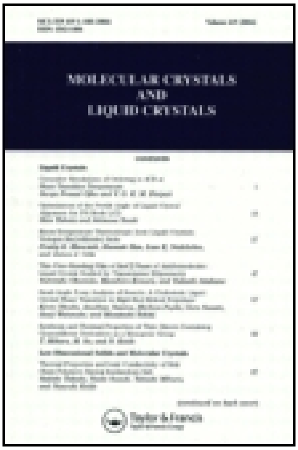

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Use of Liquid Crystals as Vapor Detectors

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The visual detection between crossed polarizers of organic vapors on various liquid crystal films is described. The liquid crystal is utilized as a smear on glass or as an impregnant in microporous polypropylene. The organic vapor induces a change of the liquid crystal from a birefringent mesophase to an isotropic liquid. The effect is generally reversible, i.e., removal of the film from the contaminated atmosphere restores the original state of the film. Non-selective detection is achieved easily in the ppm range. Of the liquid crystals examined, the most sensitive detector was found to be N-(p-methoxybenzilidine)-p-n-butylaniline (MBBA). Optical reflection from cholesteric materials, has been utilized previously for detection purposes. However, dependence on temperature and the need for instrumental monitoring to achieve high sensitivity do not currently allow the achievement of simple detector devices. In contrast, temperature effects and the need for instrumental monitoring are not as important with the systems described in the present paper. Also, opportunities exist for bettering sensitivity and selectivity.

INTRODUCTION

There has been considerable interest in the effect of bulk and surface impurities on the physical properties of mesomorphic materials. The present paper expands on a preliminary communication released previously on the visual detection of organic vapor absorption on liquid crystal films positioned between crossed polarizers.[1]

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Previous publications gave a description of the transparency characteristics of several liquid crystals from the solid to isotropic liquid phases.[2,3] The various phase transitions and in some cases, dichroic scattering could be detected easily from the transparency curves. Impurities affect the phase transitions as well as dichroic properties. Basic information has been accrued concerning the effect of bulk impurities on the transparency of cholesteryl nonanoate.[4] Also, there is information available on the fluorescence emission of impurities dissolved in cholesteryl nonanoate.[5]

Optical reflection from cholesteric liquid crystals has been utilized for the detection of organic vapors.[6-9] However, dependence on temperature and the need for instrumental monitoring to achieve high sensitivity do not currently allow the achievement of simple detector devices for use through visual observation. On the other hand, temperature effects and the need for instrumental monitoring are not as important with the polarizing system.[1] In the present paper we report details concerning the application of the crossed polarizer technique to chemical detection.

MATERIALS[†]

N-(p-Methoxybenzilidine)-p-n-butylaniline (MBBA)[10,11] was prepared by mixing p-methoxybenzaldehyde with p-n-butylaniline, heating at 105°C for two hours while allowing water to escape, then recrystallizing twice from low boiling petroleum ether. (p-Ethoxybenzilidine)-p-n-butylaniline (EBBA) was obtained from Eastman Organic Chemicals, Rochester, New York 14650.

3-N-(p-Ethoxybenzilidine)-6-n-butylpyridine was kindly supplied by CPT Rudolph A. Champa, Wright-Patterson AFB.[12] A nematic liquid crystal formulation, VL1047N, was used as obtained from the Vari-light Corp., Cincinnati, Ohio 45242. High purity butyl p-(p-ethoxyphenoxycarbonyl) phenyl carbonate (resistivity of 1×10^8 ohm cm at 85°C) was used as obtained from Princeton Organics, Princeton, NJ 08540. Cholesteryl nonanoate, decanoate and myristate were obtained from Eastman Organic Chemicals, Rochester, NY 14650, and were recrystallized three times from absolute ethanol prior to use. A nematic liquid crystal, range 18°-80°C (designated LCI 1880) was obtained from the Liquid Crystal Industries, Inc., Turtle Creek, PA 15145. Acetate capped chloral-dichloroacetaldehyde copolymer was obtained from the Diamond Shamrock Co. under Contract DAAA15-67-C-0668.

[†] Mention of a particular commercial product does not imply US Government endorsement.

Alon®, fumed alumina of 0.03 micron average particle size, was obtained from the Cabot Corp., Boston, MA. Celgard 2400 (microporous polypropylene film) was obtained from Celanese Plastics Co., Newark, NJ 07102. Typical properties listed by the manufacturer for Celgard 2400 include: thickness, 1 mil; pore size, <0.1 μm; porosity, 35%; surface area, 50 m^2/g.

