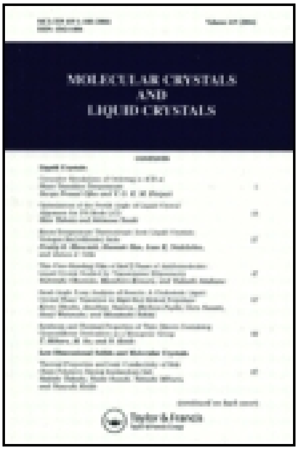

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Electrical Properties of Polypyrrole and Poly N-Methylpyrrole Organised in Manganic-Stearate Template in Langmuir Blodgett Films

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Electrical Properties of Polypyrrole and Poly *N*-Methylpyrrole Organised in Manganic-Stearate Template in Langmuir Blodgett Films

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The electrical properties of Langmuir-Blodgett (LB) films of polypyrrole and poly N-methylpyrrole fabricated on a manganic stearate template in the LB film has been studied. The LB films of polymer exhibit domains of highly organised two dimensional linear array of polymer granules sandwiched between insulating fatty acid layers along with some disorganised domains. Measured in-plane conductivity of polypyrrole and poly *N*-methylpyrrole are 1.5 S/cm and 0.012 S/cm with thermal activation energy 0.08 eV and 0.214 eV respectively. The transverse conductivity is 10^{-10} S/cm and 10^{-12} S/cm for polypyrrole and poly *N*-methylpyrrole respectively showing a high degree of anisotropy in both the LB films.

Keywords: Organised conducting polymers; Langmuir-Blodgett films; polypyrrole; poly *N*-methylpyrrole

INTRODUCTION

In the last decade the discovery that the electrical conductivity of polymers can be controlled over the insulating to the metallic range has led to substantial efforts to prepare conducting polymer for technological applications [1]. Of the many conducting polymers identified so far polypyrrole and its derivatives have been studied extensively [2–6] because of their high conductivity and environmental stability.

The use of LB technique to deposit ultra thin anisotropic conducting polymer films exhibit great promise in microelectronics and molecular electronic devices as the molecular architecture and superstructure of suitably modified polymers in such films can be controlled to achieve desired network for the device application. In our earlier work [7] this was done by organising the $FeCl_3$ molecules between fatty acid layers in the LB film which initiated the polymerization of pyrrole impregneted in the film by exposing it to pyrrole vapour. In the present work we use the same technique but a different initiator to fabricate the organised assemblies of polypyrrole and poly *N*-methylpyrrole and examine if the organization and the electrical properties of the LB film are significantly affected by the initiator used. The method involves deposition of manganic chloride within the planes of fatty acid multilayers by exposing a LB film of manganic stearate to hydrogen chloride gas. This on subsequent exposure to pyrrole and *N*-methyl pyrrole vapour leads to the formation of respective polymers. Comparing with our previous work [7, 8, 9] it is observed that manganic chloride is a better initiator than $FeCl_3$ and $CuCl_2$ and it takes shorter polymerization time. Here we have centered our investigation to the electrical and structural characterization of these polymers within fatty acid multilayers in LB film. In the case of unsubstituted pyrrole the chain is formed via σ, σ coupling, giving a linear polymer. A planar conformation allows for the highest overlap of orbitals along the conjugated system. Molecular orbital calculation indicate that the substitution of nitrogen bonded hydrogen atom with an alkyl substitution forces the chain out of planarity by twisting the monomer units relative to one another. This chain distortion decreases the mobility of charge carriers on the chain by decreasing conjugation, inhibits interchain interaction and ultimately causes a decrease in conductivity [10]. This decrease in conductivity and increase in activation energy is observed in our experimental results as we go from polypyrrole to poly *N*-methyl pyrrole.

EXPERIMENTAL

Pyrrole and N-methyl pyrrole (99% Aldrich) were purified before use by distillation in nitrogen atmosphere. Other chemicals were used as supplied. For Langmuir-Blodgett film deposition we used a Joyce-Loebl (UK) LB trough, model 4, Manganous stearate was prepared first by double decomposition of manganous chloride and sodium stearate solution. The prepared mangnous stearate was then oxidized by $KMnO_4$ to get manganic stearate [11]. Manganic stearate was dissolved in chloroform (0.1 mg/ml). This solution was spread on the surface of high purity water (from milli-Q-plus system of Millipore U.S.A.). The film was compressed to a pressure of 35 mN/m. The compression rate was 2 A^{02}/molecule/sec. The snuff coloured manganic stearate multilayers were deposited on hydrophobic glass and ITO coated glass by Y type deposition. After proper drying the film was then exposed to HCl vapour for a few minutes and then kept exposed to pyrrole/*N*-methylpyrrole (or their mixture) monomer vapour (for 15 hours in pyrrole and for 30 hours in *N*-methyl pyrrole vapour). The respective monomer molecules diffuse into the multilayer and react with manganic chloride to give polypyrrole and poly *N*-methyl pyrrole. Pyrrole reacts faster than *N*-methyl pyrrole with $MnC1_3$. Polymerization time for polypyrrole is shorter than for poly *N*-methyl pyrrole. The film is then dried in a desiccator for another day. Schematic representation of polymer formation (a) and organization in LB film (b) are shown in Figure 1.

