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FINAL REPORT

HIGH TEMPERATURE SMART SENSORS AND ACTUATORS

Submitted by

Oscar J. Almeida
Brian G. Dixon
Jill H. Hardin
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CAPE COD RESEARCH, INC.

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U. S. ARMY RESEARCH OFFICE

Research Triangle Park, NC 27709-2211

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ABSTRACT

The future of robotics, clutches and suspensions lies in discovering novel fluids whose flow can be controlled rapidly and without the use of mechanical valves. This report deals with the discovery of a smart fluid with unusual properties. More work is needed to determine whether these properties can serve as the basis for useful smart actuators.

Most smart fluids under study today are colloidal suspensions of highly polarizable particles (electrorheological fluids). Unfortunately these ER fluids have problems associated with maintaining the colloids in suspension, with the long time scale of the response, with excessive power consumption and with reproducibility of effect over thousands of cycles.

Many of the problems associated with ER fluids might be entirely avoided by using a single phase liquid whose viscosity changes with applied field strength. Effects of this type (electroviscous fluids) have been observed in the past. However, known changes in viscosity are typically less than 2% at large field strength. Thus the electroviscous effect is generally believed to be of no practical use.

The results described herein may change this view. A new class of electroviscous (EV) fluids was synthesized and found experimentally to display a 2000% increase in viscosity when placed under electric field strengths on the order of 2 kV/mm. The effect is very fast with a response time of less than 30 milliseconds. The novel fluid has good high temperature stability, is a very good insulator and may have lubricating properties.

The measured viscosity change is directly proportional to applied field strength. Thus the EV mechanism may be different from that observed in other known EV fluids.

A striking difference between this discovery and previously known EV fluids is the size of the observed effect. The results are preliminary. The observed effect has not been optimized and its origin is not completely understood.

CONTENTS

APPENDICES

ILLUSTRATIONS

1.0 INTRODUCTION

This report describes the results of a six month feasibility study, "High Temperature Smart Sensors and Actuators" funded under DAAL03-92-C-0007. This program investigated the feasibility of a novel approach to smart lubricants for reducing shock and vibration in Army ground and aircraft vehicles. A fundamentally different approach for creating smart fluids was experimentally explored. Feasibility of the concept was demonstrated for fluids formed by grafting liquid crystal groups onto the terminal ends of short linear polysiloxane chains. The results are low viscosity fluids with novel electroviscous (EV) behavior.

Research going back to the 1940s has demonstrated that slurries can have large changes in measured viscosity when exposed to strong electric fields. Modern electrorheological (ER) fluids are all colloidal suspensions of highly polarizable particles in a non-polarizable solvent. A wide variety of oils has been successfully employed as ER vehicles and the particles can consist of either polar organic materials such as starch, cellulose, polymers or inorganics, such as silica or metal oxides. In a strong electric field, the behavior of the ER fluid is dominated by the dipolar interactions between colloidal particles. When a large electric field is applied to the fluid, dielectric columns orient parallel to the field lines. While these columns form rapidly, relaxation of these columns is a much slower process.

There are a number of unsolved problems with ER fluids. Discrete particles, no matter how closely matched in density to the dielectric fluid matrix, tend to separate out over time. The polar particle phase, especially when water is absorbed on the surfaces of the colloids, renders conventional ER fluids somewhat electrically conductive. At high electric field strengths, the fluids can pass appreciable amounts of current. This in turn leads to heat generation which can be detrimental to the fluid's stability and ER performance. The presence of water tends to limit ER performance to below 100°C.

Electroviscous fluids differ from electrorheological fluids in that they contain no solids. Thus they may be able to circumvent some of the problems of ER fluids. The ideal EV fluid for reducing shock and damping vibration would have a low viscosity. On application of an electric field, it would immediately become very viscous. The effect should be fast and completely reversible for millions of cycles. To keep power requirements low, the ideal EV fluid should have low electrical conductivity and large changes in viscosity. No known EV fluid has all of these properties.

2.0 APPROACH

The overall approach was to synthesize six silicone polymers, each endcapped with liquid crystal groups. The rationale for this approach follows.

2.1 Technical Approach

The search for the ideal EV fluid begins with a liquid which has the desired combination of lubricating properties over a broad temperature range. Silicone fluids are well known for their wide useful thermal range (-40°C to 285°C) and their excellent lubricity under extreme pressure conditions. Their chemical and solvent resistance are unique. Silicones also tend to be liquids even at molecular weights which would yield waxy solids in hydrocarbon structures. This is almost entirely due to the extraordinary flexibility of the silicone chain and represents a unique feature of silicone compounds.

Silicones, however, are "stupid" fluids. They show no EV response whatsoever. Thus they must be chemically modified.

LC monomers can be dissolved in organic solvents and these solutions show small but measurable EV effects. To be useful, these subtle EV effects must be magnified hundreds of times. The hypothesis which formed the basis of this research was that EV effects depend on the statistical distance between charged groups. For monomers, this is small.

The technical approach is to attach LC groups to silicone chains. The simplest case, terminal end attachment, was chosen arbitrarily. Attaching LC groups to the terminal ends of short silicone polymers may greatly increase the atomic distance between the charges of the dipoles formed in an electric field. Structurally these liquids consist of LC microphases joined by very flexible silicone chains. The LC groups can be polarized; the silicone chain cannot. Apparently these silicone chains do not prevent the orientation of the LC microphases. A photomicrograph of one of the better EV fluids produced by this research illustrates this point on the next page.

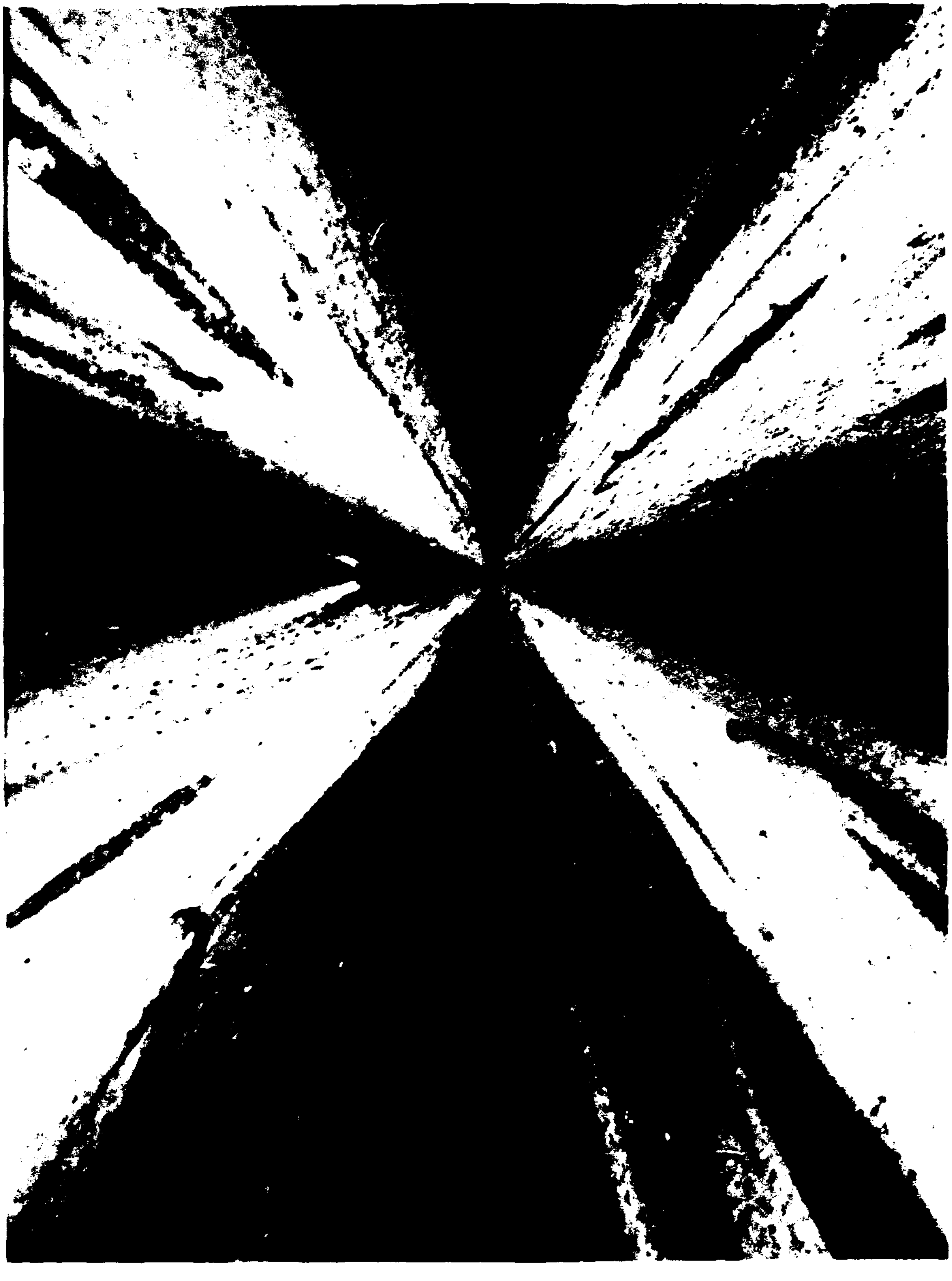


Figure 1. Photomicrograph of Electroviscous Fluid

Figure 1 illustrates the high degree of order despite the presence of silicone chains. Under hydrodynamic shear, this order is altered and the fluid behaves much like a low viscosity silicone oil.

However, on application of an electric field, there exists the possibility of dipole formation between LC groups. The result may be a network of silicone chains whose ends are tethered to LC microphases. This should result in a large increase in viscosity. This unproven hypothesis is illustrated below.

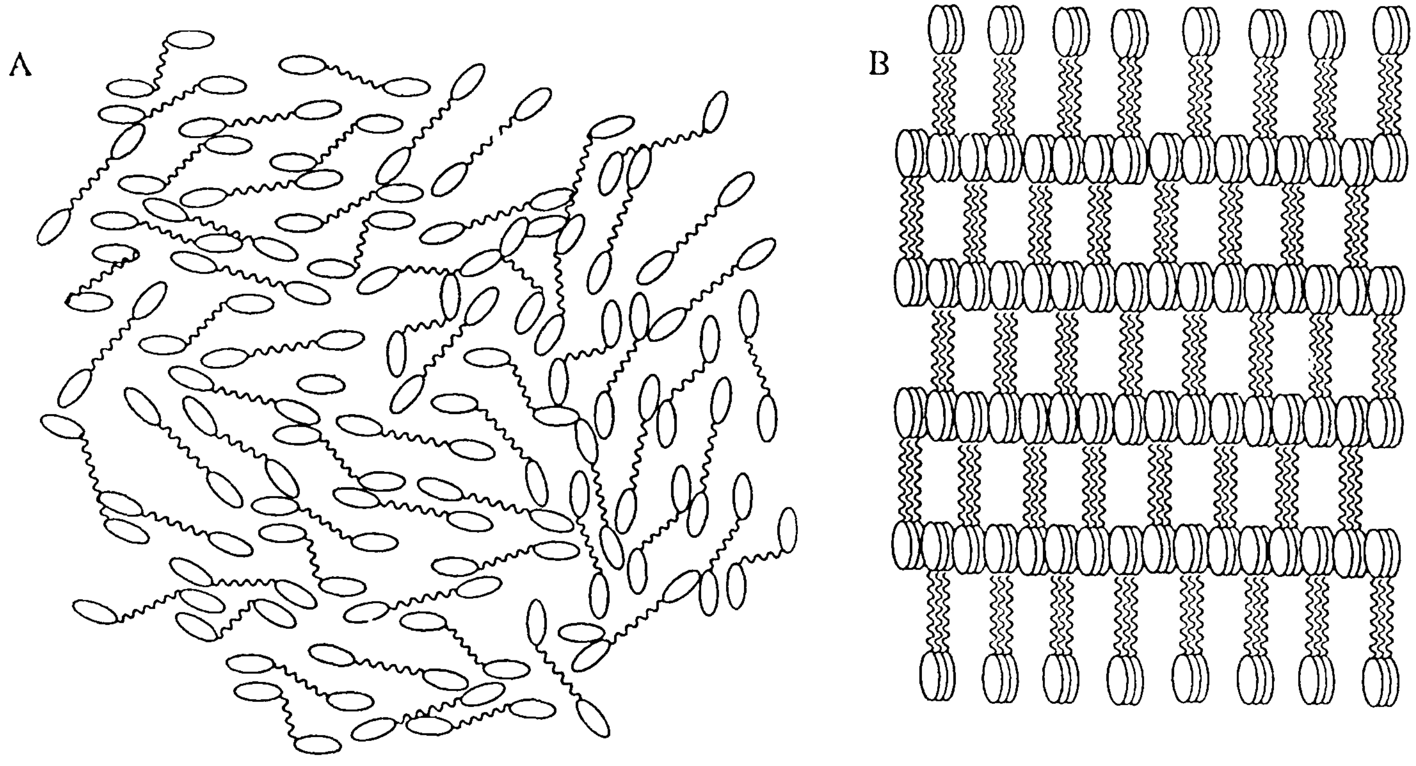


Figure 2. Electroviscous Fluid Concept

(a) Random molecular order. (b) Highly structured fluid after an electrical field is applied

2.2 Pendant Groups

The following six pendant groups were chosen for this study. Compounds A and B were chosen as charge transfer groups because of their electron rich and electron deficient nature. Compounds C through F are LC of nematic cholesteric nature and their switching times are very fast. They are structurally similar in the sense that they all contain multiple rings with different substituents in the terminal benzene ring and they all form R--CH=CH_2; allowing for a single step hydrosilation reaction to graft the R--CH_2- onto the ends of hydrogen terminated dimethyl siloxane chains.