PREPARATION OF LIQUID CRYSTAL FILMS

For the preliminary screening tests the candidate liquid crystal was smeared thinly on a microscope slide or on the inside surface of a test tube. A modification involved mixing the liquid crystal (three parts) with fumed alumina (Alon®) (one part) in order to prevent film creeping.

The normal procedure involved impregnating microporous polypropylene film (Celgard 2400) with the liquid crystal. Best results were achieved by first stretching the film using double wooden hoops. A piece (approx. 9 cm^2) of the stretched film was then mounted on a cardboard making a window. A simple method of mounting involved placing the film onto the window opening previously lined with cellophane tape which was sticky on both sides. Excess film was then trimmed off.

A drop of the liquid crystal was then placed on the film and the excess wiped off by using absorbent tissue. Actually both sides of the film were rubbed repeatedly with the tissue until a uniform color field was evident when the film was viewed between crossed polars of a hand polariscope. In some instances it was found useful to expose the impregnated polymer to CH_2Cl_2 vapors (using a hypodermic syringe) then repeat the rubbing.

Several experiments were also performed using a polarizing microscope. In these cases the film was mounted over a 0.63 cm hole in a cardboard support.

QUALITATIVE SCREENING

A qualitative screening of several different liquid crystals was conducted in order to select materials for more detailed study. The nematic, cholesteric and smectic mesophases were represented. Diethylamine was used as the test vapor. Several of the tests were performed above room temperature in order to maintain a particular mesophase for the material being examined. The procedure involved smearing some of the liquid crystal (in a fused state) around the bottom inside surface of a 10 ml test tube. The tube was mounted in hot water contained in a beaker placed on a hot plate. The beaker was placed between the crossed polars of a hand polariscope supported by means of a clamp. In these tests air saturated with diethylamine was injected into the test tube as it was viewed through the polariscope.

The liquid crystals examined other than at room temperature were was follows: cholesteryl decanoate (75°C, cholesteric), cholesteryl myristate (75°C, cholesteric), cholesteryl nonanoate (70°C, smectic, obtained by cooling from the isotropic liquid), butyl p-(p-ethoxyphenoxycarbonyl)-phenyl carbonate (62°C, nematic).

All of the liquid crystals gave a positive test but the nematics tested at room temperature responded much faster than the others. Because of the obvious advantages of working at room temperature, further work emphasized the use of materials exhibiting mesophases at room temperature.

USE OF IMPREGNATED POLYPROPYLENE FILMS

Cardboard containing a window of liquid crystal impregnated polypropylene film was mounted with cellophane tape on the inside of a 1 liter flask. The flask was positioned between crossed polars of a hand polariscope oriented to give the film a visual green color. Use of a fluorescent lamp in combination with polars from a commercial microscope gave brighter colors than did the polariscope. Also, it was found convenient to limit the viewing area of the film by covering the outside of the test flask with a 3"x5" index card punched with a 1/4" diameter hole. This allowed the observer to focus on the most uniform portion of the film. This technique was especially convenient if the impregnated film appeared color striated.

Test atmosphere was prepared by allowing microliter quantities of the substance to be detected to evaporate in the stoppered flask. The exact quantity introduced was determined by weighing the microliter syringe filled and after emptying. The flask was equipped with a miniature fan which allowed equilibration to occur rapidly. The fan was operated for 1 min after the test substance was introduced. The motor was turned off and the color of the film was checked. A change in color from green to orange was interpreted as positive detection of the vapor. The concentrations of various organic vapors required to give the color change with several different liquid crystals are shown in Table 1.

TEMPERATURE EFFECTS

Liquid crystals when examined as smears on glass between crossed polarizers give a bright light field which appears yellow or white to the observer. As illustrated in Table 1 with VL1047N, the light field remains until a sufficient amount of a particular vapor is absorbed. The disappearance of the light field can also be caused by raising the temperature beyond the mesophase-isotropic transition point of the particular liquid crystal.

TABLE I

Concentrations of organic vapors effecting a visually observable change of liquid crystal films[a]

Organic Vapor	Concentration ppm[b]
VL1047N[c]	
dimethyl methylphosphonate	3
acetic acid	10
nitromethane	25
acetonitrile	25
methylene chloride	70
methanol	70
diethylamine	110
carbon tetrachloride	110
acetone	160
petroleum ether (b.p. 30-60°C)	460
MBBA[d]	
trimethylphosphate	< 1
α-picoline	3
pyridine	5
dioxane	10
tetrahydrofuran	15
nitromethane	20
acetontrile	25
ethyl acetate	40
isopropanol	45
methanol	50
diethylamine	50
chloroform	50
acetone	60
petroleum ether (b.p. 30-60°C)	270
50% MBBA + 50% EBBA(d)	
trimethylphosphate	< 3
acetic acid	7
α-picoline	10
pyridine	19
tetrahydrofuran	24
dioxane	37
nitromethane	70
acetonitrile	110
chloroform	190
methanol	230
carbon tetrachloride	250
methylene chloride	400

