well as the sample variations for 7% CBPB coated samples were evaluated. Values of 1.6%, 3.5%, and 3.8% were obtained respectively for these integrations.

Other Measurements. The nuclear magnetic resonance (NMR) spectra were collected by using a General Electric Co. (Fremont, CA) model GN-300 spectrometer. The differential scanning calorimetric (DSC) measurements were carried out on a TA Instruments, Inc. (New Castle, DE) model 2910 differential scanning calorimeter.

RESULTS AND DISCUSSION

Two alkoxybenzoate esters, shown in Figure 1, were synthesized. The first of these, CBPB, which has a terminal nitrile group, has liquid crystal properties, and the second compound, BPB, which has an analogous chemical structure except for the absence of the nitrile group, does not exhibit mesogenic behavior. The latter compound was synthesized and coated onto silica for comparative purposes. The thermal transitions of the two materials were examined by using a differential scanning calorimeter. Figure 2 is a comparison of the DSC scans over the temperature range from 313 to 563 K. Endothermic peaks were observed at 381 and 540 K for



Temperature, K

Figure 2. Differential scanning calorimetry (DSC) determinations on CBPB (top curve) and BPB (bottom curve). Conditions: heating and cooling rates, 10 deg/min; nitrogen atmosphere.

l ab	le	1.	Values	i of	the	Adso	rption	Energy	$(q_{\rm st})$	for	Hydrocarbons	
on l	Un	no	dified F	oro	us :	Silica	Fracto	sil 500			-	

hydrocarbon	$\begin{array}{c} {f adsorption\ energy,} \\ q_{{f st}} \ ({f kJ/mol}) \end{array}$	adsorption energy, q_{st} (kJ/mol)			
ethylbenzene	57.4	49.3,° 53d			
toluene	51.6	45.5°			
benzene	45.5	41.1, ^a 55.9 ^b			
n-octane	44.4	42 ^d			
<i>n</i> -heptane	39.9	41.1, ^a 52.7, ^b 38 ^d			
n-hexane	34.5	37.3.ª 44.2. ^b 44.6°			
1-hexane	42.6	51.2°			

^a Taken from ref 30. ^b Taken from ref 31. ^c Taken from ref 32. ^d Taken from ref 33.

CBPB, which correspond to the crystal to nematic and the nematic to isotropic transitions, respectively. However, only a single peak was noted at 421 K for BPB, which is due to its crystal to isotropic phase transition.

Chromatographic Studies. The specific retention volumes (V_g) of the test solutes on the columns containing silica, CBPBsilica, and BPB-silica were measured from 353 to 403 K (i.e., the range where the crystal to nematic transition is expected for CBPB), and the adsorption energies (q_{st}) were calculated.²⁹ The resulting q_{st} values for the different solutes on unmodified Fractosil 500 silica as well as corresponding reported literature values for different silicas³⁰⁻³³ are summarized in Table 1. Figures 3 and 4 show representative plots of ln V_g vs 1/T for the six test solutes chromatographed on silica coated with BPB and CBPB. The resulting values of the adsorption energies (q_{st}) of the solutes on these two modified silicas are given in Table 2.

As can be seen from Table 1, for the unmodified silica, there is the general tendency of the q_{st} values to increase systematically as a function of the number of carbon atoms in the solute for the linear hydrocarbons and aromatic homologues. This is due to an increase in the nonspecific

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Figure 3. Experimental dependence in V_g vs 1/T for (O) ethylbenzene, (\bullet) toluene, (Δ) benzene, (Δ) *n*-octane, (\Box) *n*-heptane, and (\blacksquare) *n*-hexane on silica physically coated with 7% BPB.



Figure 4. Experimental dependence in V_g vs 1/*T* for (O) ethylbenzene, (\bullet) toluene, (Δ) benzene, (Δ) *n*-octane, (\Box) *n*-heptane, and (\blacksquare) *n*-hexane on silica physically coated with 7% CBPB.

Table 2. Values of the Adsorption Energy $(q_{\rm el})$ for Hydrocarbons on Physically Modified Silica Surfaces

CBPB-silica q _{st} (kJ/mol)	BPB-silica q_{st} (kJ/mol)
34.7	41.6
31.3	37.7
26.9	31.8
41.6	37.5
37.4	33.1
33.0	28.6
32.3	30.2
	CBPB-silica q _{st} (kJ/mol) 34.7 31.3 26.9 41.6 37.4 33.0 32.3

dispersive interactions.³³ A comparison of the thermodynamic characteristics of the *n*-alkanes with those of the aromatic compounds (Table 1) shows that the q_{st} values for the solutes with π -electrons are higher than those for the linear alkane with equivalent carbon numbers. For example, the q_{st} values for benzene and toluene are respectively 10.9 and 10.7 kJ/ mol higher than those for *n*-hexane and *n*-heptane. These results reflect the increased specific interaction of the π -electrons of the aromatic solutes with the surface silanol groups and are consistent with other published data which are listed in column 2 of Table 1. In general, the data in Table 1 indicate that the adsorption characteristics of the bare Fractosil 500 silica are similar to those expected for other similar types of silica.