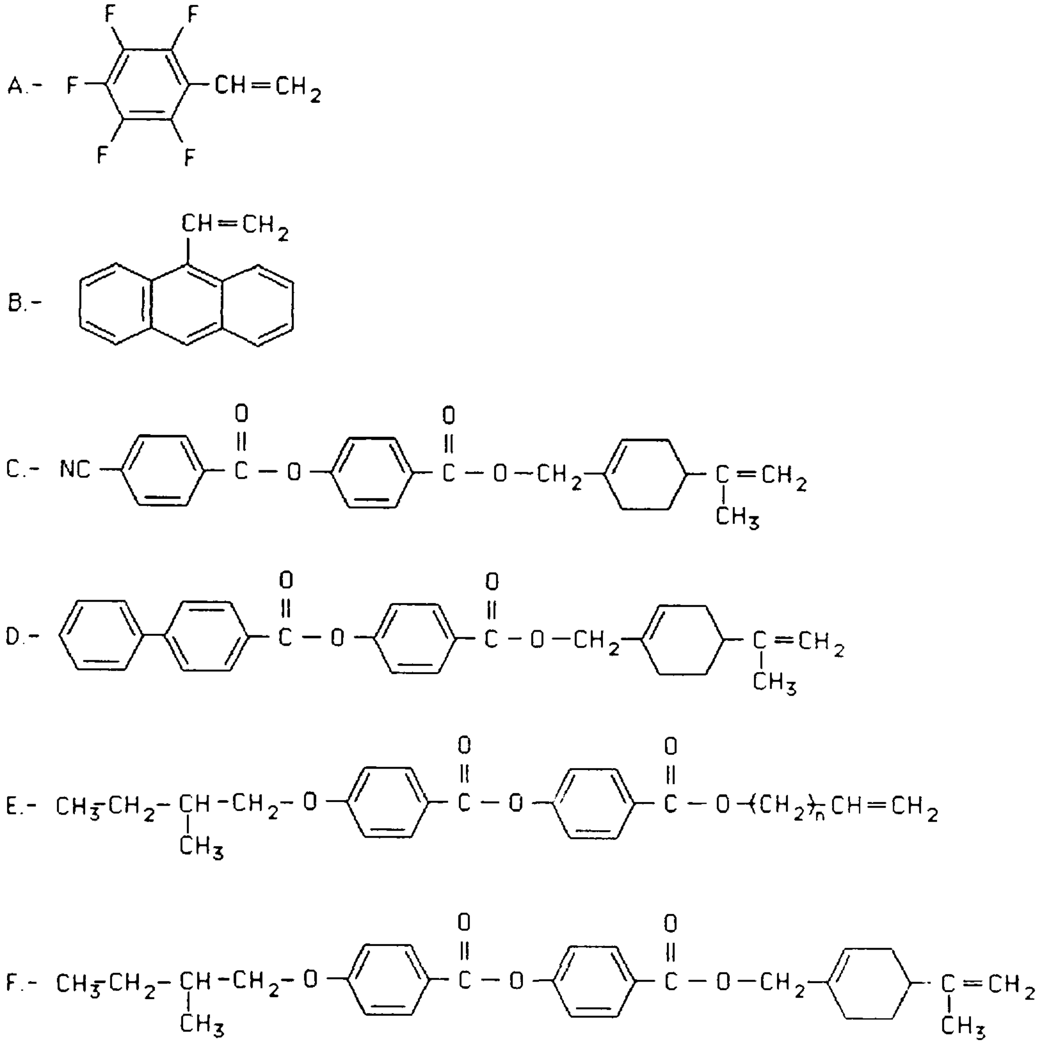


Figure 3. Six Test Pendant Groups

2.3 Liquid Crystal Background

Liquid crystal is a state of matter which exists between a crystalline solid and a liquid. Compounds which exhibit LC properties change from a solid to a liquid or from a liquid to a solid through intermediate states called mesophases, or mesomorphic states. LCs whose order may be affected by solvents are referred to as lyotropic liquid crystals, while those which are affected by thermal means are called thermotropic liquid crystals. As heat is applied to a thermotropic LC, the transitions usually follow the order: Solid -- Smectic phase -- Nematic phase or Cholesteric phase -- Isotropic Liquid. The smectic phase has a two dimensional arrangement in which the molecules not only line up in one direction but they also stack sideways to form parallel planes. The nematic phase has a one dimensional arrangement in which the molecules line up in one direction. The cholesteric phase, also called the chiral nematic phase, is formed by LCs containing chiral centers and has a twisted sheet structure. This concept is illustrated below.

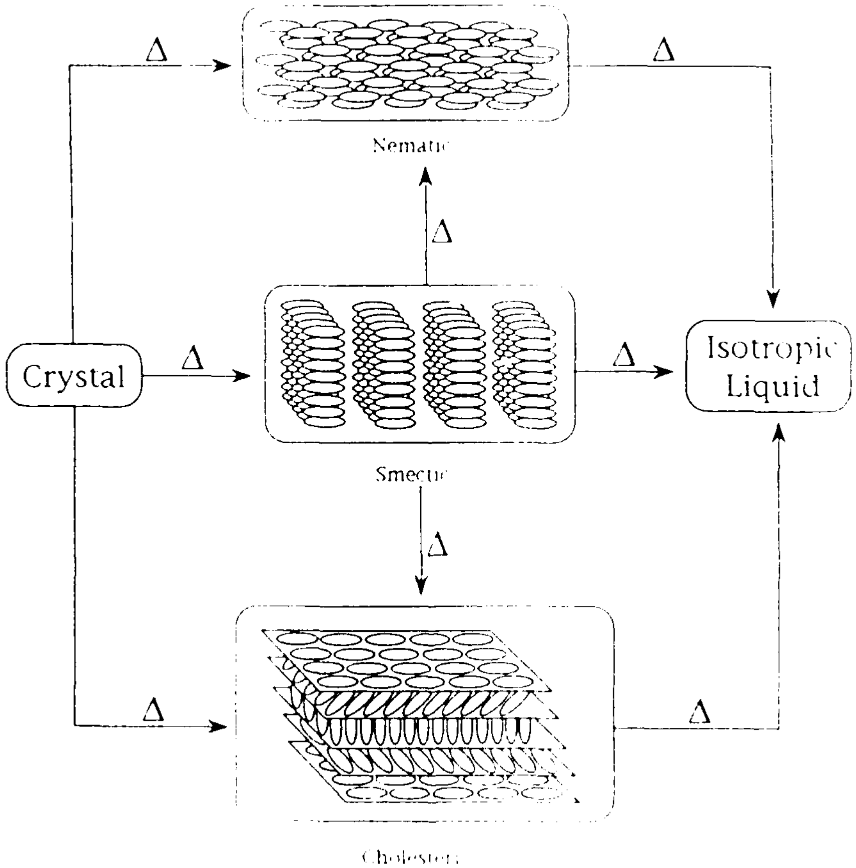


Figure 4. The Liquid Crystalline Phases

Each successive layer of a cholesteric mesophase has its principal axis rotated from the previous one so that the entire array forms an ordered helical or twisted series of layers. The repeat distance between successive layers with the same orientation is called the pitch and it is very sensitive to temperature, pressure, electric and magnetic fields, or solvents. The structural unit which is responsible for imparting LC properties to a substance is often called the mesogenic unit or mesogen. It usually consists of a linear array of two or more aromatic rings or cyclohexane rings connected in the 1,4 positions by short links of one or two bond lengths. In this manner, a rigid rod segment is formed which has an overall length that is substantially greater than the width. This molecular shape is important for forming mesophases.

Low molecular weight cholesteric LC monomers can be ordered unidirectionally in electrical fields. Display devices such as those found in wrist watches and pocket calculators use this property.

The study of LCs is a relatively new field and has aroused considerable current interest among scientists. LCs appear to be a fertile field for searching for smarter fluids.

3.0 EXPERIMENTAL RESULTS

3.1 LC Thermal Properties

The thermal properties of the LC mesogens were determined by Differential Scanning Calorimetry. Some of the LC-endcapped four-siloxane-chain compounds were also evaluated by DSC; however, because of their pasty characteristics, some of them could not be tested.

Table 1: LC Mesogens DSC Thermal Analysis

Sample	T_K-S_A/C (^oC)	S_A/C-I (^oC)	T_K-I (^oC)	I-S_A/C (^oC)	S_A/C-T_K (^oC)
perillyl-4-cyano-benzocarbonyloxy-benzoate	58	62	----	----	----
perillyl-4-phenyl-benzocarbonyloxy-benzoate	----	----	116	56	48
Ω hexene-4-t-butoxy-benzocarbonyloxy-benzoate	----	----	77	38	32
perillyl-4-t-butoxy-benzocarbonyloxy-benzoate	60	69	----	2	2

T_K-S_A= crystalline solid to smectic A transition.
T_K-C= crystalline solid to Cholesteric transition.
S_A-I = smectic A to isotropic liquid transition.
C-I = Cholesteric to isotropic liquid transition.

All mesogens showed liquid crystal behavior, and although they are thermotropic liquid crystals, none of them are enantiotropic LC (LC behavior on both heating and cooling curves). The perillyl-4-cyano-benzocarbonyloxy-benzoate and perillyl-4-t-butoxy-benzocarbonyloxy-benzoate show monotropic LC behavior on the heating curves while perillyl-4-phenyl-benzocarbonyloxy-benzoate and Ω hexene-4-t-butoxy-benzocarbonyloxy-benzoate show monotropic LC behavior on the cooling curves.

The perillyl-4-cyano-benzocarbonyloxy-benzoate and perillyl-4-phenyl-benzocarbonyloxy-benzoate compounds show Smectic A texture, while Ω hexene-4-t-butoxy-benzocarbonyloxy-benzoate and perillyl-4-t-butoxy-benzocarbonyloxy-benzoate show cholesteric texture. The analysis of the textures was performed by polarizing microscopy since they cannot be determined by DSC.

Table 2: DSC Thermal Analysis of grafted LC Mesogens onto siloxanes

Sample	T_k-S_A/C (°C)	S_A/C-I (°C)	T_k-I (°C)	I-S_A/C (°C)	S_A/C-T_k (°C)
perillyl-4-cyano-benzocarbonyloxy-benzoate	----	----	60	----	----
Ω hexene-4-t-butoxy-benzocarbonyloxy-benzoate	----	----	81	----	----

Upon chemical bonbing of the LC mesogens to the siloxane chains, LC behavior is no longer recorded by DSC. However; studies carried out by polarizing microscope show the existence of the LC mesophases (Section 3.2). A possible explanation is that siloxane chains tend to decrease the order of the LC compounds to the point that their thermal behavior becomes so slow that DSC can no longer record it.

3.2 Optical Characterization of LC Compounds

The experimental LC mesogens and LC-endcapped four-siloxane-chain compounds were optically analyzed by polarizing microscopy. Photographs of the compounds follow.

Figure 5. Photomicrograph of perillyl-4-cyano-benzocarbonyloxy-benzoate

Figure 6. Photomicrograph of perillyl-4-phenyl-benzocarbonyloxy-benzoate

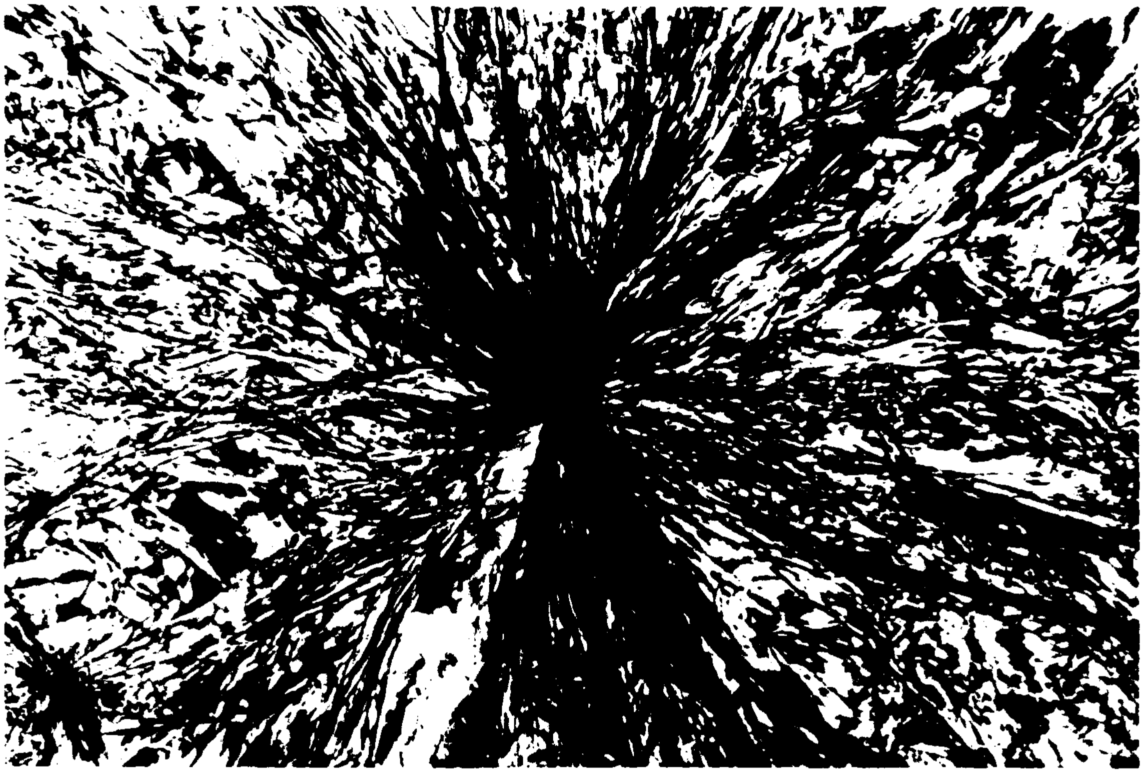


Figure 7. Photomicrograph of Ω hexene-4-t-butoxy-benzocarbonyloxy-benzoate

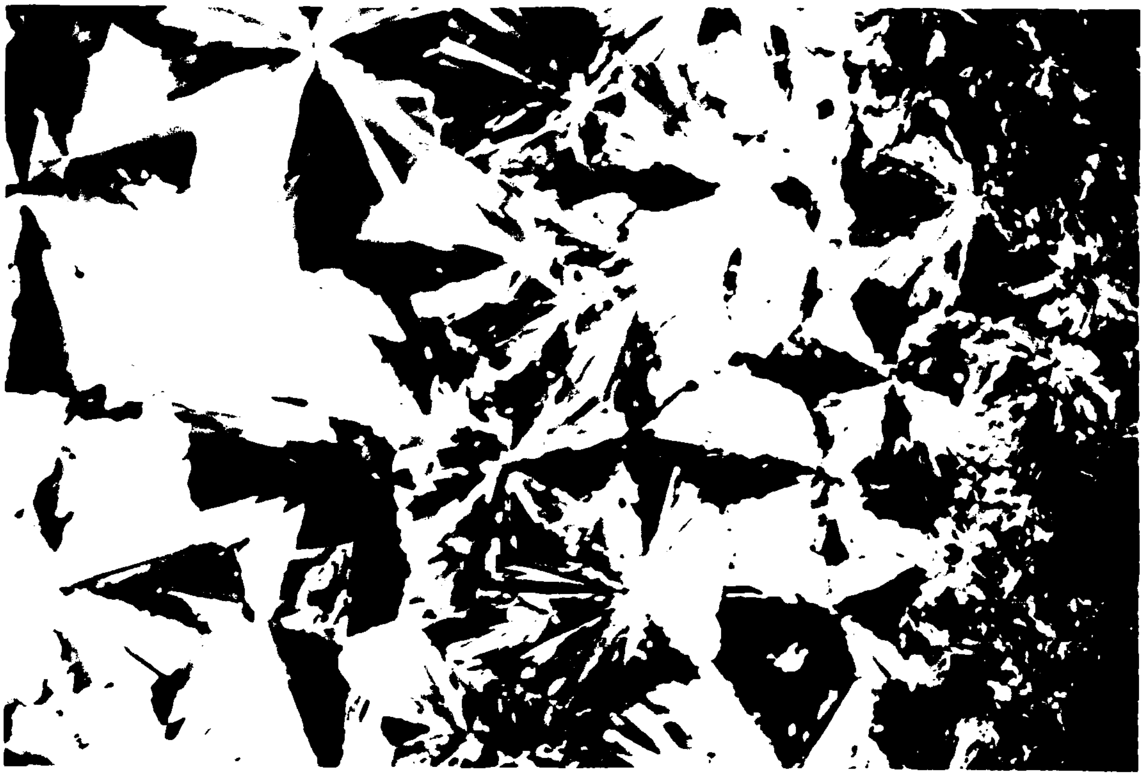


Figure 8. Photomicrograph of perillyl-4-t-butoxy-benzocarbonyloxy-benzoate

The following photographs correspond to the LC grafted onto the siloxanes.