Scanning electron micrographs of the film surface were taken in a Hitachi scanning electron microscope model S-415 A. In-plane conductivity was measured by four probe method. Point contacts were made with silver paste. For transverse measurements, conducting ITO coated glass and silver electrode were used. For temperature dependence studies the substrate with LB film was placed in a suitably designed chamber [12] in which the substrate could be maintained at any desired temperature in the range 200–400°K by regulating a local heater in combination with liquid nitrogen. The temperature was measured with copper-constantan thermocouple stuck to the substrate and a digital panel meter (model HIL 2301, India). The thickness of the film was measured with the help of a surfometer by mechanical stylus method.

RESULTS AND DISCUSSION

Pressure-Area (π-A) Isotherm of Monolayer in the Subphase

The manganic stearate films spread on the water subphase exhibited a pressure area (π-A) isotherm closely resembling that of copper stearate [9]. In Figure 2 we show the (π-A) isotherm of manganic stearate. In the condensed phase, the area per molecule is 50 Å [2].

In Figure 3 we show area-vs-time plot for the film. The result show that initially the film is unstable but finally attains stability at longer time. The transfer ratio is close to unity and proper alignment of manganic stearate molecules in the film is achieved.

Scanning Electron Micrograph

In Figure 4 (a, b, c) we show the scanning electron micrographs for polypyrrole and poly *N*-methyl pyrrole LB films. The micrographs reveal dense packing with spherical granules, a feature characteristics of polypyrrole film [7]. This

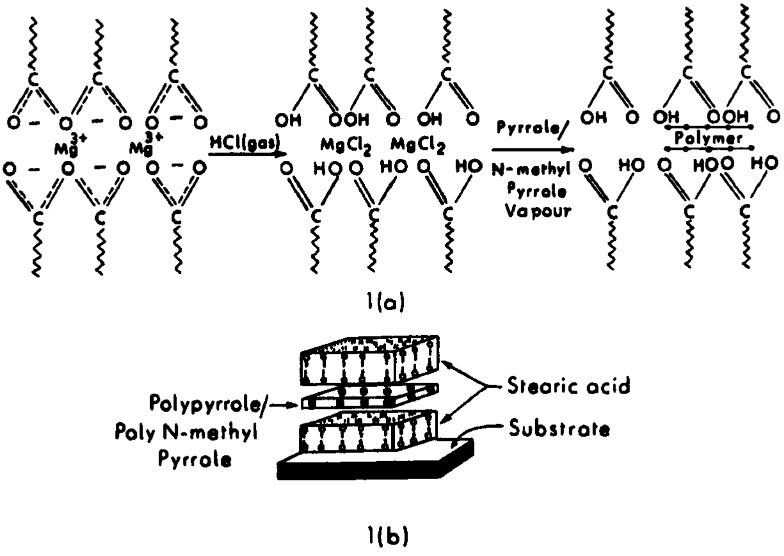

FIGURE 1 Schematic representation of (a) polymer formation by chemical modification of manganic stearate multilayers and (b) the mode of stacking of polymer on a substrate.

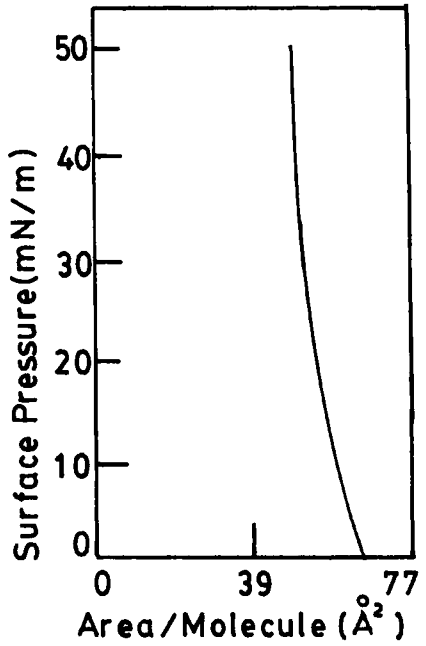

FIGURE 2 Surface pressure-area/molecule (π-A) plot of manganic stearate.

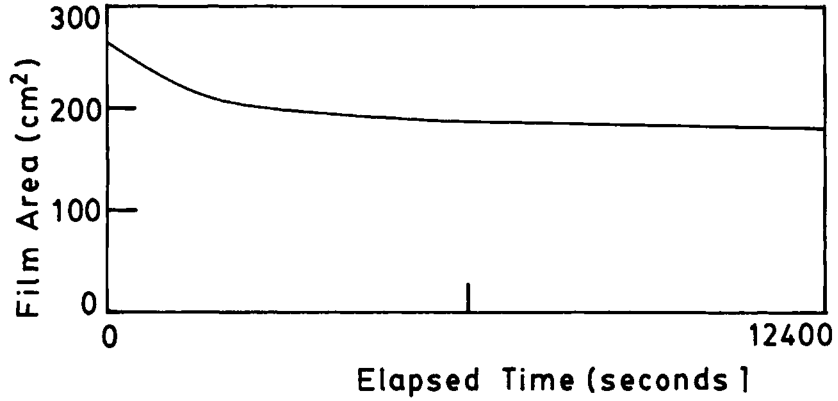

FIGURE 3 Area vs time plot for manganic stearate monolayer film.

