AD-A191 200 QUASI-LIQUID CRYSTALLINE MATERIALS WITH SPECIAL ELECTRO-OPTIC PROPERTIES(U) WEIZMANN INST OF SCIENCE REHOVOTH (ISRAEL) V KRONGAUZ NOV 87 DAJA45-85-C-0030 1/1

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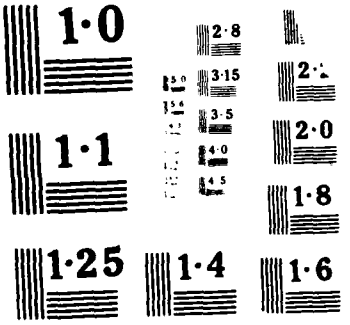
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QUASI-LIQUID CRYSTALLINE MATERIALS WITH SPECIAL ELECTRO-OPTIC PROPERTIES

1st Periodic Report

Dr. Valeri Krongauz

December 1985 - January 1986

United States Army

European Research Office of the US Army

London, England

Contract number DAJA45-85-C-0030

THE WEIZMANN INSTITUTE OF SCIENCE

"The Research reported in this document has been made possible through the support and sponsorship of the U.S. Government through its European Research Office of the U.S. Army. This report is intended only for the internal management use of the Contractor and the U.S. Government".

In the research proposal submitted to the European Research Office of the US Army we have described a new type of organic material, quasi-liquid crystals (QLC's) obtained by us from thermochromic spiropyrans with mesogenic substituents. We have defined some basic properties of the material, that can be of practical importance [1-4]. During the past two months the studies on QLC's have been concentrated on further investigation of the structure of this new material.

For structural studies the thin films of QLC's were aligned in the electrostatic field. We examined polarization absorption spectra of the films in tne UV and visible regions and polarization ESR spectra. Recently the FTIR technique was used for IR observation of polarization of different groups in the spiropyran molecules aligned in the films. We used different coloured and fluorescent additives as probes in absorption and emission spectroscopy and a paramagnetic probe in ESR studies. Analysis of these data allowed us to suggest a structure of QLC, which can be described as a phase resembling reentrant nematic LC's with rudimental bilayered domains.

Our research plans include examination of nonlinear optical properties of QLC's and synthesis of new spiropyrans with liquid crystalline properties.

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QUASI-LIQUID CRYSTALLINE MATERIALS

WITH SPECIAL ELECTRO-OPTIC PROPERTIES

2nd Periodic Report

Dr. Valeri Krongauz

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United States Army

European Research Office of the US Army

London, England

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During the past four months the studies on the project have been concentrated on examination of nonlinear optical properties of Quasi-liquid crystals (QLC's).

The work is being conducted in cooperation with Prof. Shen's group at the Physics Dept., University of California, Berkeley. Measurements of the second harmonic generation (SHG) of the aligned QLC films could give an adequate characterization of the optical non-linearity of the material. These experiments gave very promising results: The QLC films give singificant second harmonic signals. To get some qualitative idea on the efficiency of the SHG, we compared the signals from QLC's and from quartz. The QLC film of 1 m thickness gave a signal comparable with that from a 1mm thick quartz plate.

The signal grows substantially when an electrostatic field is applied. Some other very interesting and more complicated electro-optical properties of the QLC films were disclosed, and are now being investigated. All these effects open new possibilities for a variety of practical applications.

Our research plans include completion of SHG measurements.

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QUASI-LIQUID CRYSTALLINE MATERIALS

WITH SPECIAL ELECTRO-OPTIC PROPERTIES

3rd Period Report

Prof. Valeri Krongauz

June-November 1986

United States Army

European Research Office of the US Army

London, England

Contract number DAJA45-85-C-0030

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During the past six months we have finished to examine the second harmonic generation (SHG) from the quasi-liquid crystal (QLC) films, aligned in the electrostatic field. In addition to the results mentioned in the previous periodic reports we have found a very strong temperature effect on luminescence and SHG with temperature rise: the SHG disappears but luminescence intensity increases.

The main efforts were directed towards synthesis and investigation of structure and properties of side chain liquid crystal polymers containing thermochromic, spiropyran groups (item C in the plan of operation, section IV of the Research Proposal). We have studied structural transformations occuring in these polymers. The spiropyran-merocyanine dye conversion occurs on heating of the polymers. Physical crosslinking of the macromolecules due to aggregation of the dye moieties gives rise to a network formation responsible for apppearance of the dynamic birefringence, observed above the clearing point[1].

Our research plans include further examination of optical properties of the thermochromic liquid crystal polymers.