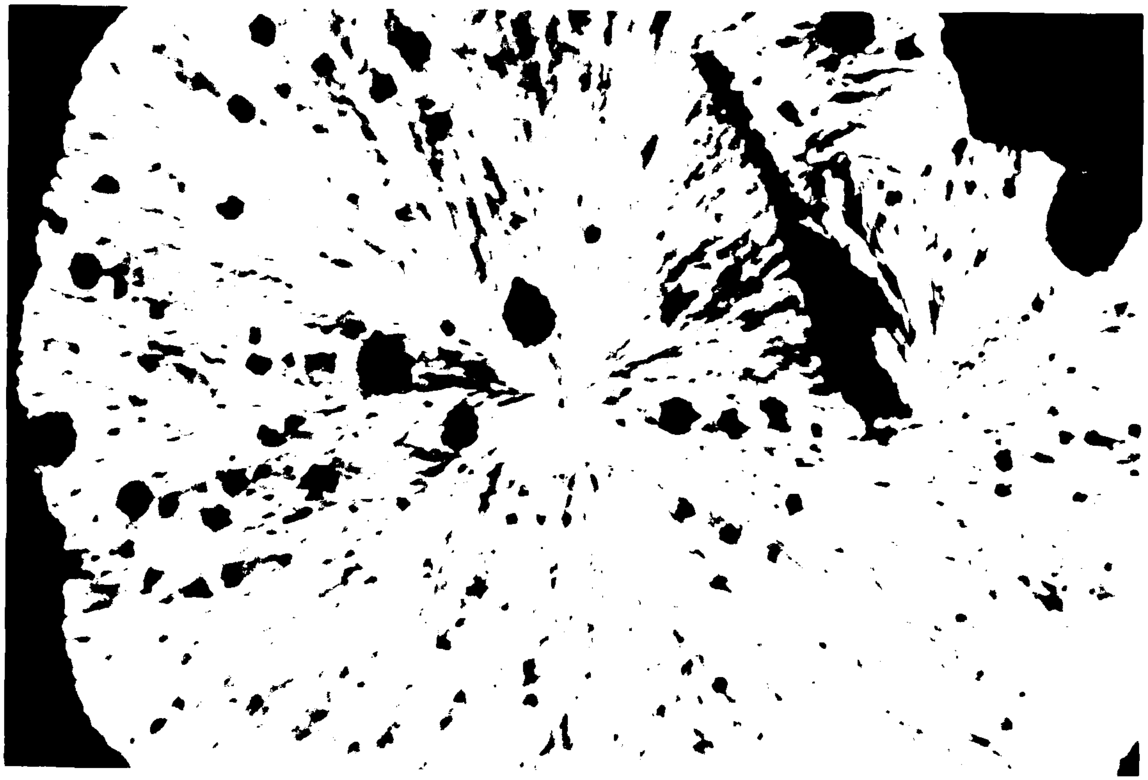


Figure 9. Photomicrograph of Grafted perillyl-4-cyano-benzocarbonyloxy-benzoate

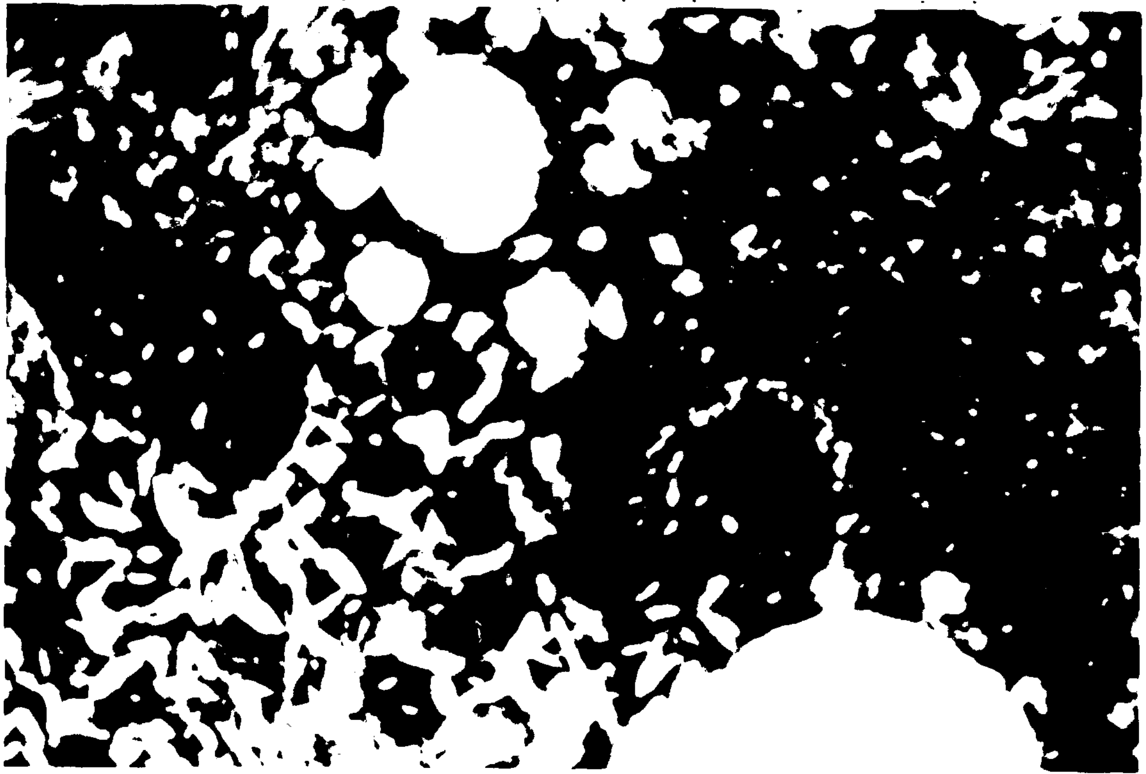


Figure 10. Photomicrograph of Grafted perillyl-4-phenyl-benzocarbonyloxy-benzoate

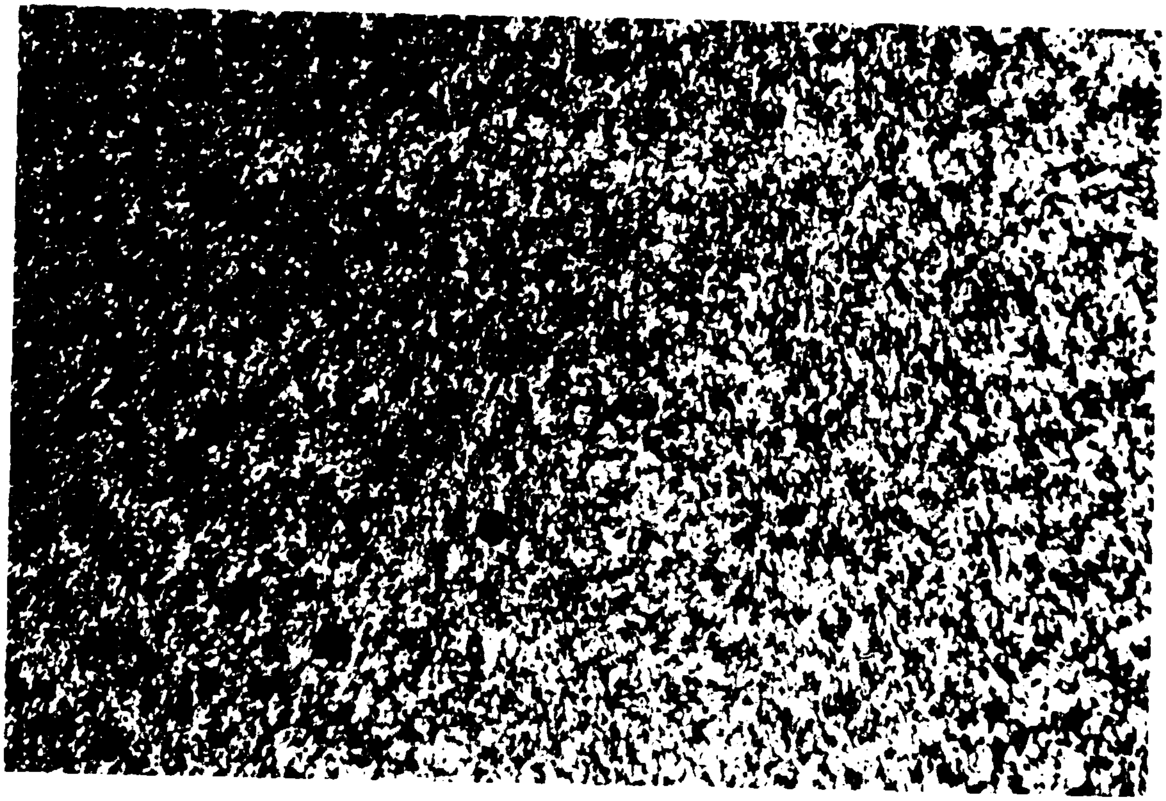


Figure 11. Photomicrograph of Grafted Ω hexene-4-t-butoxy-benzocarbonyloxy-benzoate

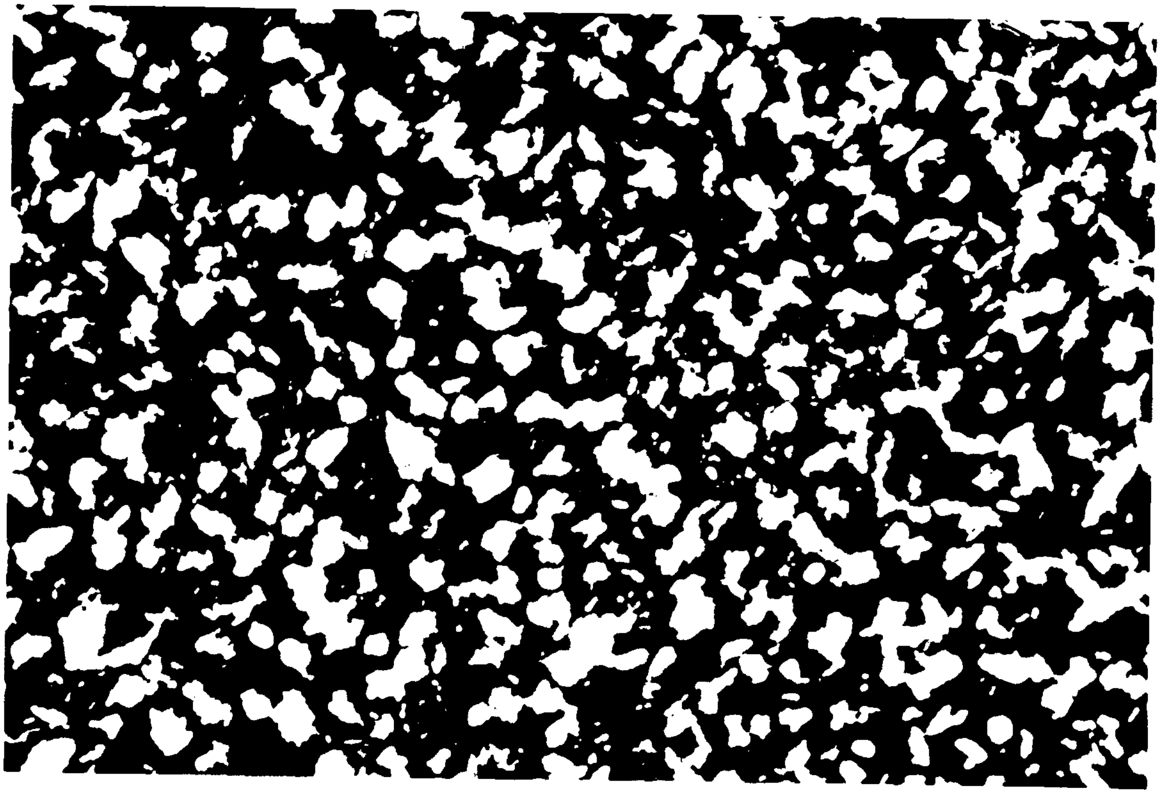


Figure 12. Photomicrograph of Grafted perillyl-4-t-butoxy-benzocarbonyloxy-benzoate

3.3 EV Fluid Test Results

In order to determine the effectiveness of the modified Brookfield viscometer apparatus for evaluating ER and EV behavior, a conventional ER fluid was prepared and tested in this apparatus. This fluid was prepared according to details given in reference 1 and consisted primarily of 40w/o -400 mesh silica gel and fumed silica in a conventional silicon oil [poly(dimethylsiloxane)]. The results of these tests are shown in the Figure 13 below:

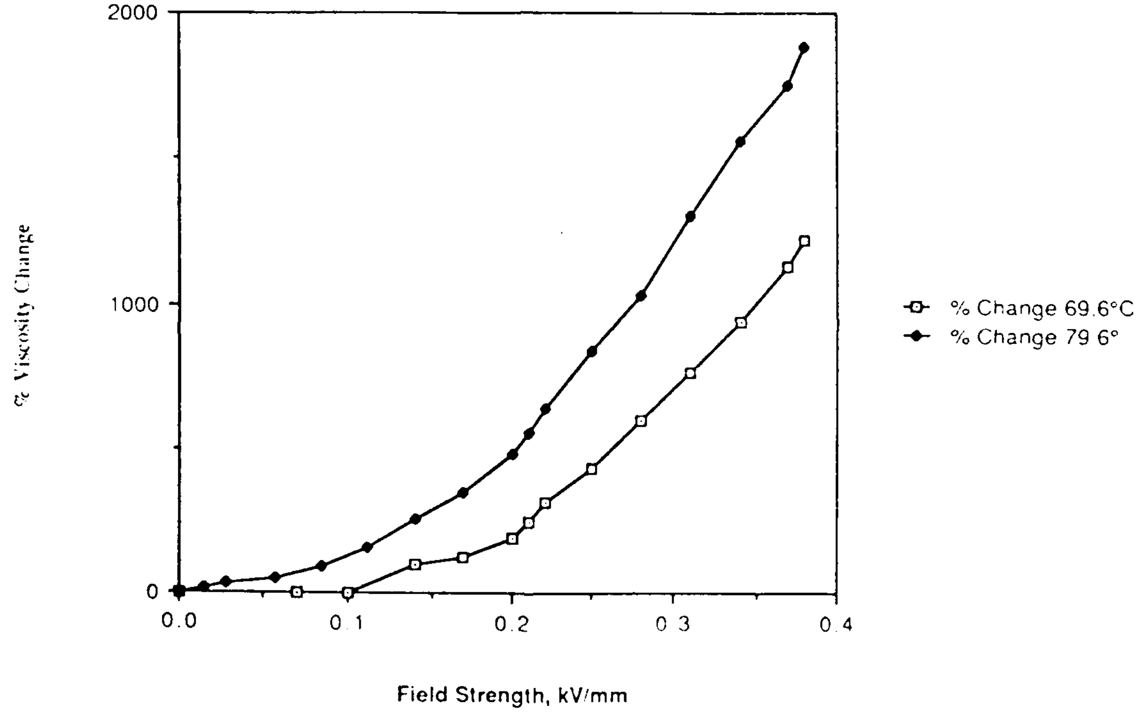


Figure 13. Electrorheological Behavior of Control Fluid

As can be seen, the viscosity of this ER fluid increased dramatically at all temperatures under the influence of the electric field. In addition, this viscosity change was quite rapid and reversible.

Having established that the test apparatus measures ER behavior, a variety of fluids including the proposed family of liquid crystal polysiloxanes was tested for the EV effect.