3-N-(p-Ethoxybenzilidine)-6-n-butylpyridine[e]	
tetrahydrofuran	6
α-picoline	7
pyridine	15
dioxane	35
nitromethane	40
acetonitrile	52
diethylamine	77
acetone	110
methylene chloride	240
carbon tetrachloride	290
petroleum ether (b.p. 30-60°C)	1200

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[a] Tests performed at room temperature (approx 27°C). The films were viewed using a hand polariscope.

[b] Weight/volume

[c] Nematic liquid crystal. Thin smear containing 3 parts by weight of VL1047N and 1 part of fumed alumina. Change from bright light field to no field.

[d] Nematic liquid crystal. Impregnated on Celgard 2400 microporous polyproplene film. Color change from green to orange with several colors in between.

[e] Smectic mesophase. Impregnated on Celgard 2400 microporous polypropylene film. Color change from red to orange with several colors in between.

Microporous polypropylene impregnated with a liquid crystal (mesomorphic state) and placed between crossed polars gives any one of several colors depending on the orientation of the polars. Rotation of the film or the polars lead to the appearance of several different colors. As mentioned, if the film is fixed so that the observed color is green, sufficient absorption of organic vapor will change the color to orange. The same color can be caused by heating the film above the isotropic transition point of the crystal impregnant. Actually, different colors are observed within a 6° range of the transition point (Table 2). The initial green is much lighter than the green noted in the sequence of colors near the transition point.

DETECTION ASPECTS

The liquid crystal smears and impregnated films are essentially acting as birefringent retarders when viewed through a polariscope. A smear on glass appears as a bright yellow-white field. Impregnated polypropylene films give different colors depending on whether the liquid crystal is in a mesophase or an isotropic phase. It should be emphasized that the polypropylene itself is birefringent. The same color effects noted in raising the temperature of the impregnated films were also noted in the chemical detection aspects irrespective of the organic vapor tested. Undoubtedly, the effect of the organic vapor absorption is to lower the isotropic transition to the test temperature (in most cases, the ambient one). Colors are observed when the unimpregnated film is rotated between crossed polars. Furthermore, droplets of any of the twenty-five organic liquids tested (including liquid crystals in the isotropic state) give the same color against a particular background color of the unimpregnated film, e.g., orange against green. Liquid crystals in a mesomorphic state show a different color than the isotropic liquids. The observed difference was utilized in the design of the organic vapor detector.

Of the nematics examined, the most sensitive detector was MBBA. This was also the one with the lowest isotropic transition temperature. Nematics with high isotropic transition temperatures were much less sensitive. In other words, more organic vapor needs to be absorbed in order to effect a transition from mesophase to isotropic liquid. The transition point for VL1047N is similar to

TABLE II

Effect of temperature on observed colors of liquid crystal films[a]

Liquid crystal	Temperature, °C	Colors
MBBA	20–34	green
	34–37	red
	37–39	green
	39–40	purple
	>40 [b]	orange
50% MBBA + 50% LCI 1880	20–43	green
	43–45	red
	45–47	green
	47–49	purple
	>49 [b]	orange
LCI 1880	20–52	red(c)
	52–55	green
	55–58	purple
	>58 [b]	orange
EBBA	20–72	green
	72–74	red
	74–76	green
	76–78	purple
	>78 [b]	orange

[a] Celgard 2400 impregnated with the liquid crystal, supercooling effect noted with EBBA; colors viewed through a polariscope during the heating of the films. The same colors are observed when the films are cooled.

[b] This figure corresponds to the isotropic transition temperature.

[c] An initial green color could not be obtained by rotating the polars.

that for the p-methoxybenzilidine derivative. However, the VL1047N does not appear as sensitive. This is due to the method of testing. VL1047N was tested as a thicker film, i.e., a smear on a microscope slide. Polypropylene films impregnated with VL1047N behaved essentially as did films containing MBBA.

In comparison to the other detectors listed in Table 1, the 3-N-(p-methoxybenzilidine)-6-n-butylpyridine was found least attractive. The detection sensitivity is low and the observed colors are not bright. The poor response does not appear totally related to the isotropic transition temperature. The pyridine derivative is smectic at room temperature and goes through other phase changes (including a nematic one) before reaching the isotropic state.