REFERENCE

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QUASI-LIQUID CRYSTALLINE MATERIALS

WITH SPECIAL ELECTRO-OPTIC PROPERTIES

4th Period Report

Prof. Valeri Krongauz

December 1986 - May 1987

United States Army

European Research Office of the US Army

London, England

Contract number DAJA45-85-C-0030

THE WEIZMANN INSTITUTE OF SCIENCE

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During the past six months we continued the synthesis and investigation of side chain liquid crystal polymers containing spiropyran groups (item C in the plan of operation, Section IV of the Research Proposal). We synthesized new polymers with polyacrylic backbone and spiropyran and mesogenic side groups connected to the backbone through the flexible hydrocarbon spacers of different length (C_2 - C_{11}). The polymers exhibit both photo - and thermochromic properties. The structural transformations of the polymers on heat, light and an electric field exposure were the main direction of our studies.

Our research plans include synthesis of photochromic liquid crystal polymers with the polysyloxane backbone.

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See also G. Attard and G. Williams, Nature, 326, 544 (1987).

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QUASI-LIQUID CRYSTALLINE MATERIALS

WITH SPECIAL ELECTRO-OPTIC PROPERTIES

5th Period Report

Prof. Valeri Krongauz

June - November, 1987

United States Army

European Research Office of the US Army

London, ENGLAND

Contract number DAJA45-85-C-0030

THE WEIZMANN INSTITUTE OF SCIENCE

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During the past six months we have completed synthesis and investigation of side chain liquid crystal polysiloxanes containing photochromic spiropyran side groups (item C, Section IV of the Research Proposal). The polymers exhibit both thermo- and photochromic properties. By changing temperature and wavelength of light we could control the polymer color. Three primary colors (yellow, blue and red) were obtained. The color changes stemmed from spiropyran-merocyanine conversion and aggregation of the merocyanine side groups.

Our research plans include further examination of optical properties of the photo-thermochromic liquid crystal polymers, including laser irradiation effects.

REFERENCE

I. Cabrera and V. Krongauz, Angew. Chem. 99 (11), 1204 (1987).

QUASI-LIQUID CRYSTALLINE MATERIALS WITH SPECIAL ELECTRO-OPTIC PROPERTIES

Complimentary Report

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Structural Chemistry, Weizmann Institute of Science,
Rehovot, Israel

Submitted to

The United States Army,
European Research Office
London, England

Contract No. DAJA45-85-C-0030

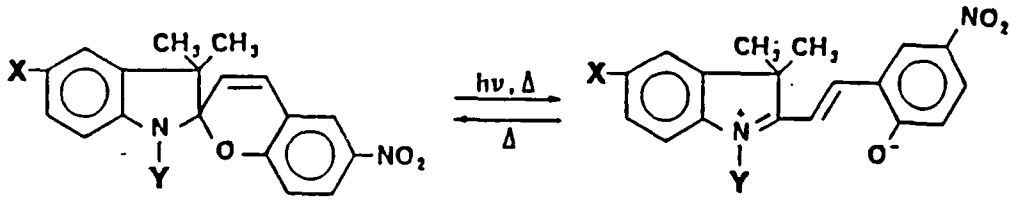
"The Research reported in this document has been possible through the support and sponsorship of the U.S. Government through its European Research Office of the U.S. Army. This report is intended only for the internal management use of the Contractor and the U.S. Government".

ABSTRACT

Photo/thermochromic liquid crystals and liquid crystal polymers were synthesized by combination of spiropyran and mesogenic groups in one low molar mass molecule or macromolecule. The spiropyran - merocyanine conversion affects the mesophase structure and results in formation of non-centrosymmetric non-linear optical material, generating second harmonics. Aggregation of merocyanine molecules leads to a new photomechanical effect in low molar mass compounds and to a rheo-optical effect in the side chain liquid crystal copolymers containing spiropyran side groups. Polychromic phototransformations in the copolymers as well as accompanying structural changes enable use of the polymer films for optical information storage.

BRIEF DESCRIPTION OF THE PROJECT AND ITS SCIENTIFIC AND TECHNOLOGICAL IMPLICATION

Spiropyrans are the most important organic photo- and thermo-chromic molecules.[1] They can be reversible converted to a merocyanine dye by u.v. irradiation or heating:



SPIROPYRAN MEROCYANINE

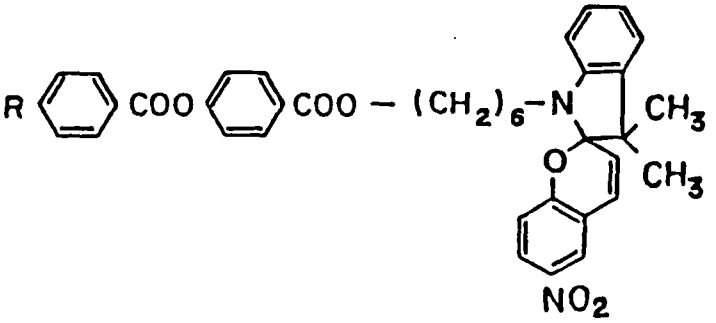
Since this transformation leads to drastic changes in such molecular properties as polarity, tendency to aggregate, molecular geometry, etc., we anticipated that the combination of spiropyrans and mesogenic groups in a single molecular structure should lead to novel types of molecular organizates with new interesting properties.