Generally, all of the new class of EV fluids gave some degree of electroviscous behavior, whereas the unsubstituted fluorosiloxane fluids, the pentafluoro styrene, the vinyl anthracene and Ω-hexene-4-t-butoxy-benzocarbonyloxy-benzoate fluids did not exhibit electroviscous effects; therefore, no other data are given for them in this section.

The most promising EV fluid discovered to date contains perillyl-4-t-butoxy-benzocarbonyloxy-benzoate and yielded an increase in viscosity of over 5000% in an electric field of 4.5 kV/mm when tested at 62.4°C. The EV testing results for this particular novel fluid are shown below in Figure 14.

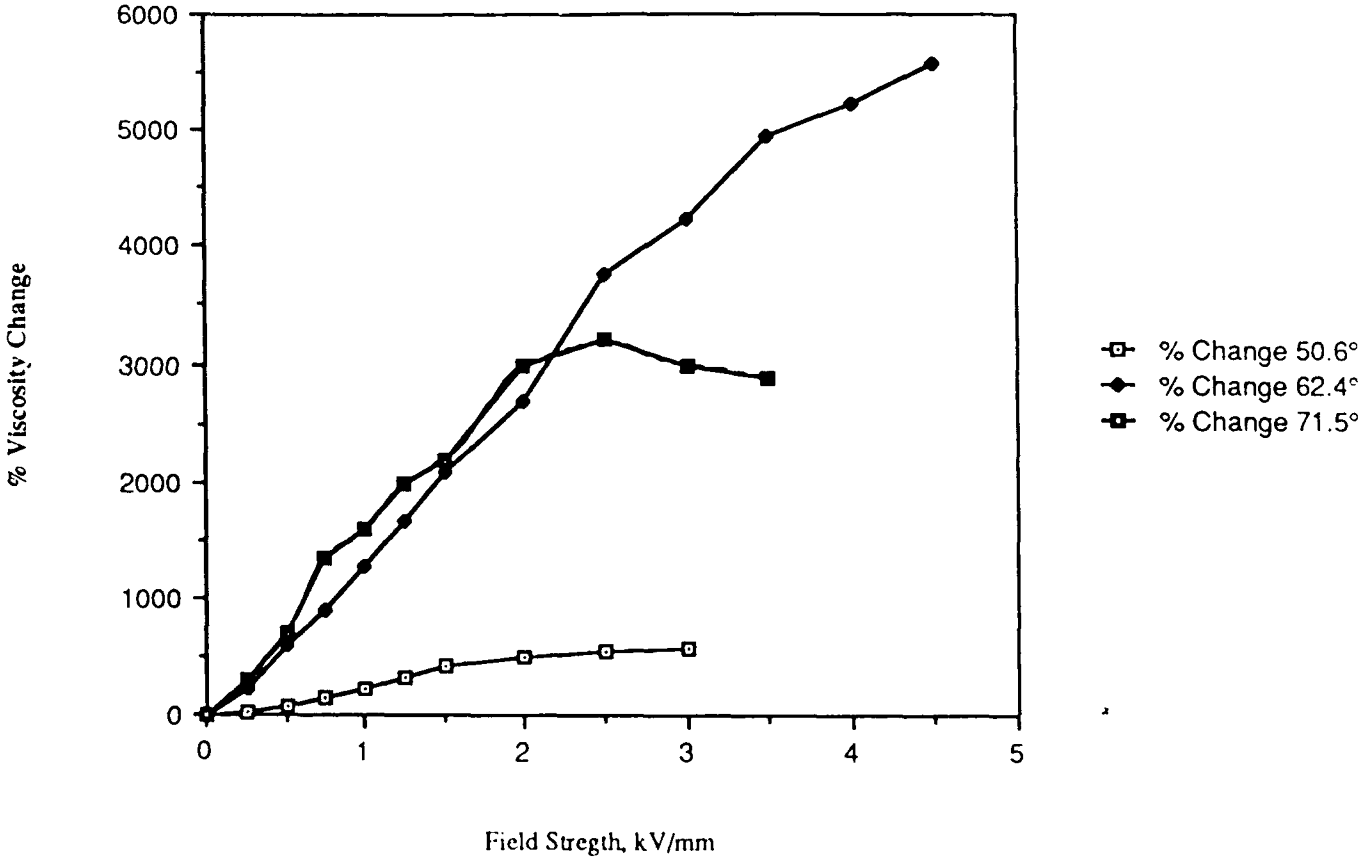


Figure 14. Electroviscous Behavior of perillyl-4-t-butoxy-benzocarbonyloxy-benzoate product

Although not as dramatic as the perillyl-4-t-butoxy-benzocarbonyloxy-benzoate product; the remaining fluids, those containing perillyl-4-phenyl-benzocarbonyloxy-benzoate and perillyl-4-cyano-benzocarbonyloxy-benzoate, yielded increases in viscosities of 900% and 500 % respectively. The EV testing results for the latter novel fluid, are shown below in Figure 15 and Figure 16 respectively.

There is a dramatic linear increase in the viscosity of the fluid as the strength of the electric field is increased. This effect appears to be temperature sensitive.

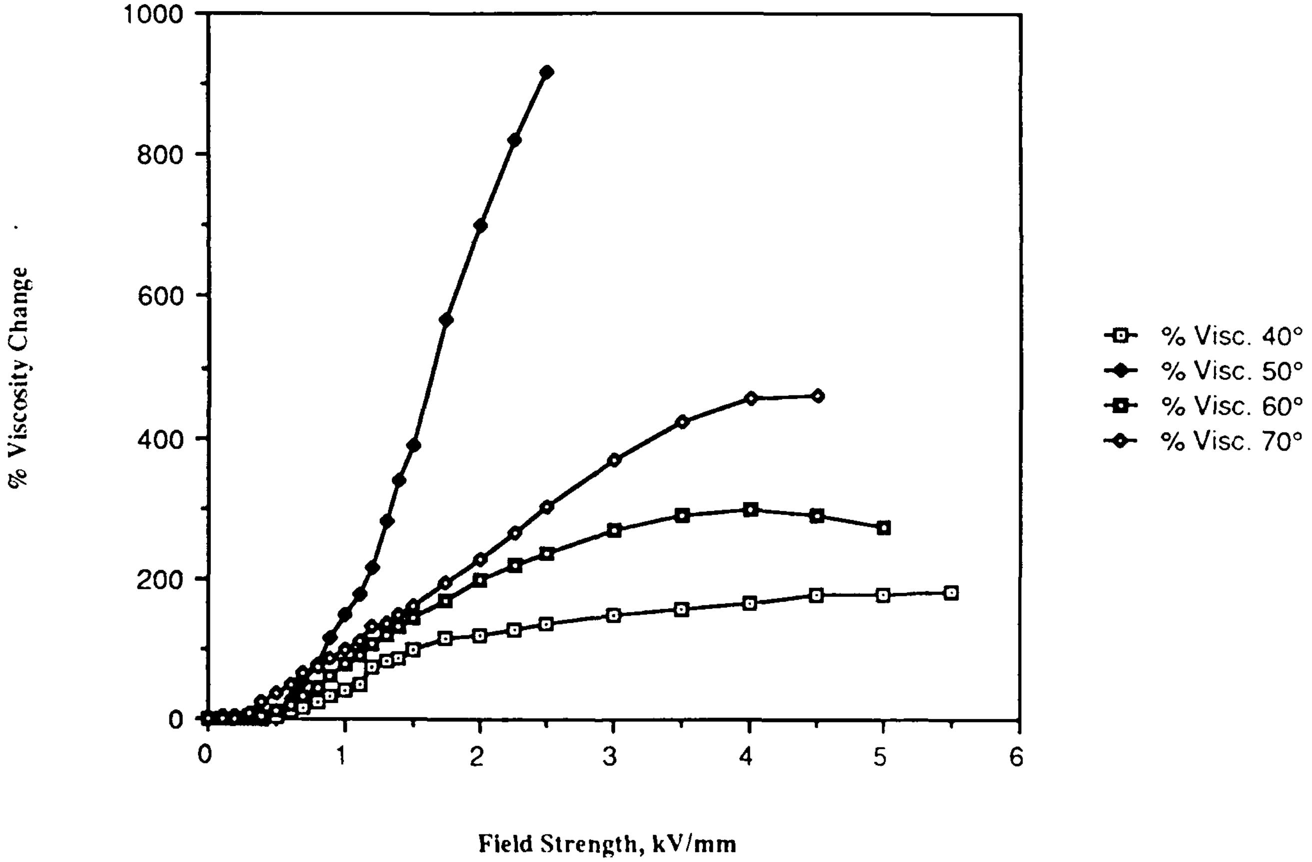


Figure 15. Electroviscous Behavior of perillyl-4-phenyl-benzocarbonyloxy-benzoate product

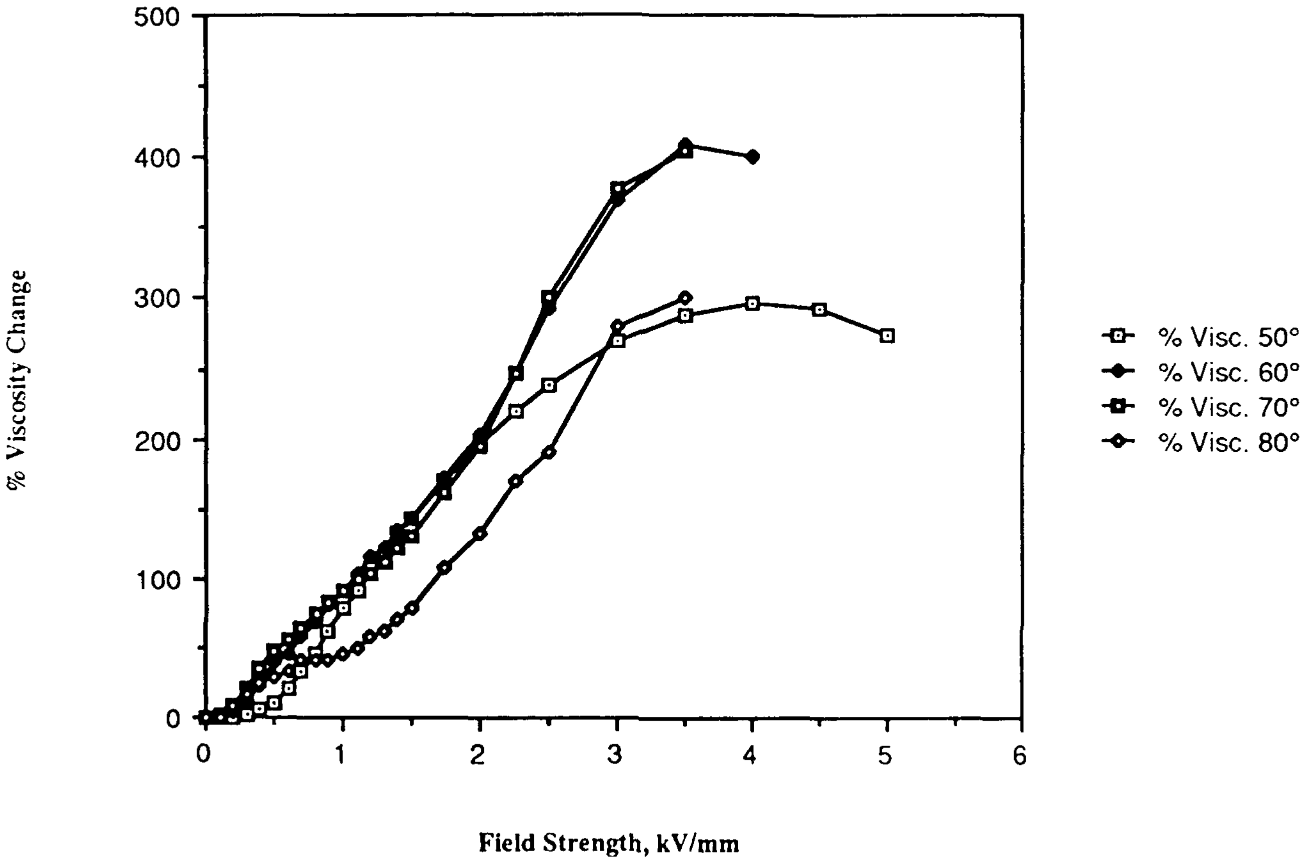


Figure 16. Electroviscous Behavior of perillyl-4-cyano-benzocarbonyloxy-benzoate product

4.0 CONCLUSIONS AND RECOMMENDATIONS

The main conclusions from the Phase I research are:

* The new class of lubricants shows pronounced electroviscous (EV) response which is temperature dependent. Over 5000 % increase in viscosity was measured for some samples.

* The EV response is completely reversible and may be *very fast*. The response time for optical changes was measured as faster than thirty milliseconds.

* No EV response was observed for poly(methyltrifluoropropylsiloxane), the control fluid.

* No EV response was observed for fluids containing pentafluoro styrene and vinyl anthracene .

* LC polysiloxane fluids show typical optical effects for materials with liquid crystalline phases as measured by polarizing microscopy.

* Magnitude of EV response depends on mesogenic group substitution and mesogenic group spacer length.

* Electrorheological behavior was observed for a slurry of silica gel and fumed silica.

The EV approach avoids the need for solid particle suspensions and water-based materials to achieve electrically induced changes in viscosity. The preliminary results of the Phase I clearly and for the first time demonstrate the feasibility of electrically achieving large changes in viscosity in a single phase fluid.

The technical feasibility of making very substantial advances in smart fluids now appears very achievable. The rich variety of possible structures, active groups, and blending liquids is, as yet, unexplored. Recommendations for future research in this area include a comprehensive Phase II investigation of the structure-property relationships which govern the EV effect in this class of compounds; refinements in the measurement of the EV effect, expanded viscosity range capability, and monitoring other rheological properties under applied electric fields; and evaluating these advanced materials in typical EV applications. Some of the structural parameters which should be further examined are the type and degree of substitution, the spacer group linkage, the composition and microstructure of the lubricant.

Improvements in the measurement of the EV effect include using more sample vessel-spindle combinations to expand the range of viscosity measurement, and a computer interfaced to the voltage source and viscometer to remotely monitor and control field strength, and monitor viscosity as well as the time element of the process. Promising EV materials could be evaluated by the Army during Phase II for Phase III applications such as robotic actuators, vibration damping, lubrication, flow control and torque transfer.

The proposed research has the potential to revolutionize robotics and provide next generation devices having importance for both military and commercial applications. The integration of actuators with computational/control capabilities enables electroviscous fluids to provide "intelligent" responses including adapting, self diagnosis, and microcontrol of moving surfaces. The devices of the next century will contain smart active damping and other mechanical controls controlled locally by voltage differences across electroviscous fluids. Examples include clutches, linear actuators and hydraulic dampers. This seminal research leads directly to commercial devices for vehicle control.

5.0 EXPERIMENTAL PROCEDURES

Figure 5 illustrates the synthetic procedures adopted in order to prepare the six desired EV fluids. The synthesis involves first blocking the carboxy group of 4-hydroxy benzoic acid with benzyl chloride followed by the reaction of the phenolic hydroxyl (I) with the desired 4-R-benzoyl chloride (III) and then deblocking the acid to yield the desired LC mesogen precursor (IV). This precursor is then transformed into an acid chloride via thionyl chloride and then reacted with (S)-(-)-perillyl alcohol to form the LC mesogen (V).

