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Thermo- and Photostimulated Currents in Bioequivalent Liquid Crystalline Structures

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Voltage-current characteristics are reported for several bioequivalent structures with liquid crystalline ordering. Measurements were carried out at different temperatures with or without irradiation by UV light. Three types of structures were studied: (1) a liquid crystalline mixture of Schiff bases (MBBA+EBBA), (2) a eutectic mixture of liquid crystalline cyanobiphenyls, and (3) non-saturated long chain carboxylic acids (e.g., oleic). For systems (1) and (2), characteristic local minima on current-temperature curves were observed, with corresponding temperatures decreasing at higher voltages. Tentative mechanisms are discussed in terms of thermoactivation of traps and liquid crystalline ordering. For systems (1) and (3), thermostimulated currents were clearly increased under the influence of UV-irradiation. This phenomenon was completely absent with system (2), which suggested a possibility of interpretation in terms of bioequivalence of liquid crystalline structures.

Keywords: liquid crystals, bioequivalent structures, conductivity, photo-stimulated current.

INTRODUCTION

The creation of artificial materials which would, to some extent, imitate biological tissues as to their structure and response to external factors, has been a problem of current interest. Specifically, great attention has been paid to artificial structures modeling biological membranes^[1]. Such structures are prepared, speaking in general terms, by formation between the substrates

(electrodes) of an ordered film consisting of a certain number (from one to several hundred) of layers formed by anisometric molecules. Such layers can be applied using various methods (e.g., Langmuir-Blodgett technique, vacuum deposition, etc.). Among the examples are bioequivalent sensors of odor, taste, humidity, concentration of certain ions or substances in a solution, etc., prepared on the basis of synthetic bilayers^[2-4]. Recently it has been shown^[5,6] that thin layers of certain substances in the liquid crystalline state can be used as model bioequivalent objects sensitive to small (< 1 R) doses of ionizing radiation. In this case, the radiation response mechanism was related not to the irreversible chemical destruction of the molecules, but to reversible changes of the molecular structure (e.g., cis-trans transitions). The radiation sensitive material which was used for the same purposes in^[7] was a thin layer of lithium stearate applied to the metal substrate by means of vacuum deposition; small dose gamma-irradiation led to a sharp increase of the thermostimulated current.

Thin (20 mcm) layers of long-chain non-saturated fatty acids were used in^[8]. The layers were formed by capillary drawing from the melt between metal electrodes; the authors claimed that elements of liquid crystalline ordering were inherent for such a structure. After irradiation by thermal neutrons^[9], this structure showed a marked increase of electrical conductivity accompanied by narrowing of the hysteresis loop on the voltage-current curve; partial relaxation to the initial state was observed after several hours. Our studies were aimed at clearing up the character and nature of electrical conductivity in several potentially bioequivalent organic systems with liquid crystalline or liquid crystal-like ordering. For these systems, voltage-current characteristics were measured at different temperatures with or without irradiation by UV-light.

EXPERIMENTAL

The systems of three types were studied:

- (1) liquid crystalline mixture of Schiff bases, namely eutectic mixture of 4-methoxy-benzylidene-4'-butylaniline (MBBA) and its ethoxy homologue

(EBBA), for which reversible changes of molecular configuration (trans-cis-transitions) had been observed under small doses of ionizing radiation^[5,6] and UV light^[10];

(2) eutectic mixture of liquid crystalline 4-alkyl- and 4-alkoxy-4'-cyano-biphenyls, which was used as a standard reference liquid crystalline system;

(3) non-saturated long-chain carboxylic acids (namely, oleic), which is a substance of biological origin and for which some features of liquid crystalline ordering and radiation-stimulated response were observed under certain conditions^[9,10].

Schematic drawing of the experimental setup and the measurement cell is shown in Fig.1.

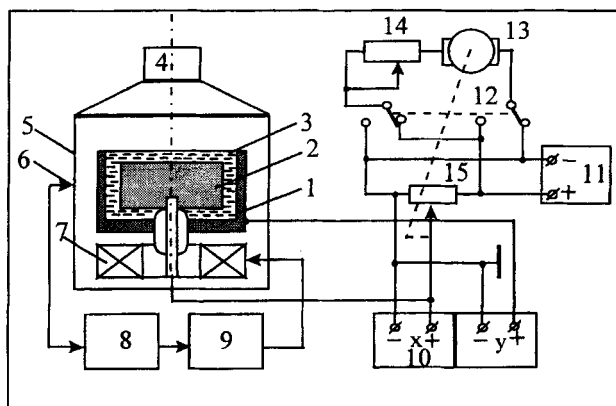


FIGURE 1. Schematic drawing of experimental setup and the measurement cell.

The cell contains cylindrical hollow electrode 1 made of brass, inside which the second electrode 2 (another brass cylinder of smaller size) is placed. The space between the electrodes is filled with the tested substance 3 (a viscous liquid or liquid crystal). The measurement cell is placed inside the chamber 5, with source of radiation 4 mounted above the upper (opened) part of the cell. Heater 7 is installed below the lower part of the cell, with programmed temperature control in the chamber effected using thermocouple 6, temperature controller 8 and power amplifier 9. The signal related to the

cell current was recorded by a two-coordinate chart recorder 10, and the voltage applied to the cell came from power source 11.