Indeed, there was good reason to believe that such "hybrid" molecules should show not only photo- and thermo-chromic mesophases but that many of the physical properties could be manipulated by heating and light. In particular the transformation of the molecules into the merocyanine form by heat or irradiation and their alignment in an electrostatic field would allow us to obtain a dipolar non-centrosymmetric structure with high optical non-linearity.

Our efforts in this direction include the synthesis of both low molecular weight

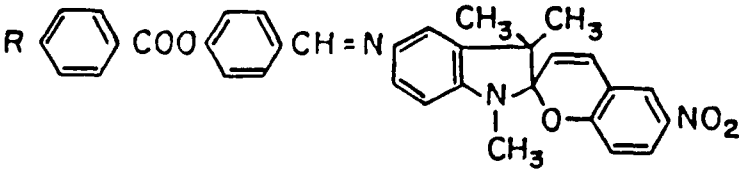
molecules and macromolecules containing spiropyran and mesogenic groups.

The initial experiments with low molar mass compounds showed that the combination of photo/thermochromic and mesogenic moieties in one molecule often led to impairment of one of the properties. Which one of the properties was lost depended markedly on the position and type of "bridge" by which the mesogenic group was connected to the spiropyran molecule. The T-shaped molecules of the general formula



show good photo- and thermo-chromic behavior but do not exhibit mesomorphic properties. However, in the melt of one of them, that with R=CN-, we discovered a very unusual and intriguing photocontraction effect.[2] This melt, produced by the irradiation and heating of amorphous films of the material, contracts markedly under u.v. irradiation. The unprecedented character and importance of such effect was emphasized in a review of this work published in Chemical Engineering News[3]

The rod-liked "hybrid" molecules, on the other hand,



displayed very special thermochromic and structural properties resulting in the appearance of a new kind of molecular organization.[4,5]

The latter compounds can be crystallized from solution and give crystals with sharp melting points and crystal-isotropic liquid phase transition. However, under certain conditions the compounds form amorphous metastable films that exhibit a characteristic birefringent texture upon heating. Appearance of this texture coincides with a sharp increase of merocyanine concentration due to the thermochromic spiropyran - merocyanine conversion.

Further increase in temperatures leads to the disappearance of this texture. The temperature of the birefringent texture is wide (80 - 90 °C), and lies much below the melting point of the crystals. Since these materials show some features of liquid crystals, but behave differently from conventional mesophases, we named them Quasi-liquid Crystals (QLCs).

Substantial efforts were made to determine the structure of these materials, which proved to be a nematic-like mesophase with a structure that is strongly affected by the presence of the highly dipolar merocyanine groups.[5-8]

QLCs can be aligned in an electrostatic field of more than 0.5 kV/mm. The electric field induced orientation of the films stabilizes the quasi-liquid crystalline state (crystallization no longer occurs), to such an extent that at room temperature the orientation and the glass like properties are preserved practically indefinitely.[4,5]

It was discovered that such polar oriented films generate second harmonics on irradiation with a laser beam.[8] The studies on second harmonic generation proved the unique character of the QLCs.

Indeed, in contrast to conventional nematic liquid crystals, where polar ordering has never been observed, in quasi-liquid crystals a polar ordering of

molecules can be observed in external fields and can be modified in a manner predictable by a mean field theory.

We finally accomplished the synthesis of photochromic liquid crystals by preparing polyacrylate[9,10] and polysiloxane[11] copolymers containing spiropyran and mesogenic side units. The culminating point in our studies of these materials was the observation that structural changes of the mesomorphic systems can be induced by the reversible spiropyran merocyanine photoconversion. As a result, these liquid crystals form an exceptional class of optical materials, in which many of the physical properties of the mesophase, such as birefringence, viscosity, etc can be changed by light. The photoinduced aggregation of the merocyanine dyes, for example, leads to a network formation and a new rheo-optical effect[9], observed above the clearing point.

Since these materials combine photosensitivity with the physical properties of liquid crystal polymers, they open innumerable possibilities for applications in optical technology. The possibility to control by light and temperature the formation of the three primary colors[11], for example, makes them interesting materials for new applications in display technology. Moreover, they can be used for the storage of optical information because, as was already mentioned, changes in absorption and birefringence can be induced by light.

In this respect we have used these materials as a medium for the storage of digital intensity distributions. The merocyanine to spiropyran isomerization, which influences locally the liquid crystal orientation, causes the optical induction of a birefringence pattern in a pre-oriented polymer liquid crystal film. This may result in the recording of information.

There are many scientific implications and potential applications for photo- and thermo-chromic liquid crystals. A measure of the promise of these materials is given in a recent scientific review of our work in Nature.[12]

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