Shape-Selectivity with Liquid Crystal and Side-Chain Liquid Crystalline Polymer SAW Sensor Interfaces

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SUMMARY
A liquid crystal (LC) and a side-chain liquid crystalline polymer (SCLCP) were tested as surface acoustic wave (SAW) vapor sensor coatings for discriminating between pairs of isomeric organic vapors. Both exhibit room temperature smectic mesophases. Temperature, electric-field, and pretreatment with self-assembled monolayers comprising either a methyl-terminated or carboxylic acid-terminated alkane thiol anchored to a gold layer in the delay path of the sensor were explored as means of affecting the alignment and selectivity of the LC and SCLCP films. Results for the LC were mixed, while those for the SCLCP showed a consistent preference for the more rod-like isomer of each isomer pair examined.

Keywords: vapor sensor; SAW sensor; liquid crystal; self-assembled monolayer; shape selectivity.

INTRODUCTION
The selectivity achievable among multiple organic vapors with coated surface-acoustic-wave (SAW) vapor sensors or sensor arrays depends on the interfacial coating film(s) applied to the sensor(s). With commonly employed isotropic sensor coatings, such as rubbery amorphous polymers and chromatographic stationary phases, responses are governed by bulk sorption which, in turn, depends on the volatility of the vapor and the vapor-coating functional-group interactions. While successful measurement and discrimination of organic solvent vapors have been demonstrated using such materials in small arrays, structural homologues and isomers can be difficult to resolve [1-5].

Sensor coating materials with controlled pore sizes or with inherent anisotropy that exhibit size and shape selective sorption may afford enhanced discrimination of structurally similar vapors. Among those materials shown to provide shape selectivity are liquid crystals (LC). The use of LC stationary phases for separating isomers in gas chromatography is well-known, and a number of reports have appeared on their use as interfacial films in chemical sensors [6-9].

In this presentation, we describe work with two LC materials - a low-molecular-weight alkyl cyano biphenyl compound and a side-chain liquid crystalline polymer (SCLCP). Responses to three pairs of isomeric organic vapors were measured as a function of concentration, temperature, surface pretreatment, and pre-alignment in an electric field. Results are used to assess the extent of shape selectivity achievable with these coating materials.

METHODS
The LC, 4-n-octyl-4'-cyanobiphenyl (K24, Figure 1) was obtained from EM Science (Hawthorne, NY). According to the manufacturer it has a crystalline-to-smectic transition at 21°C, a smectic-to-nematic transition at 32.5°C, and an isotropization temperature of 41°C. The SCLCP (Fig. 1) was synthesized by a modification of a known procedure. The product had a number-average molecular weight of 7500 (GPC), (Xn = 50), a Tc of 13°C, and an isotropization temperature of 121°C.

The isotropic polymers polyisobutylene (PIB, Aldrich) and bis-cyanoallylpolysiloxane (OV-275, Supelco) were used as reference sensor coatings in most test sequences. The former interacts with vapors solely by dispersive forces and the latter contains pendant cyano groups — a feature shared with both of the liquid crystalline materials.

The ST-quartz SAW delay-lines employed were configured as oscillators with a center frequency of 97 MHz. Up to six sensors were operated simultaneously within a thermostatted test case which was plumbed to allow simultaneous flow over all of the sensors. The isomers examined were: n-octane and iso-octane; p-xylene and m-xylene; and 4-methylstyrene and α-methylstyrene. Test atmospheres were generated using bubblers and a
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programmable dilution stage with dry N₂ as the carrier gas. Typical exposures were in the range of 0.5-10% of saturation (i.e., p/pₛₑᵥ = 0.5-10%).

Self-assembled monolayers (SAMs) having either methyl (ME) or carboxylic-acid terminal groups (COOH) were prepared with 1-octadecythiol and 1-thioundecanoic acid, respectively, by a known procedure using SAW devices with a thin Au/Cr layer in the delay path [10]. The LC and SCLCP were deposited by spray coating from solution.

FTIR-ERS measurements were performed as described previously [11]. For electric-field alignment tests, a standard cavity cell was constructed of two electrically conductive indium-tin-oxide (ITO) coated glass plates separated by a 50-µm-thick Teflon spacer. Using a function generator in series with a voltage step-up transformer, the electric field (ac) was applied across the ITO-coated plates while the cavity cell was gently heated with a heat gun and the temperature monitored via a thermocouple mounted at surface of the top ITO-coated glass plate.

FTIR-ERS measurements of K24 films gave CN stretch signals that were much less intense for the K24-Me-SAM than for the K24-COOH-SAM, suggesting a significant difference in average alignment as a function of the SAM terminal group. Changes in both the FTIR spectra and SAW frequency measurements collected during temperature cycling of the K24 from 25 to 50 °C were consistent with reversible alignment changes accompanying the phase transitions at 33 and 41 °C.

Linear response isotherms were observed at low vapor concentrations and the SCLCP exhibited consistently higher ratios of sensitivities (rod-like:non-rod-like isomer) at 25°C than the LC (Table 1), with sensitivity ratios ranging from 1.17 to 1.77 for the SCLCP and 0.93 to 1.42 for the LC. In fact, there is little evidence of shape selectivity between either the xylenes or octanes with the K24 coating, while the SCLCP selectivity for the rod-like isomers is consistent and significant. For the styrenes, both the K24 and the SCLCP show significantly greater selectivity for the 4-methyl isomer, presumably due to the pendant methyl group in α-methylstyrene lying out of the plane of the ring [12].