Voltage-current characteristics could be measured both in manual and automatic modes. In the latter case, the applied voltage was controlled by potentiometer 15, which is rotated through a reduction gear by electric motor 13. The motor rotation rate and hence the rise and decay times of the current were set by potentiometer 14. The setting for voltage increase or decrease was made by switch 12.

RESULTS AND DISCUSSION

In Fig.2-4 the measured values of current under different applied voltages are shown as functions of temperature, which, apart of its conventional role in the conductivity processes, determined the phase state of the substance in the measurement cell.

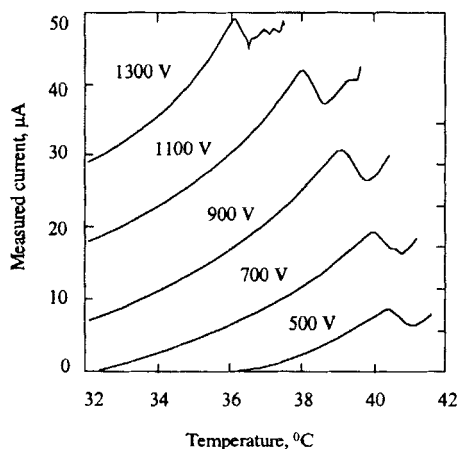


FIGURE 2. Temperature dependence of the measured current under different applied voltages for MBBA-EBBA mixture

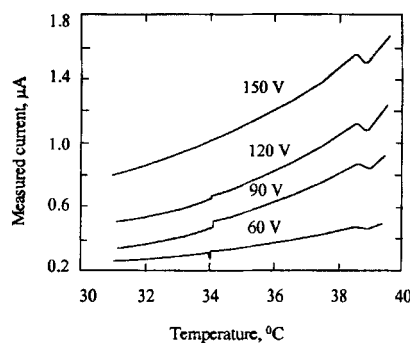


FIGURE 3. Temperature dependence of the measured current under different applied voltages for the cyanobiphenyl mixture.

A characteristic feature was observed on the $I(t)$ curves, which was especially clear with the MBBA+EBBA mixture (Fig.2). The temperature at which this splash of the current is observed becomes higher under lower voltages, and the splash itself becomes less marked, practically disappearing below 100 V. This is the case for the cyanobiphenyl mixture (Fig.3), where, due to its low breakdown voltage, higher voltages could not be used. At the same time, even under 1300 V no similar features were noted for the oleic acid (Fig.4).

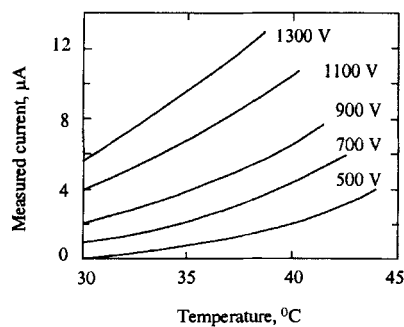


FIGURE 4. Temperature dependence of the measured current under different applied voltages for the oleic acid

Comparing the temperatures of the observed or expected current splash with phase transition temperatures of the substances studied (nematic-

isotropic transition temperatures are 61.5 C and 59 C, respectively, for MBBA+EBBA and the cyanobiphenyl mixture, while for oleic acid the melting temperature to a presumably isotropic liquid is 13.4 C), one may use two different ways of reasoning. Really, the observed features may be related to the liquid crystalline ordering with some peculiar structural or phase transformation occurring under combined action of voltage and temperature (the higher is voltage, the lower are temperatures which are required to initiate the transformation). This is strongly supported by the absence of the current splashes with oleic acid which, at the temperatures used, is expected to be an isotropic liquid. From the other point of view, mechanisms more typical for organic semiconductors, like those involving thermoactivated traps, could also contribute.

Voltage-current characteristics for MBBA+EBBA mixture are shown in Fig.5. Characteristic hysteresis loop similar to that reported in^[8,9] was noted. Small but clearly distinct increase of the measured current values was observed under irradiation by UV light, which could be considered similar to that reported in^[9] as an effect of ionizing radiation. The observed behavior was generally similar to the other two substances studied, with the effects observed being less marked with oleic acid and practically absent for the cyanobiphenyl mixture. This result, however preliminary, can be considered as a supplementary argument supporting the idea of^[5,6] to use liquid crystalline azomethine systems as model bioequivalent objects sensitive to radiation factors.

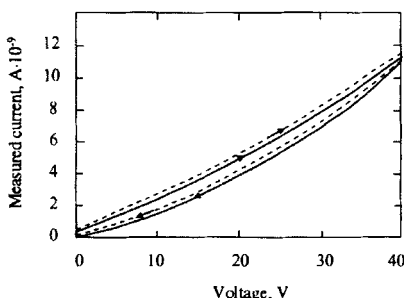


FIGURE 5. Voltage-current characteristics for MBBA-EBBA mixture at 20 C with (dashed line) and without (solid line) irradiation by UV lamp.

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