The LC mesogen is then grafted onto 1,1,3,3,5,5,7,7-octamethyltetrasiloxane via a platinum-complex-catalyzed hydrosilation reaction to yield product (VI). All of the EV fluids are prepared by the acid-catalyzed, ring-opening polymerization of hexamethyldilsiloxane with (VI). Details of the syntheses follow.

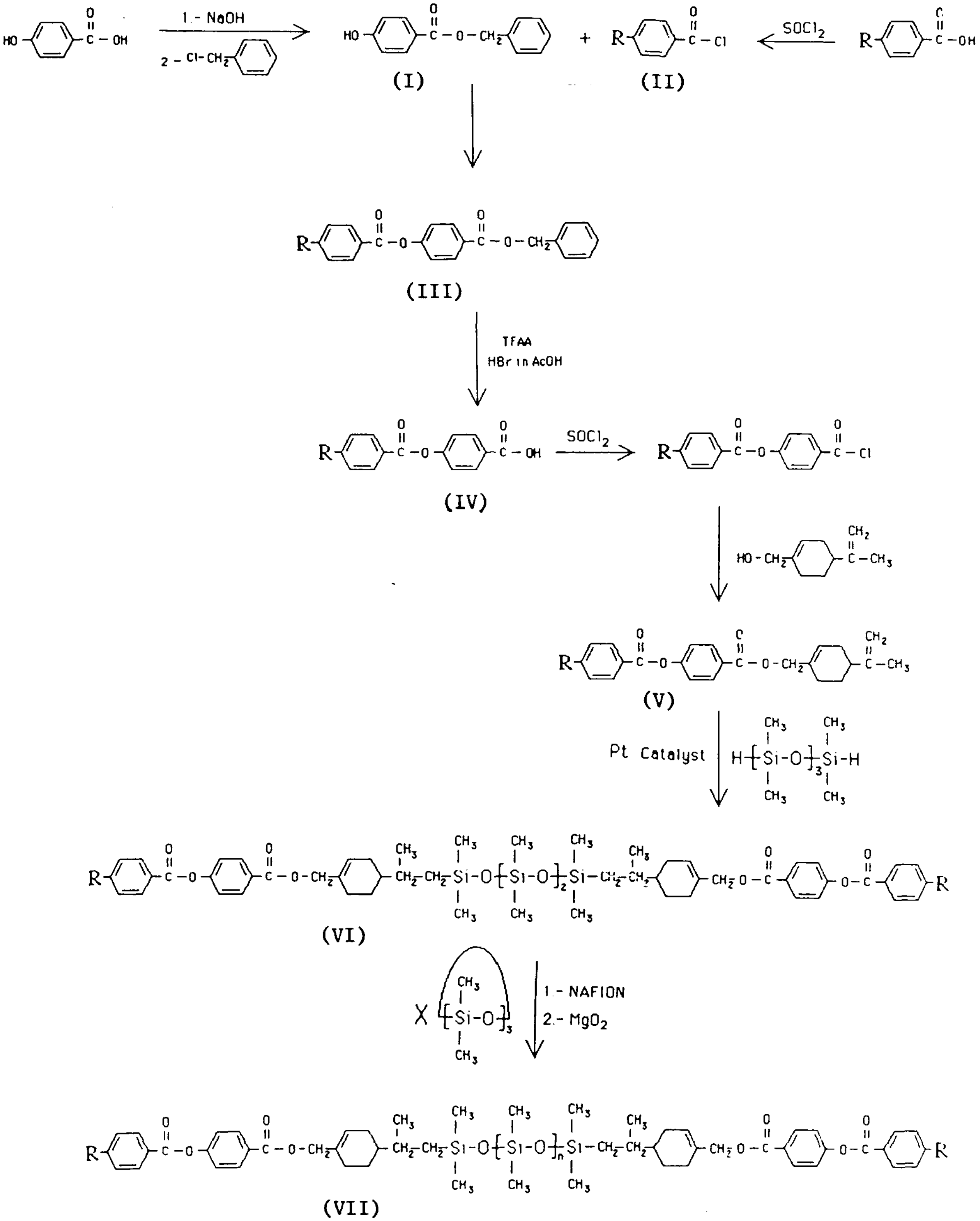
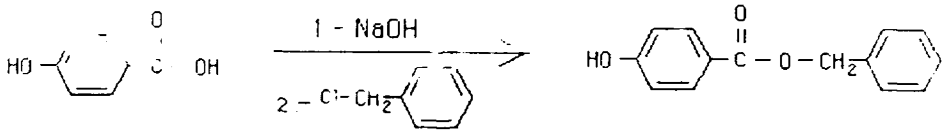


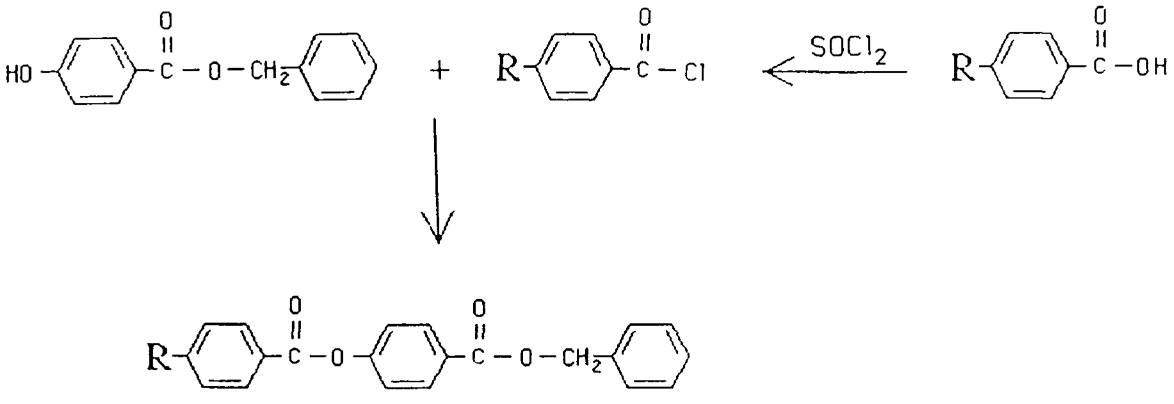
Figure 17. EV Liquid Synthesis Routes

5.1 Preparation of EV Liquid Crystal Materials

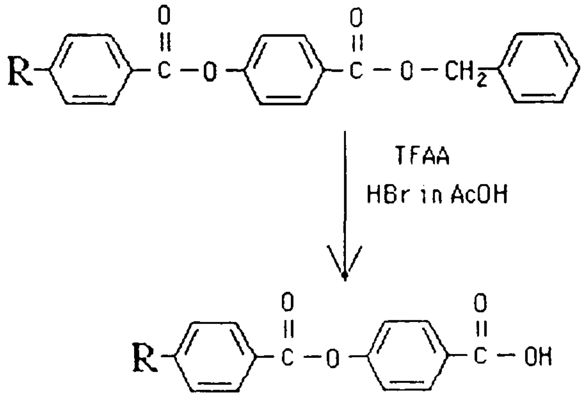
5.1.1 Synthesis of benzyl-4-hydroxy-benzoate (I) 4-Hydroxybenzoicacid (276 g, 2 mol) and potassium hydroxide (132 g, 2 mol) were dissolved in 1400 mL and 600 mL of ethanol respectively. The two solutions were mixed and stirred for 0.5 h. The solvent was evaporated by rotovap. The white solid product was then dissolved into 1400 mL of DMF in a 2 L 3-neck round bottom flask. A solution of 40 g of tetrabutylammonium iodide in benzyl chloride (230 mL, 2 mol) was added through a dropping funnel. The mixture was stirred under mechanical stirring for 24 h at 50° C. After cooling, the product was poured into 7 L of ice water. The mixture was stirred for 1 h, filtered, and dried by vacuum oven. The dried solid was dissolved in carbon tetrachloride and treated with decolorizing charcoal; filtered hot and recrystallized from the same solvent. The reaction scheme is given below.



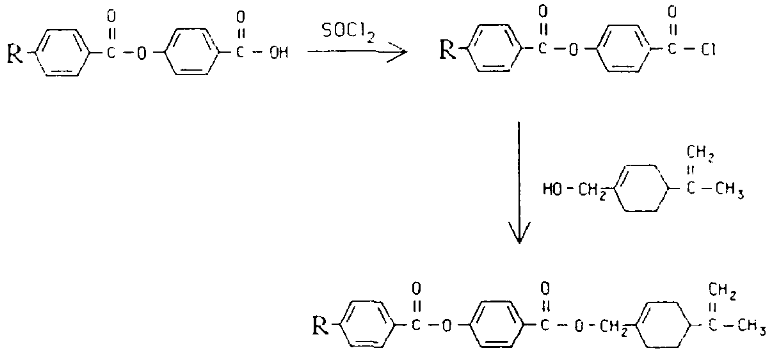
5.1.2 Synthesis of 4-benzylbenzoate-4'-R-benzoate (III) The required 4-R-benzoic acid (0.360 mol) was placed in a dry 500 mL round bottom flask fitted with a condenser, N_2 gas inlet, drying tube, dropping funnel. A slurry of 4-R-benzoic acid was made with 40 mL of anhydrous 1,2-dichloroethane, 31.41 mL of thionyl chloride and 10 drops of DMF. The mixture was allowed to reflux for 1.5 h, then diluted with another 100 mL of 1,2-dichloroethane and allowed to reflux for 1 h. Then, a mixture of benzyl-4-hydroxy benzoate (90.49 g, 0.3965 mol) and 70 mL of pyridine was added through a dropping funnel over a period of 1 h. The reaction was carried out for 24 h and then allowed to cool. Upon cooling, most of the pyridinium hydrochloride salt had precipitated; therefore, the solution was filtered before evaporating the solvent. The solvent was removed by rotary evaporation and the solid residue was washed with water and then with methanol. The reaction scheme is given below.



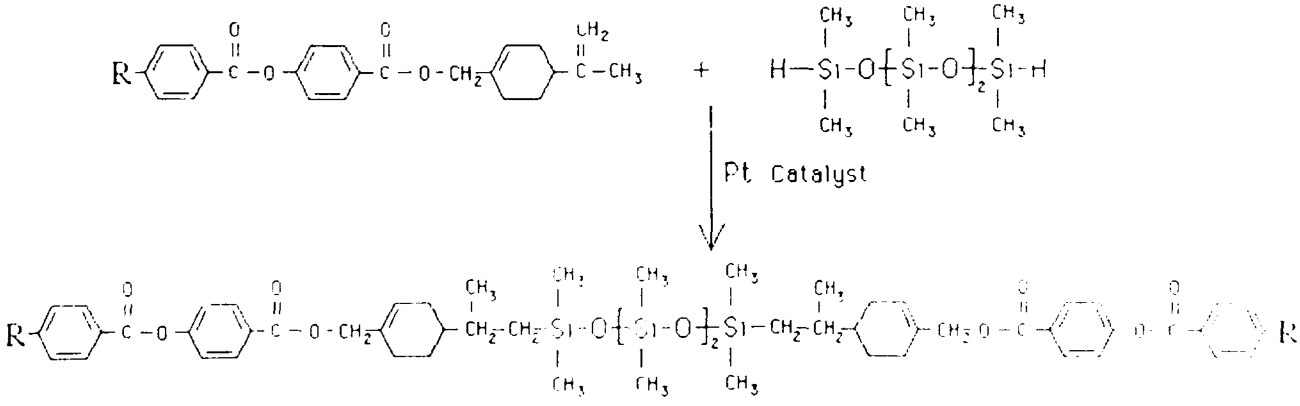
5.1.3 <u>Synthesis of 4-R-benzocarbonyloxy-benzoic acid (IV)</u> 4-benzylbenzoate)- 4'-R-benzoate (0.140 mol) was dissolved in 300 mL of trifluoroacetic acid and allowed to stir for 0.5 h as 28 mL of 30% HBr in acetic acid was added dropwise. A white precipitate began to form within the first 30 min after addition and the reaction was allowed to stir at room temperature for 5 h. The reaction was stopped by adding 30 mL of acetone and then filtering. The white solid was washed with excess methanol and dried under vacuum. The reaction scheme is given below.



5.1.4 Synthesis of perillyl-4-R-benzocarbonyloxy-benzoate (V) 4-R-benzocarbonyloxy-benzoic acid (0.0374 mol) was placed in a dry 100 mL round bottom flask with 20 mL of anhydrous 1,2-dichloroethane, 4.1 mL of thionyl chloride and 5 drops of DMF. The mixture was allowed to reflux for 1.5 h, then diluted with another 50 mL of 1,2-dichloroethane and allowed to reflux for 1 h. A mixture of perillyl alcohol (5.70 g) and pyridine (3.26g) in 50 mL of 1,2-dichloroethane was then added drop-by-drop and the reaction was allowed to continue under reflux for 24 h. After allowing to cool and placing the reaction vessel in an ice bath for 1 h, the mixture was filtered. The solvent was removed by rotoevaporation and the solid was purified by recrystallization or column chromatography; depending on the product. The reaction scheme is given below.

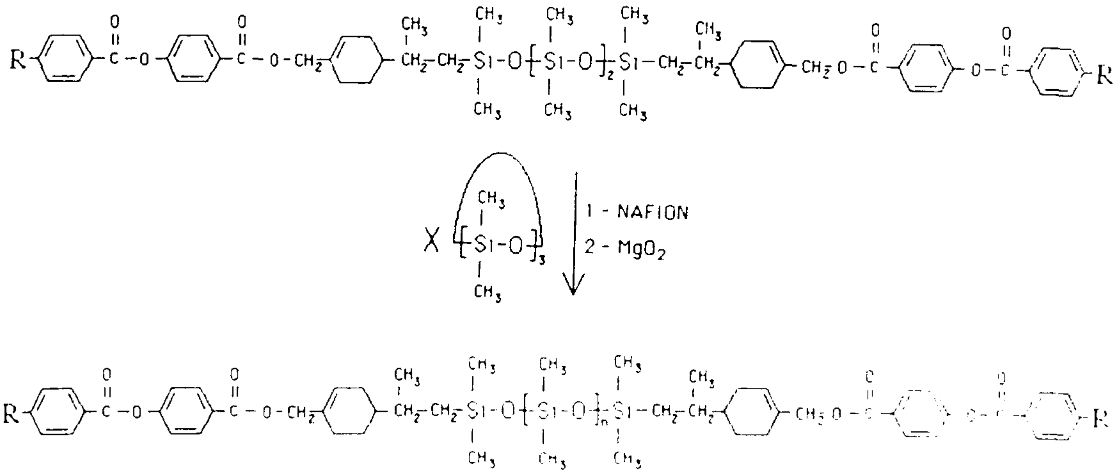


5.1.5 Grafting of LC Groups onto Siloxanes (VI) The perillyl-4-R-benzocarbonyl-oxy-benzoate (0.02588 mol) is reacted in a 2:1 ratio with 1,1,3,3,5,5,7,7-octamethyltetrasiloxane via a platinum complex-catalyzed hydrosilation reaction. The general reaction scheme is given below.