At high concentrations of the methyl styrenes (p/pₛₑᵥ = 8%) an increase in the slopes of the response isotherms was observed with the K24-COOH-SAM and the ratio of responses also increased dramatically. The dynamic response of the coating became slower, as well. This suggests a vapor-induced smectic-nematic phase change in the LC. The effect was reversible. FTIR-ERS data confirm alignment changes at high vapor concentrations.

Results

Photomicrographs of the deposited K24 films on the COOH-terminated SAM showed reasonably good wetting, while those on the Me-terminated SAM were discrete beads indicative of poor wetting. SCLCP films were smooth and continuous on both SAM pretreated surfaces.

Table 1: SAW sensor sensitivity ratios of rod-like to non-rod-like isomers for all coatings at 25°C.¹

<table>
<thead>
<tr>
<th>Vapor pair</th>
<th>b.p. (°C)</th>
<th>PIB</th>
<th>OV-275</th>
<th>K24 LC</th>
<th>K24 LC</th>
<th>K24 LC</th>
<th>SCLCP</th>
<th>SCLCP</th>
<th>SCLCP</th>
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<tbody>
<tr>
<td>p-xylene/m-xylene</td>
<td>138/139</td>
<td>1.00</td>
<td>1.05</td>
<td>1.14</td>
<td>1.01</td>
<td>0.93</td>
<td>1.17</td>
<td>1.18</td>
<td>1.18</td>
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<tr>
<td>std dev</td>
<td>NA</td>
<td>0.03</td>
<td>0.05</td>
<td>0.06</td>
<td>0.09</td>
<td>0.01</td>
<td>0.00</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>n</td>
<td>NA</td>
<td>19</td>
<td>8</td>
<td>15</td>
<td>12</td>
<td>8</td>
<td>2</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>n-octane/iso-octane</td>
<td>125/99</td>
<td>1.00</td>
<td>0.74</td>
<td>1.02</td>
<td>1.05</td>
<td>1.10</td>
<td>1.27</td>
<td>1.65</td>
<td>1.77</td>
</tr>
<tr>
<td>std dev</td>
<td>NA</td>
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<td>0.11</td>
<td>0.13</td>
<td>0.01</td>
<td>0.07</td>
<td>0.08</td>
<td>0.18</td>
<td></td>
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<tr>
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<td>NA</td>
<td>8</td>
<td>8</td>
<td>4</td>
<td>2</td>
<td>8</td>
<td>2</td>
<td>8</td>
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<tr>
<td>4-methylstyrene/α-methylstyrene</td>
<td>170/165</td>
<td>1.00</td>
<td>1.15</td>
<td>1.42</td>
<td>1.35</td>
<td>1.37</td>
<td>1.47</td>
<td>1.44</td>
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<tr>
<td>std dev</td>
<td>NA</td>
<td>0.02</td>
<td>0.03</td>
<td>0.21</td>
<td>0.11</td>
<td>0.02</td>
<td>0.04</td>
<td>0.05</td>
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<td>16</td>
<td>13</td>
<td>8</td>
<td>6</td>
<td>13</td>
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</table>

¹All sensitivity values were calculated using vapor concentrations expressed in terms of the fraction of the saturated vapor pressure for each solvent so that the expected sensitivity ratio (in the absence of size/shape effects) is 1.0 in all cases. PIB ratios were adjusted to a value of unity, and all other sensitivity ratios were adjusted accordingly, to account for small changes in bubbler temperatures between tests of isomeric vapors.
The SAM pretreatment did not affect the SCLCP selectivity and had little effect on that of the K24. Curiously, positive frequency shifts were always observed in response to all vapors for the K24-Me-SAM films, indicating a predominance of film stiffening vs. mass loading. The poor surface wetting is thought to contribute in some way to this phenomenon.

Operating the sensor in the LC nematic temperature range gave larger, but slower responses and did not affect selectivity. Selectivities were retained above the isotropization temperature for the LC on the methyl-terminated SAM, suggesting surface-induced retention of alignment.

Application of an ac field to thick K24 films while heating and cooling led to distinct changes in film morphology, suggesting an increase in LC alignment that is retained upon cooling to room temperature. Initial tests of selectivity between films of K24 on quartz SAW sensors with and without pretreatment with electric field and thermal cycling, however, indicated no significant differences. It may be that surface interactions with the relatively thin coating films on the SAW sensors mitigate electric-field induced alignment.

CONCLUSIONS

Apparent shape selectivity has been demonstrated between several isomeric organic vapors using SAW sensors coated with liquid crystalline materials. The degree of selectivity was greater for the polymeric SCLCP than for the low-molecular-weight K24, and the former was unaffected by pretreatment with SAMs. SAM pretreatment did affect the alignment and vapor-sorption characteristics of LC films, however it did not affect the vapor selectivity. The finding of consistent positive frequency shifts with the K24-Me-SAM system bears further investigation as a means to enhance the range of responses obtainable with SAW sensors. Electric-field treatment of the K24 films apparently affected alignment with thick films but not with the thinner films used as sensor coatings.

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REFERENCES