It is apparent on examining Table 1 that the detection is nonspecific. There is no particular correlation evident between detectable concentration and properties of the organics other than that the more polar materials are more easily detected. Neither water vapor nor water droplets affect the liquid crystal impregnated detector films.

The detection effects shown in Table 1 are relatively insensitive to fluctuations in room temperature since the isotropic transition of the liquid crystals examined lie well above room temperature. Also, the effects are reversible, i.e., removal of the films from the organic vapor atmosphere restores the original color.

The polypropylene detector films are visually clear and do not feel wet or "greasy" to the touch. It is recommended that the films be used within a day of being prepared because of the possibility of their absorbing nonvolatile compounds or chemically reactive ones over a period of time. The benzilidine aniline derivatives are not especially stable since the -C=N- group is a particularly labile one.

The major advantage of the detection technique reported in this paper over the one utilizing optical reflection from cholesteric liquid crystals is simplicity. Uniformly thin films are easily prepared and handled. Temperature control is relatively unimportant. Instrumental monitoring is not required but could be adapted easily if an application deems it. A hand polariscope with an electric light source was used but natural light could serve as well. In contrast, optimum utilization of techniques based on optical reflection from cholesteric liquid crystals requires instruments such as a temperature regulator, incident light source and photocell as well as electronic output. Achievement of detection by visual observation is complicated since the observed color depends on the angle of viewing. This is not as critical with the nematogen-polyproplene film.

OPTIMIZATION OF SENSITIVITY AND SELECTIVITY

Higher sensitivity (while retaining nonspecificity and reversibility) can be obtained by:

a) operating at temperatures closer to the isotropic transition temperatures,

b) operating at room temperature but choosing a liquid crystal system with a lower isotropic transition temperature, or

c) using as the detection signal a color change which occurs prior to the formation of an isotropic phase.

Each of the above possibilities requires closer control on temperature and more careful monitoring. The sensitivity can be bettered by at least one order of magnitude (depending on the material detected and the choice of liquid crystal

TABLE III

Colar changes of liquid crystal films exposed to various concentrations of organic vapors[a]

Concentration ppm[b]		Color
liquid crystal:	70% MBBA	
organic vapor:	tetrahydrofuran	
< 1.0		green
1.5		red
3.0		orange
4.5		green
6.0		blue
7.5		violet
>15.0		orange
liquid crystal:	70% MBBA + 30%	EBBA
organic vapor:	acetonitrile	
< 35		green
55		blue
70		red
80		orange
90		green
95		blue
100		violet
> 110		orange

[a] Celgard 2400 microsporous polyproplene films impregnated with the liquid crystal, exposed to organic vapor and examined between crossed polars of a polariscope.

[b] Weight/volume.

detector) if the first color change is used as the detection signal. This is illustrated with several examples in Table 3.

A combination of increased sensitivity, selectivity and non-reversibility can be achieved if:

a) the liquid crystal reacts with the material to be detected, or

b) the liquid crystal system is combined with a chemical which reacts with the material to be detected.

For example, it was found that chloroacetaldehydes cause an irreversible loss of the bright light field of VL1047N films viewed between polarizers.

It was reported previously that amines cause degradation of chloraldichloroacetaldehyde copolymer with production of chloroacetaldehyde monomers[13,14] VL1047N films themselves are only moderately sensitive to amines as illustrated in Table 1 with diethylamine. Overall sensitivity was increased by taking advantage of the previous results with the polymer. A layer of pulverized polymer (about 0.1 g) was spread on a microscope slide. Another slide containing the liquid crystal paste with fumed alumina was positioned one slide thickness above the polymer slide. The 1 cc quantities of various concentrations of diethylamine vapor were injected into the space between the two slides, giving a positive test within one minute. The results (obtained at room temperature) are shown in Table 4. Use of the copolymer in conjunction with VL1047N gives a 200-fold increase in sensitivity to DEA over that if the liquid crystal alone. For this particular system, the copolymer and liquid crystal could not be combined because the mixture decomposes with time. The sensitivity could be further increased if a polyproplene film impregnated with VL1047N had been used instead of VL1047N-Alon® paste. Decreasing the thickness of the liquid crystal film should generally increase sensitivity.

TABLE IV

Detection of diethylamine vapor

Amine Concentration, ppm[a]	VL1047N[b]	VL1047N Copolymer[c]
100	+	
50	–	+
1		+
0.5		+
0.1		–

[a] Volume/volume.

[b] VL1047N-Alon® film alone.

[c] System as described in the text.

In another case, N-(p-methoxybenzilidine)-p-n-butylaniline was doped with 0.5% p-butylaniline. A polypropylene film impregnated with this mixture was sensitive to 0.5 mg/l of acetic anhydride The effect was irreversible.

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