The LC mesogen was placed in a three-necked round bottom flask fitted with dropping funnel, nitrogen gas inlet, Dean-Stark trap, and condenser. The compound was dissolved in 60 mL of toluene and heated to reflux until 20 mL of toluene were collected. This process ensures dryness of the solution to avoid hindrance of the hydrosilation. Then 5 drops of platinum-divinyl-tetramethyldisiloxane were added. The siloxane was then added dropwise over a period of 0.5 h. The reaction was carried out at 80-90°C for 22 h. Then, activated charcoal was added and the solution vacuum filtered. Finally, the toluene was removed under reduced pressure.

5.1.6 **Preparation of LC Containing Fluid (VII)** The desired EV fluids were prepared by the acid-catalyzed, ring-opening polymerization of hexamethyldilsiloxane with the perillyl-4-R-benzocarbonyl-oxy-benzoate terminated 1,1,3,3,5,5,7,7-octamethyltetrasiloxane. The reaction was carried out in a 1:30 ratio of cyclic siloxane to LC functionalized siloxane. A 100 mL one-necked round bottom flask was fitted with (0.001895 mol) of perillyl-4-R-benzocarbonyl-oxy-benzoate, 12.64 g (0.05685 mol) of hexamethyldilsiloxane and 0.3 g of Nafion powder. The reaction was heated to 80°-90°C and kept at that temperature for 24 h. After cooling, the reaction was diluted with CH_2Cl_2 and MgO and $MgSO_4$ were added to remove any acid and to dry the system. The solution was then filtered and the solvent removed by rotary evaporation. The reaction scheme is given below.



5.2 Material Analysis

5.2.1 Chemical Characterization of LC Compounds

The liquid crystal compounds were chemically characterized by proton nuclear magnetic resonance spectrometry (^{1}HNMR) and Fourier Transform Infrared (FTIR) spectroscopy. The NMR analysis was carried out by dissolving the copolymers in deuterated chloroform and using tetramethylsilane as a reference. A Varian Model EM-360 60 MHz spectrometer was used. FTIR analyses were performed by Diffused Reflectance or Transmittance. A Perkin-Elmer FTIR 1600 spectrometer was used for these analyses.

The thermal properties of the LC mesogens were measured by Differential Scanning Calorimetry (DSC). A Perkin-Elmer Delta Series DSC7 was used. However, this instrument cannot handle liquid samples; therefore, thermal characteristics of the fluids could not be determined. The heating or scanning rate used for each thermal scan was 10 ^{o}C/min and the temperature range typically was -20 to 130 ^{o}C.

5.2.2 Optical Characterization of LC Compounds

The liquid crystal samples were analyzed by polarizing microscopy. The optical analyses were carried out on a Zeiss Microscope (standard lab 16) fitted with polarizing filters.

5.2.3 Fluid Viscosity Characterization

The viscosity characterization of the experimental fluids were performed with a Brookfield viscometer (Model LVT), placed in a Faraday cage and outfitted with a Bertran high voltage power supply (Model 205 B-20R). Viscosity measurements were performed at a number of temperatures, field strengths and shear rates.

5.3 Electroviscous Testing

A diagram illustrating the viscosity test apparatus is shown on the next page.

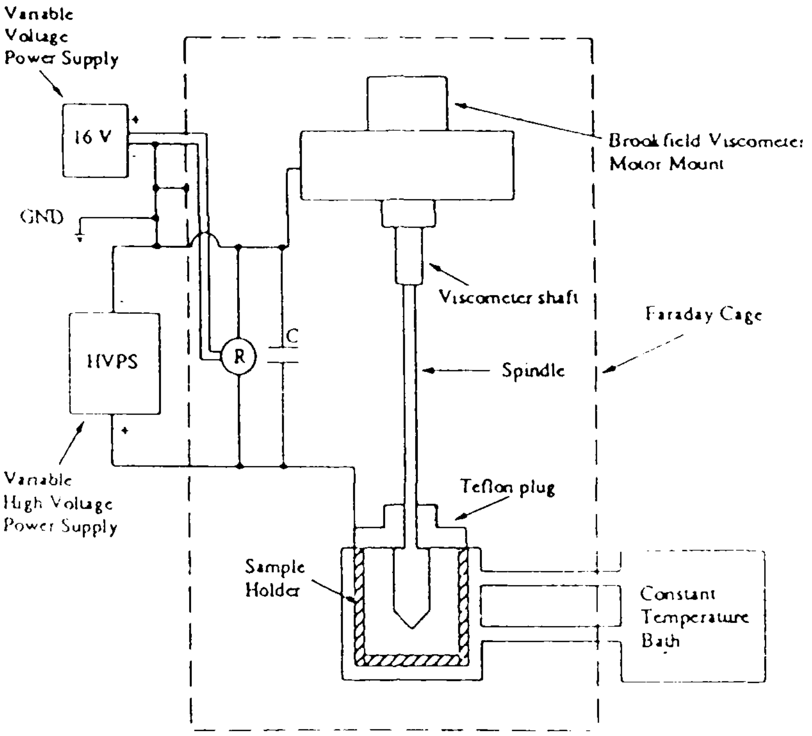


Figure 18. Electroviscosity Test Apparatus

A Brookfield viscometer (Model LVT) was modified for electroviscosity experiments. Basically, the steel sample chamber was connected to the hot side of a Bertran high voltage DC power supply (Model 205 B-20R) and the steel spindle was connected to ground so that a large voltage gradient could be imposed across the fluid sample while the viscosity was being measured. The sample chamber was also jacketed to allow control of sample temperature by means of an external circulating bath. For further safety the apparatus was placed within a 2 ft. cube Faraday cage. Measurements are taken by monitoring the viscometer dial from outside the cage. This allows continuous measurement of the viscosity of the fluid as temperatures and voltages are varied.

The testing procedure involves first preparing the sample by placing it in the sample holder and placing the sample holder in the viscometer. The apparatus is then prepared by setting the circulation bath temperature to the desired temperature and the viscometer to the desired shear rate. Typically the samples were tested at temperatures ranging between 50-100^{o}C and field strengths from 0-5 kV/mm.

5.4 Response Time Test Apparatus

To measure the response time for a change in the optical properties of the EV fluids, a test apparatus and instrumentation package was designed and constructed. The test instrument illustrated in Figure 19 uses a set of polarizing lenses, a light emitting diode (LED) light source, and a silicon photodiode detector in combination with an electronic timing circuit. A schematic of the timing circuit is shown in Figure 20.

The instrument uses the polarization properties of the liquid crystalline EV fluids to measure the time for a change in rest orientation due to exposure to an electric field. The second polarizing lens is adjusted such that it is crossed perpendicular to the first lens, blocking light from the high-intensity GaAlAs LED from the CLD31 photodiode detector. The EV fluid is placed in the test cell which consists of a number of glass slides fixed in place with epoxy. Wide pieces of nickel foil are attached to the top and bottom of the test cell with epoxy to connect to the high-voltage power supply leads. An electric field is formed across the 3 mm gap between the two nickel foil strips. Application of a large electric field to the EV fluid causes a change in the polarization angle of the system, allowing light to strike the photodiode detector.

The heart of the electronic timing circuit is an ICM7226A IC. The ICM7226A is a fully integrated universal counter combining a high frequency oscillator, an 8 decade data counter, a decade timebase counter, and segment and digit drivers to drive large LED displays. When used with a 10 MHz timebase, the ICM7226A can time events with a 0.1 µS resolution. Other sections of the timing circuit include switching circuitry for the high-intensity LED, amplifier level shifting circuitry for the CLD31 photodiode detector, and buffering for driving the high-voltage power supply control lines. The timing circuit is completed by a custom TIBPAL16R4-25CN programmable array logic IC which is used as a state machine to sequence all of the control signals for ICM7226A.

A Bertran 205B-20R power supply is used to apply an electric field to the test apparatus. The precision regulated linear power supply can output a maximum of 20 kV @ 1 mA with only 300 mV ripple. The Bertran 205B-20R includes a remote programming connector which allows the output of the power supply to be turned on/off and to be varied with an external voltage source.

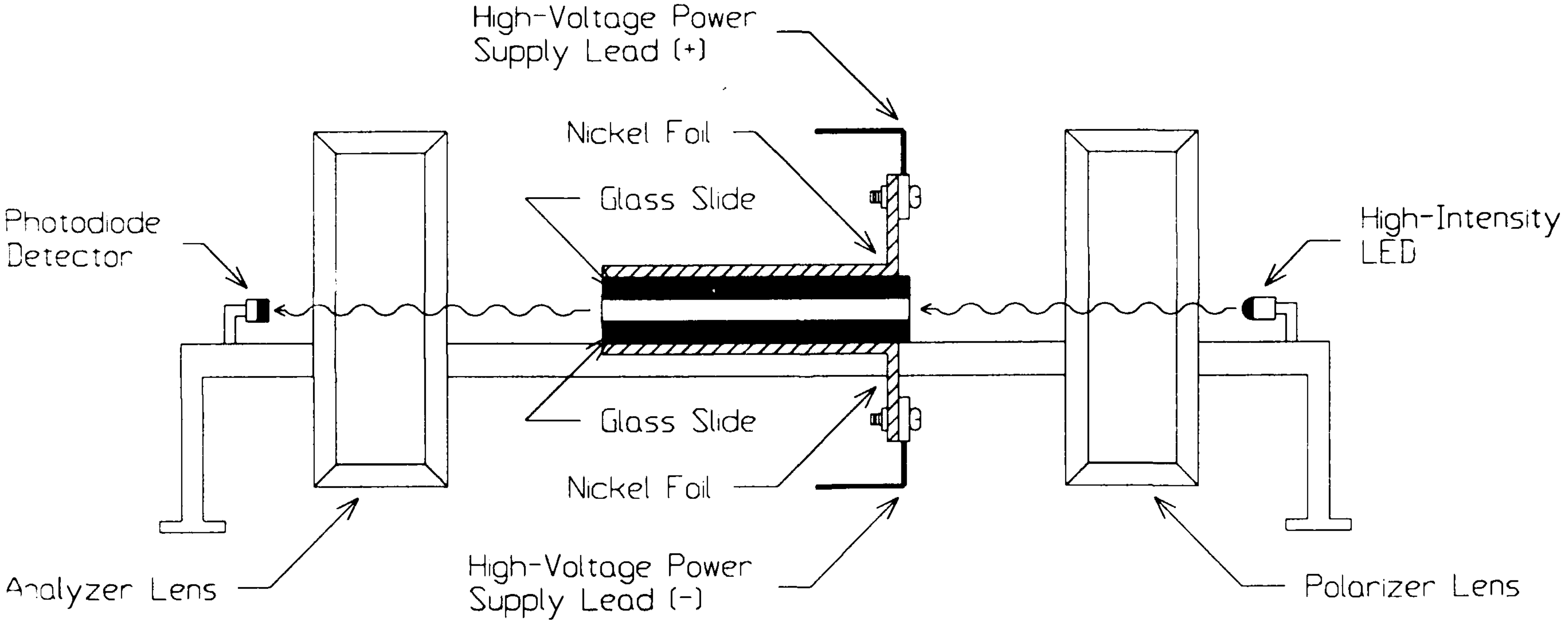


Figure 19. Response Time Test Apparatus.

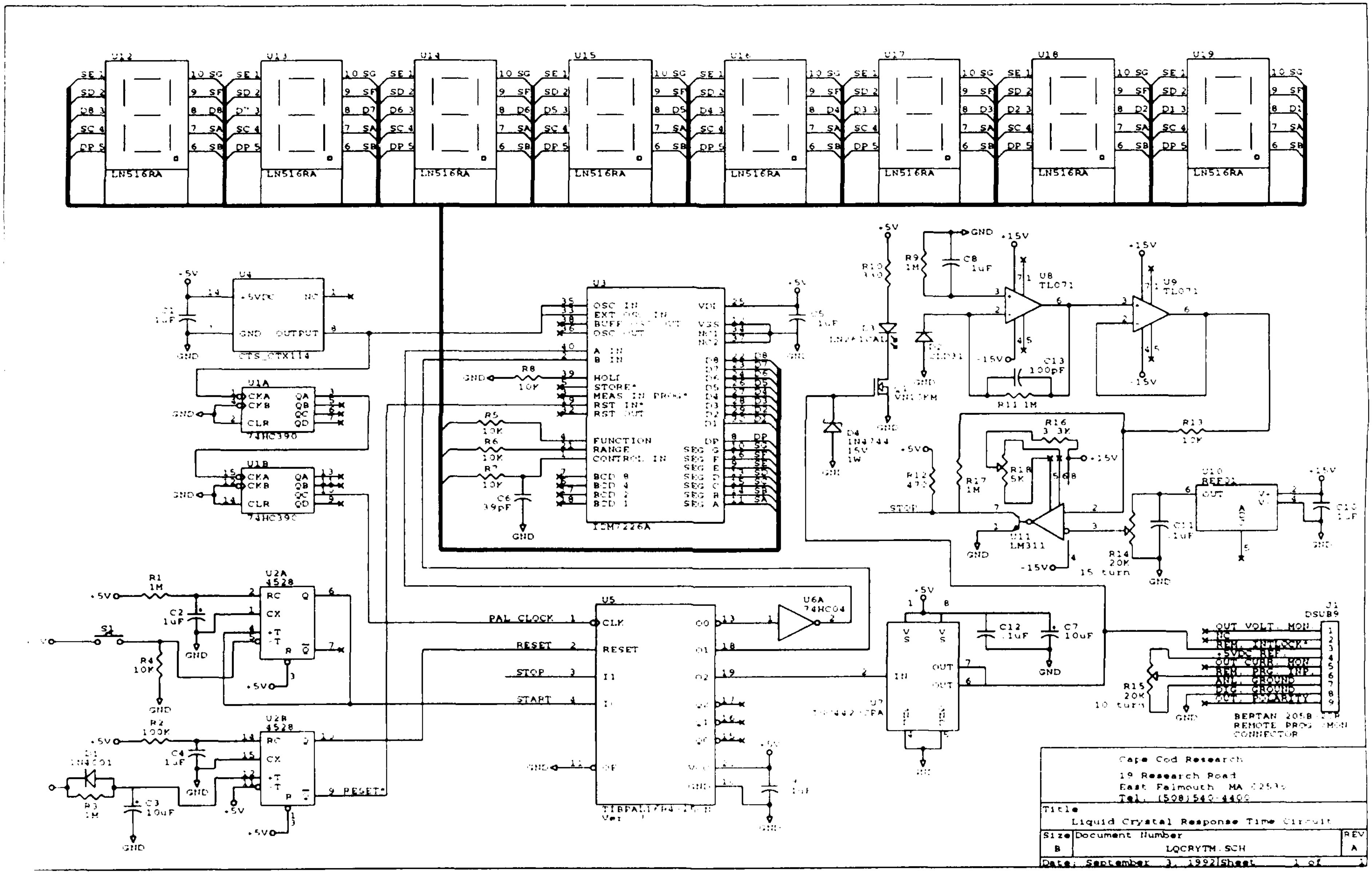
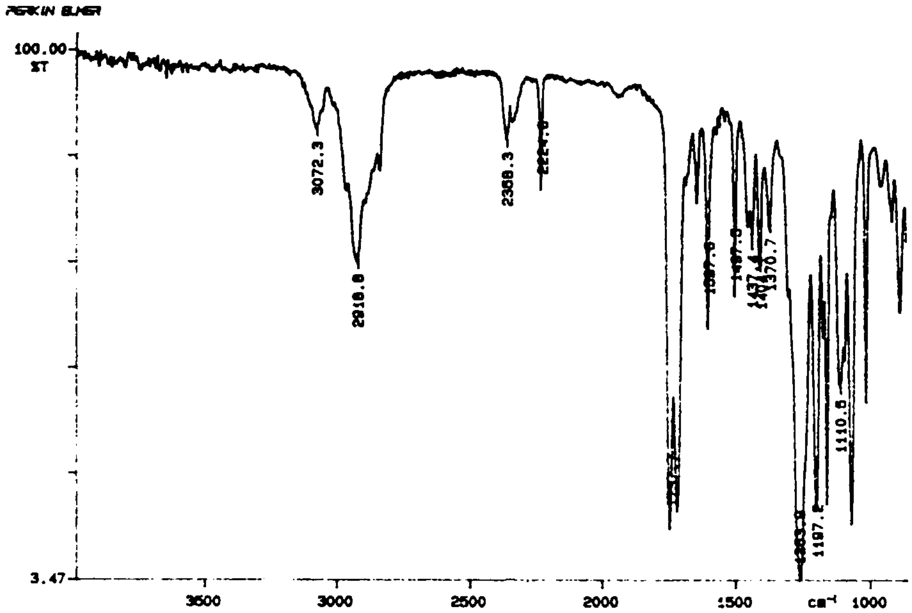


