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Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

To cite this article: Olaf Karthaus, Takeo Koito, Norihiko Maruyama & Masatsugu Shimomura (1999): Mesoscopic Patterns of Polythiophenes for Electronic Applications, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 327:1, 253-256

To link to this article: http://dx.doi.org/10.1080/10587259908026826

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Mol. Cryst. Liq. Cryst., 1999, Vol. 327, pp. 253-256
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Mesoscopic Patterns of Polythiophenes for Electronic Applications

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(Received July 9, 1998; In final form July 31, 1998)

Ordered arrays of micron-size (i.e. mesoscopic) lines of conducting polymers can be deposited from solution by a simple casting process. The arrays were characterized by optical microscopy and AFM and the darkconductivity and photoconductivity of single poly(3-hexylthiophene) lines was measured by using microelectrodes. Doping with iodine leads to an increase of the darkcurrent.

Keywords: poly(3-hexylthiophene); mesoscopic pattern; electric conductivity; photoconductivity; microelectrode

INTRODUCTION

The concepts of supramolecular chemistry can be successfully implemented for molecular assemblies with electrical and/or optical functions. It could be shown that the ordered molecular arrangement in Langmuir Blodgett films, self - assembled monolayers or liquid crystals can be used for directional electric conductivity[1] and other transport processes. In these cases, the conductivity was measured with at least millimeter-sized electrodes, thus averaging conductivity on a macroscopic scale . Other work focusses on the measurement of conductivity on the single molecular scale[2] and the observation of quantum-size effects on electrical properties. There, only rigid conductors, like carbon nanotubes can be imaged.

Here we show the possibility for measuring the electric properties of conducting polymers in the mesoscopic scale, i.e. an intermediate size range

of a few micrometer. When cast from dilute solutions many polymers are known to form regular patterns on surfaces.[3]-[5] The origin of these patterns are convective processes in the solution that lead to instabilities at the edge of the solution droplet and to the deposition of the polymer stripes in an orderly fashion.[6]

RESULTS AND DISCUSSION

By casting a 20 mg/l $CHCl_3$ solution of regioregular poly(3-hexylthiophene) (PHT) (Aldrich), [7] onto freshly cleaved mica, or onto cover glass slides (Matsunami, NEO, Japan) line structures can be prepared. Fig. 1a shows a fluorescence micrograph (ex:510-550 nm, em:>600 nm) of such an array of lines, each of the lines is ca. 10 μm wide and several 100 μm long. The thickness, determined by AFM, is 20 nm. Absorption- (three peaks at 520 - 620 nm) and emission spectra (max. at 640 nm) of the pattern are the same as for homogeneous cast films, reported in the literature.[7] It is possible to make an electric contact of a single line by placing a droplet of Ag-paste (DOTITE, Fujikura Kasei, Japan) at one end of the lines and using a micromanipulator-positionned microelectrode (Tungsten, 1 μm tip, 0.5MΩ impedance, World Precision Instruments) as the opposite electrode (Fig.1b). The setup is then illuminated with actinic light (510-550 nm) and the dark- and photoconductivity (direct current from 0 V to 230 V) are recorded by using an electrometer (Advantec).

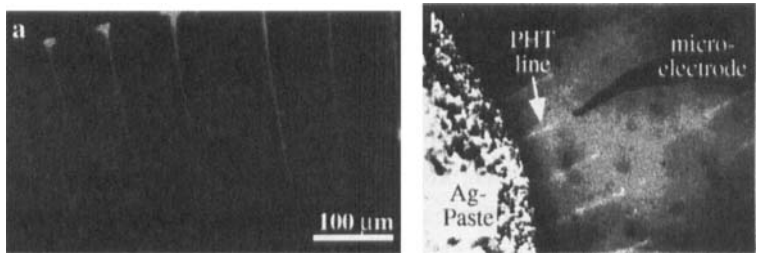

FIGURE 1 Fluorescence micrograph of a line pattern of PHT on mica (a). Optical micrograph of a single PHT line on glass connected by Ag-paste and a microelectrode (b).

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The graphs in Fig. 2a and 2b show the ohmic response of the dark conductivity of a single PHT line. The response is very fast and after an initial overshooting of the current, due to charging of the electrodes, a stable darkcurrent is obtained. Also the photocurrent (Fig. 2c) shows a fast response towards illumination. After less than 10 s a stable current is obtained. The decay of the photocurrent after switching of the light seems to consist of two components, with a decay time of a few seconds and a few minutes, repectively. The origin is not clear yet, but it might be due to a low carrier mobility in the PHT sample. Fig. 2d shows the I-V characteristics of the sample. Both dark- as well as photocurrent show a linear behaviour. From the cross section of the line (measured by AFM to be 0.1 μm^2) a current density of 25 $nA/\mu m^2$ (at 90 V and a gap of 20 μm) can be calculated.

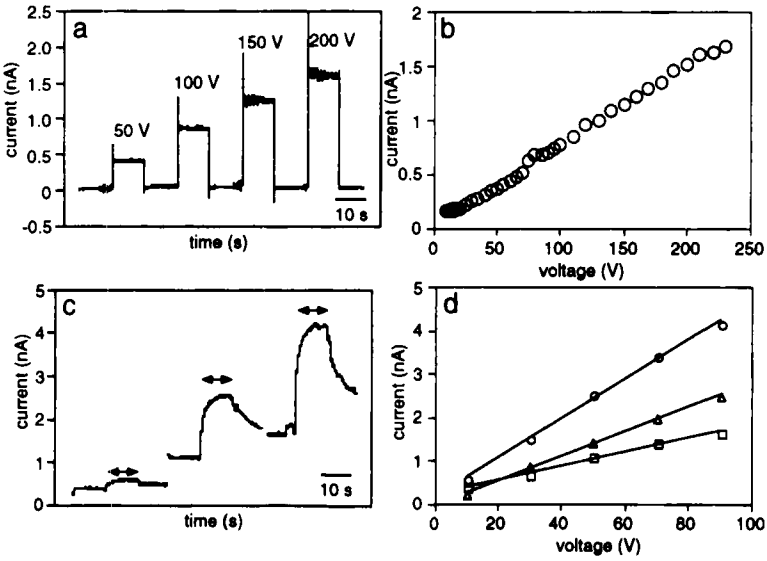

FIGURE 2 Time course of the darkcurrent of a single PHT line at various voltages (a). Current-voltage dependence of darkcurrent (b). Time course of the current of a single PHT line at various voltages. The arrow indicates the illumination period (c). Current-voltage dependance of total current (o), photocurrent (Δ) and darkcurrent (□) (d).

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Doping of the PHT with iodine vapour increases the dark conductivity by a factor of 20 -40. In these experiments, the darkconductivity of a single line was measured. Then the sample was subjected to iodine vapour for 1 min and replaced under the microscope.After contacting the same line at the same position by using the microelectrode, the darkcurrent was measured again. Table 1 shows the voltage dependance of the darkconductivity of the undoped and doped line.

TABLE I Conductivity of undoped and iodine-doped poly(3-hexylthiopene)

Voltage (V)	Darkcurrent (nA) before doping	Darkcurrent (nA) after doping
30	0.070	1.49
50	0.091	2.63
70	0.107	3.94
90	0.119	5.44

CONCLUSIONS

We could show that the photofunctional poly(3-hexylthiophene) forms oriented line structures upon casting from dilute solution. The size of the lines is in the micrometer range and the conductivity of single lines could be measured.

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