Coating the silica with either CBPB or BPB leads to reduced $a_{\rm st}$ values for the solutes compared to the adsorption energies on the unmodified silica (Table 1 and 2). A possible explanation for this behavior is that during the coating process the higher energy adsorption sites, which are contained in the smaller pore or on the surface, are blocked by the physically sorbed organic layer, leading to a decrease in the surface heterogeneity.^{32,34} Although the interactions of the solutes with the BPB-silica were reduced compared to those on bare silica, they reflected the same general trends. For example, the adsorption energies of aromatic solutes on BPB-silica (Figure 3, Table 2) as in the case of the unmodified silica were larger than those of the corresponding normal hydrocarbons. These results indicate that solute retentions of the aromatic solutes are still influenced by specific interaction but that they are only about 30-40% of that on the unmodified surface.

With the introduction of a nitrile group in the BPB molecule, the adsorption behavior of the modified silica is changed significantly. The absorption energies of the aromatic compounds vs those of the linear hydrocarbons with equivalent numbers of carbon atoms are reversed on the CBPB-silica compared to those of the corresponding solutes on either the unmodified silica or BPB-modified silica (Figure 4, Table 2). These results reflect a reduction in the specific interactions of the aromatic compounds with the CBPB-silica surface and are consistent with the attenuation of the residual silanol interactions via the nitrile groups of CBPB as well as the possibility of a different surface alignment of CBPB compared to BPB (i.e., a flat vs a perpendicular orientation). On a relative basis, the higher values of q_{st} for the linear alkanes also are consistent with these latter alignment arguments.

It is well-known that at higher surface coverages the distinct phase transitions of mesogenic compounds appear as discontinuities in plots of $\ln V_g$ vs $1/T^{2,4,5,14-17,35}$ Likewise, it has been demonstrated that liquid crystalline behavior is not observed without multilayer coverage.^{5,12,25} As such, a significant feature of the current work is that linearity was observed in the $\ln V_g$ vs 1/T plots (Figure 4) under the coating conditions studied (i.e. silica modified with 7% CBPB). These results indicate that the coverage used in the current study was insufficient to obtain mesogenic behavior.

Infrared Studies. In order to further examine the orientational and interaction arguments presented above, a series of infrared experiments were carried out. Spectra were collected as a function of increasing temperature (323-403 K) from both the pure CBPB liquid crystal and 7% CBPBmodified silica. Representative sets of spectra covering the nitrile stretch region of the pure CBPB sample at temperatures near the phase transition are shown in Figure 5. In the crystalline phase (Figure 5a-c), the central frequency and intensity of the nitrile band remain almost constant with increasing temperature; however, between the crystal and nematic phases (Figure 5c-e), the band shifts to higher frequency and its integrated intensity increases. Beyond the phase transition (Figure 5e,f), the frequency and shape of the band vary little with temperature. Such changes in spectral features have been reported previously^{36,37} and can be utilized

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Figure 5. Nitrile stretching bands for CBPB at selected temperatures: (a) 378 K, (b) 379 K, (c) 380 K (crystalline phase), (d) 381 K, (e) 382 K (nematic phase), (f) 383 K.



Figure 6. Changes in the normalized integrated intensity as a function of temperature for (\bullet) pure CBPB and (\blacktriangle) 7% CBPB-silica samples.

to investigate the thermotropic behavior of compounds such as CBPB in the pure state and when it is deposited on silica.

Shown in Figure 6 are plots of the normalized integrated intensities of the nitrile band vs temperature for pure CBPB and the 7% CBPB-silica sample. In the case of the pure CBPB sample (data shown as filled circles), an abrupt increase in the plot was observed at 381 K, which is the reported temperature²⁶ for the crystal to nematic transition as well as that measured by our DSC experiment (Figure 2). This characteristic infrared behavior was not observed on the 7% CBPB-modified silica (i.e., the normalized integrated band intensity remained constant within the precision of the measurements as a function of increasing temperature) (Figure 6, filled triangles). These latter results are in agreement with the previously discussed GC results and indicate the absence of detectable mesomorphic properties for the 7% CBPBmodified silica sample by using the current approach.



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Figure 7. Comparison of the nitrile stretching bands at (A) 7% CBPB coating and (B) 20% CBPB coating.

An additional feature of the infrared experiments is illustrated in Figure 7a. The spectra of the nitrile stretching region for the 7% CBPB-silica samples contained a complex band which suggests the presence of at least two species. This is further illustrated at a higher level of coverage (20%) in Figure 7b. In the latter figure, the component at lower wavenumber increases on a relative basis compared to the higher wavenumber component. On the basis of these observations as well as other infrared studies of hydrogen bonding for nitrile groups with silica,^{19-21,23-25,38} the higher wavenumber component arises from nitrile groups that form hydrogen bonds with free surface silanols, whereas the lower wavenumber peak is due to nitrile groups that do not form hydrogen bonds with the substrate. Although quantitation of the individual spectral components is not possible without further experiments (i.e., without a measurement of the molar absorptivities), the data indicate that both types of species are present to a significant degree for the level of coverages studied.

CONCLUSION

The current combined approach appears to provide a means of correlating liquid crystalline behavior and alignment properties with molecular recognition of solutes when these materials are used as chromatographic supports. Similar experiments are now in progress to examine changes in mesogenic behavior as a function of coating thickness in order to further elucidate questions concerning molecular alignment of the surface film and molecular recognition.

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