Figure 20. Timing Circuit

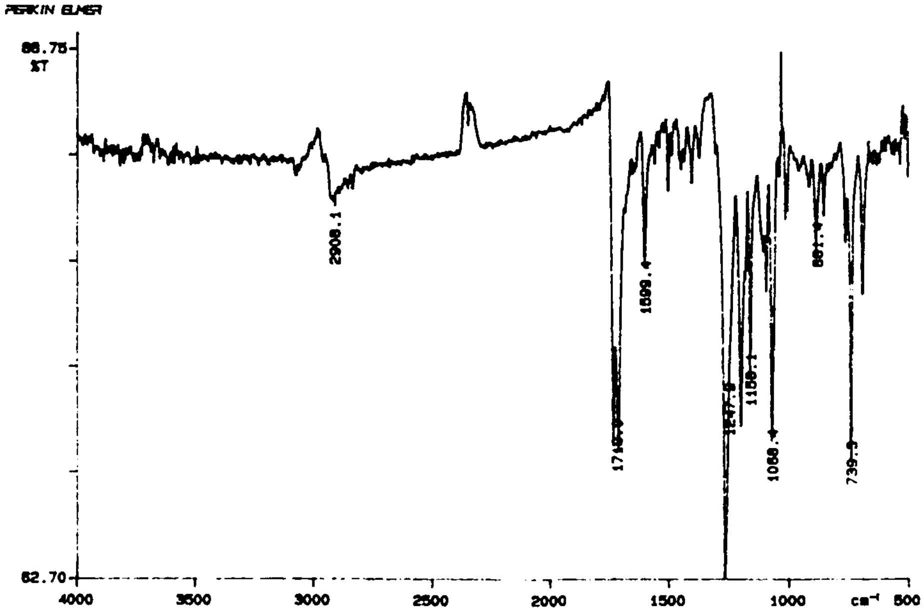
6.0 REFERENCES

1. J. Goossens, G. Oppermann, W. Grape, and V Haertel, U.S. Patent, US 4,645,614, February, 1987

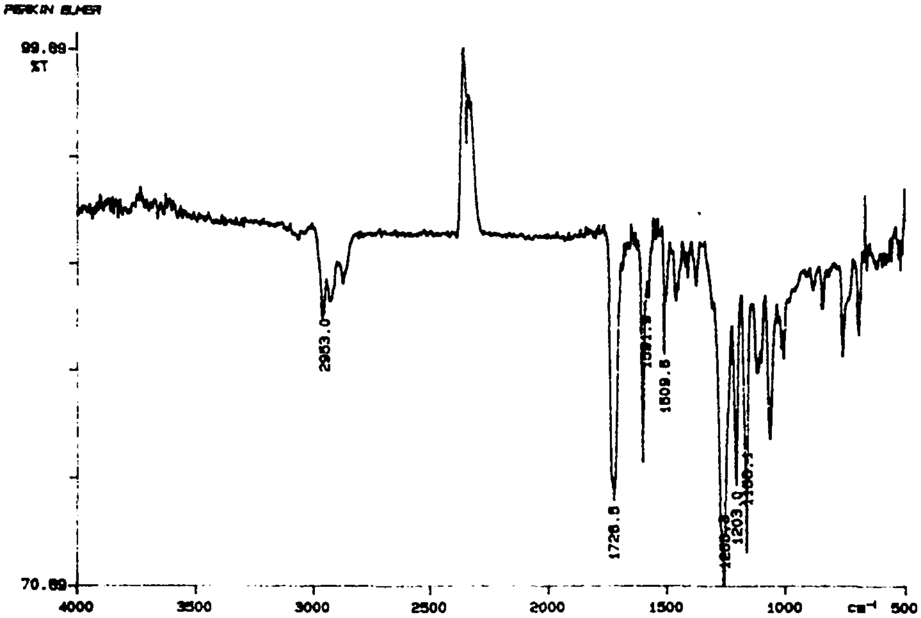
APPENDIX I



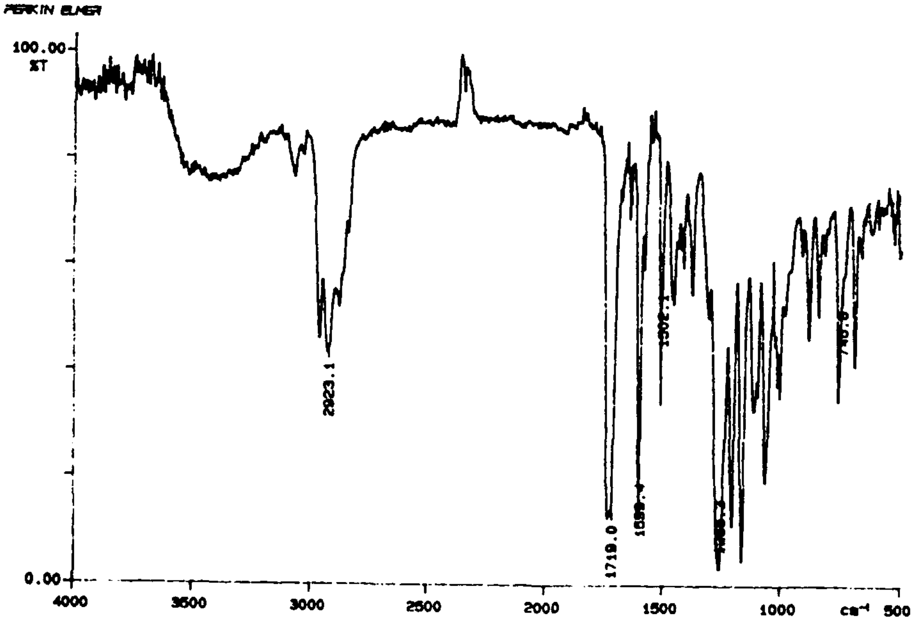
FTIR Scan of perillyl-4-cyano-benzocarbonyloxy-benzoate



FTIR Scan of perillyl-4-phenyl-benzocarbonyloxy-benzoate



FTIR Scan of Ω hexene-4-t-butoxy-benzocarbonyloxy-benzoate



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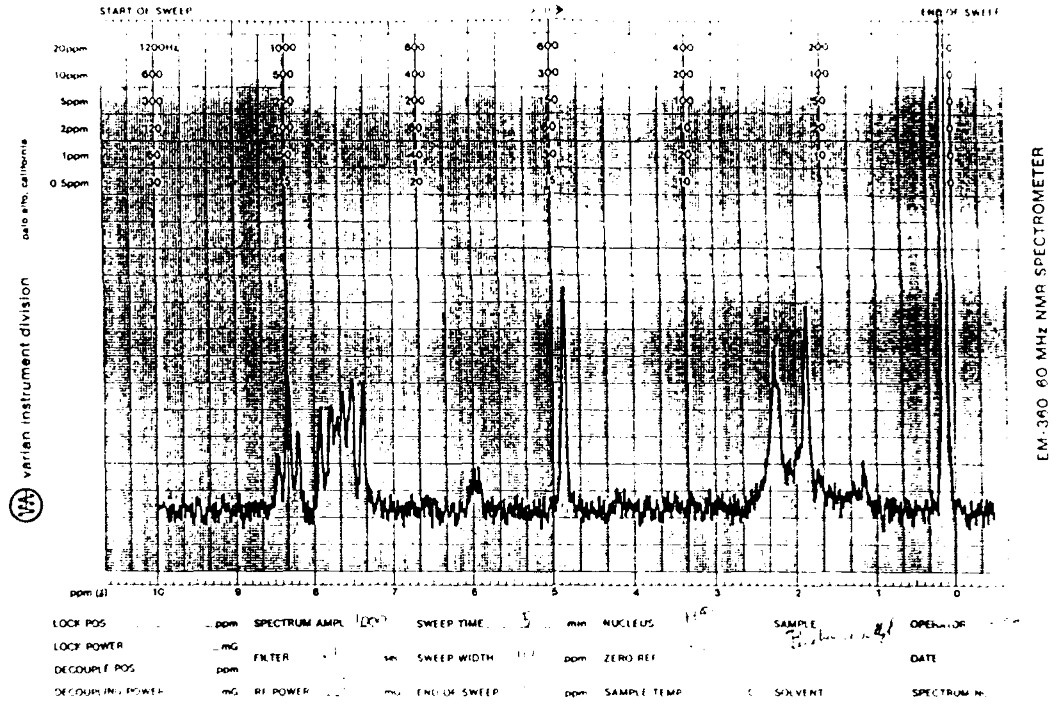

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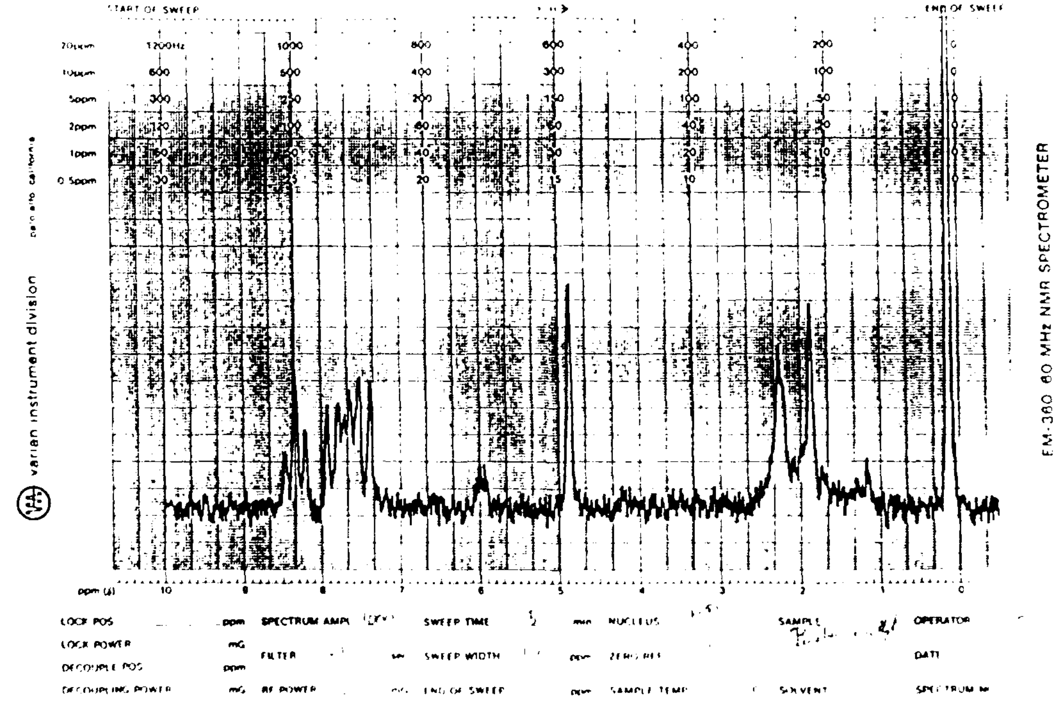
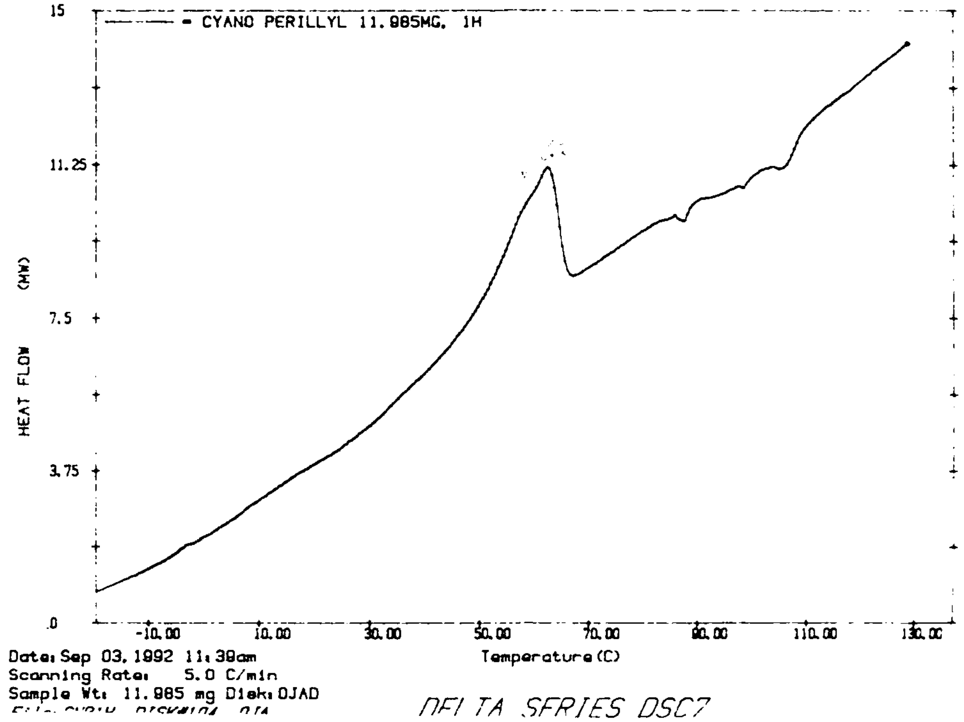
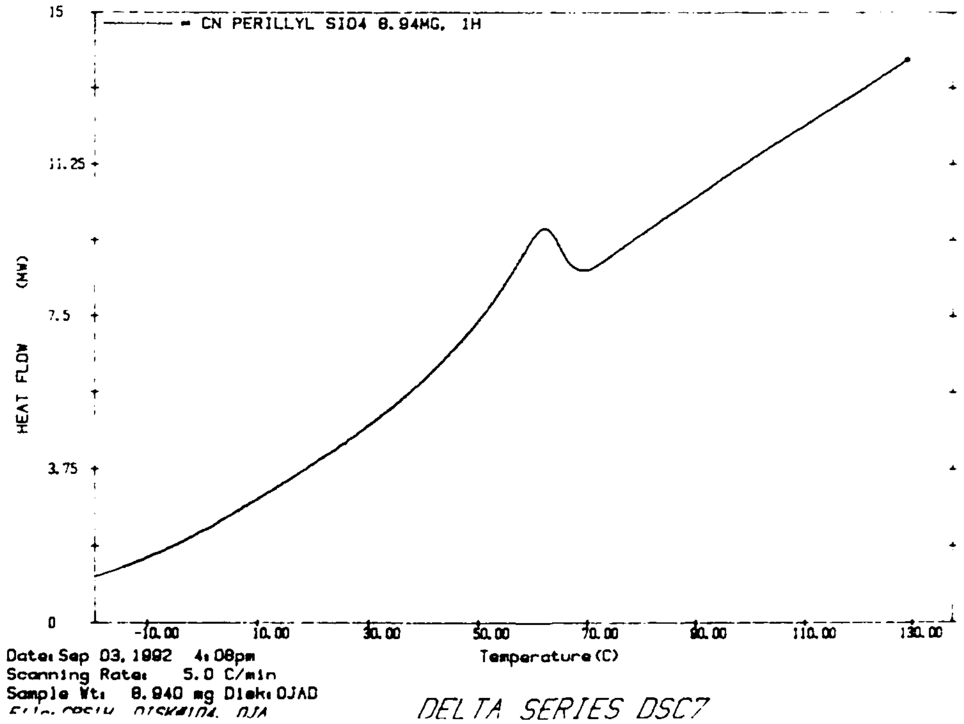


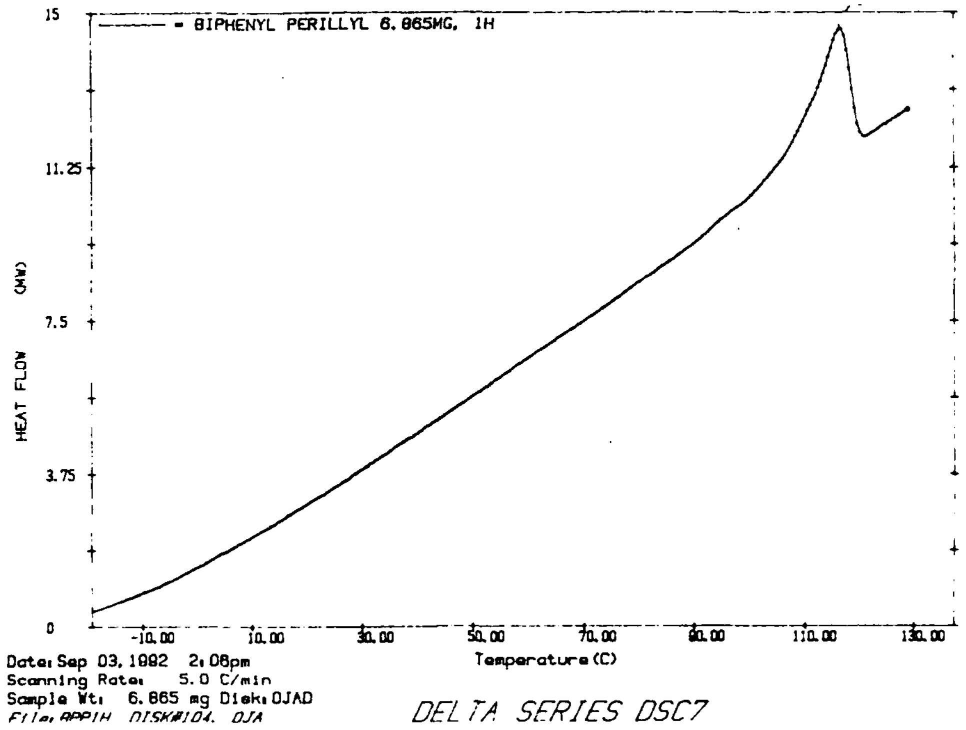
NMR Scan of perillyl-4-t-butoxy-benzocarbonyloxy-benzoate



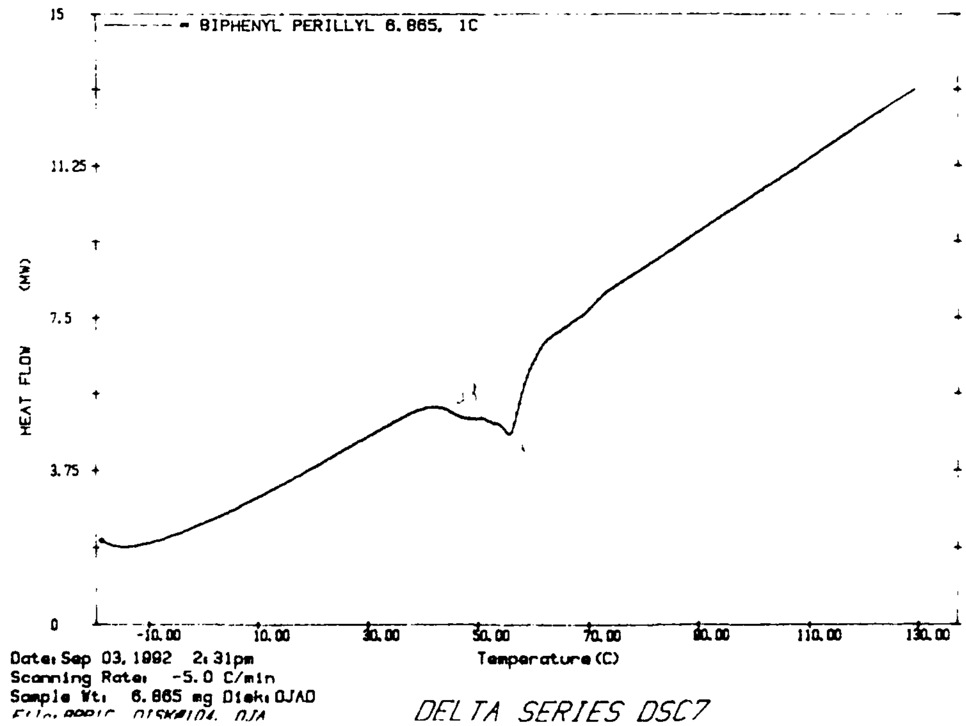
DSC Scan of perillyl-4-cyano-benzocarbonyloxy-benzoate -- heating curve



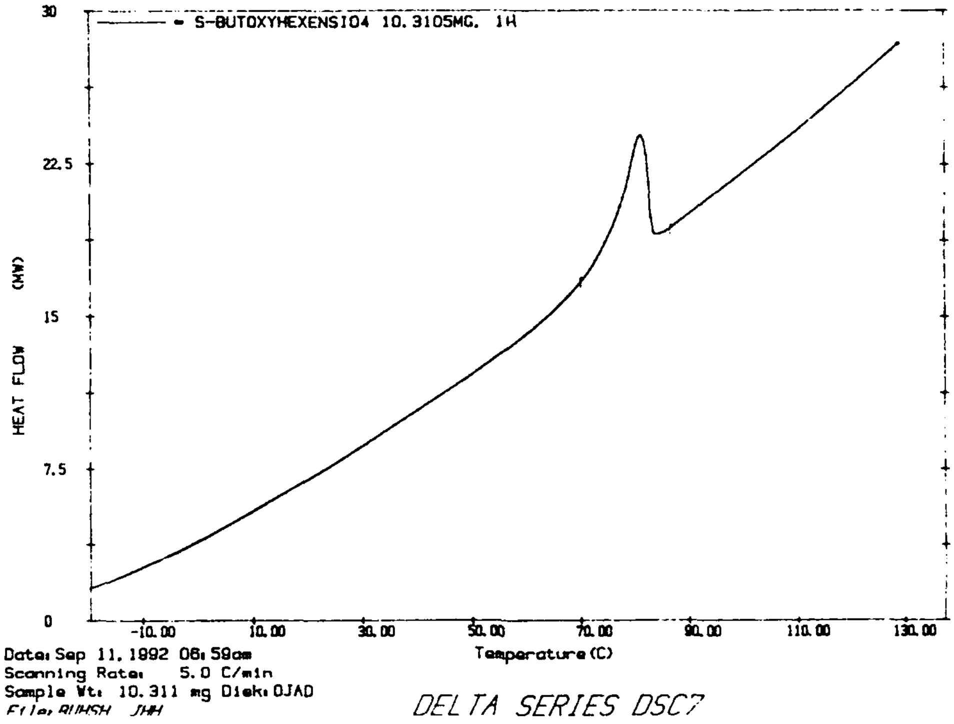
DSC Scan of grafted perillyl-4-cyano-benzocarbonyloxy-benzoate -- heating curve



DSC Scan of perillyl-4-phenyl-benzocarbonyloxy-benzoate -- heating curve



DSC Scan of perillyl-4-phenyl-benzocarbonyloxy-benzoate -- cooling curve



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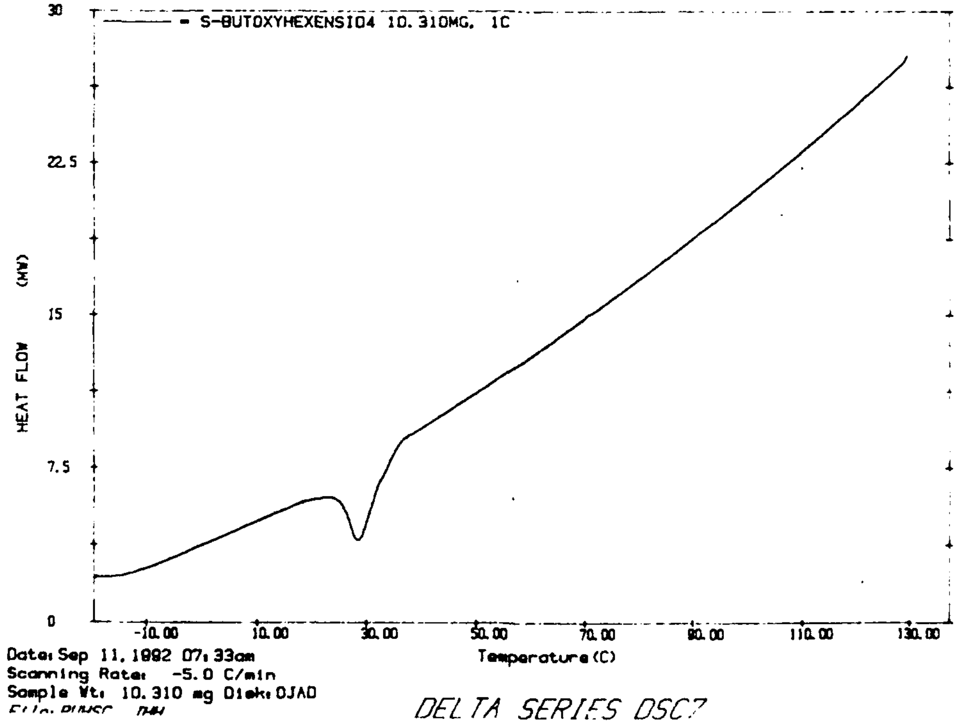

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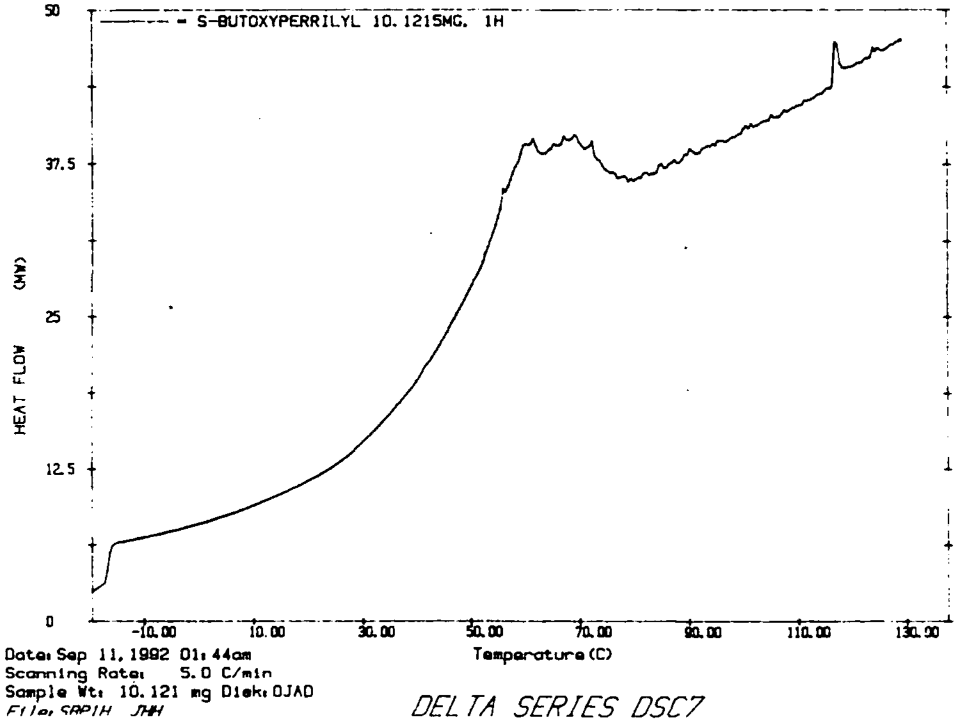
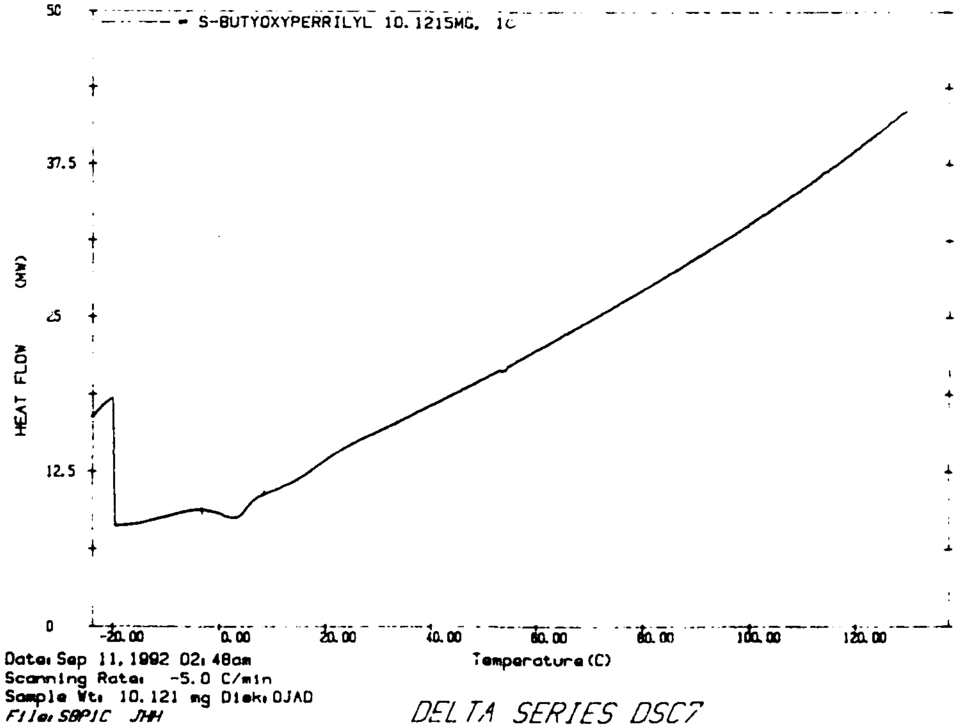


DSC Scan of perillyl-4-t-butoxy-benzocarbonyloxy-benzoate -- heating curve



DSC Scan of perillyl-4-t-butoxy-benzocarbonyloxy-benzoate -- heating curve