property has been extensively utilized to coat semiconductors and photocells as polypyrrole forms an impermeable membrane over a substrate (unlike polyethylenes, which have a fibrillar structure and cannot be deposited as an impermeable coating) [7]. The grain size as calculated from scaling shown in the micrographs taking into consideration the respective magnification factors is of diameter 11 A° for polypyrrole and 242 A° for Poly *N*-methyl pyrrole films. From the micrograph (4a) it is observed that the polypyrrole LB film shows a very good two dimensional organization as expected in the LB film deposition methodology we have used. Unfortunately such organisation is not uniform through out the film. In some other areas of the same film as shown in Figure 4b, no such organisation is observed. The LB film fabricated by us thus consists of domains of organised and disorganised conducting polypyrrole granules. SEM of *N*-methylpyrrole reveal dense packing but no linear organisation is observed.

ELECTRICAL PROPERTIES OF THE LB FILMS

The electrical properties of polypyrrole and poly *N*-methyl pyrrole LB films (31 layers on hydrophobic and ITO coated glass) have been studied. Four probe technique has been used for in-plane conductivity measurement. Transverse conductivity has been measured by standard sandwich cell technique. In-plane conductivity is 1.5 S/cm and 0.012 S/cm for polypyrrole and poly *N*-methyl pyrrole respectively. Current-Voltage characteristics (Fig. 5) shows

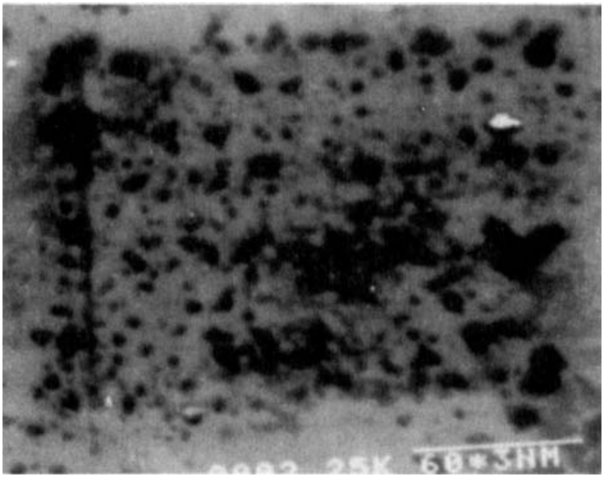

FIGURE 4 (a) Scanning electron micrographs at 15 K of polypyrrole LB film. (Magnifcation 2000x): a specific domain.

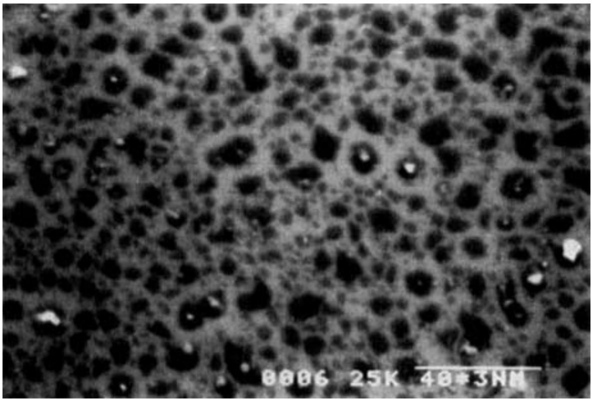

FIGURE 4 (b) SEM at 15 K of polypyrrole LB film (magnification 2000x): a different domain from that in Fig. 4(a).

linear behaviour for in-plane conduction for both the films. In-plane conductivity does not show any anisotropy. This is also reflected in the SEM pictures where some disorganized array along with some organized domains are observed in the LB films. Transverse conductivity is 10^{-10} S/cm and 10^{-12}

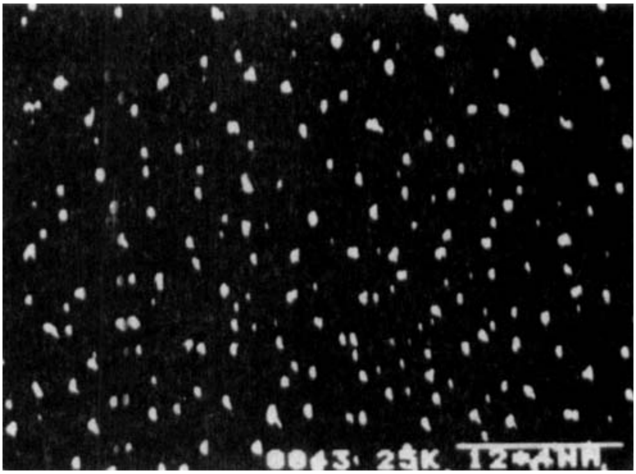

FIGURE 4 (c) Scanning electron micrograph at 15 K of poly-*N*-methylpyrrole (magnification 250x).

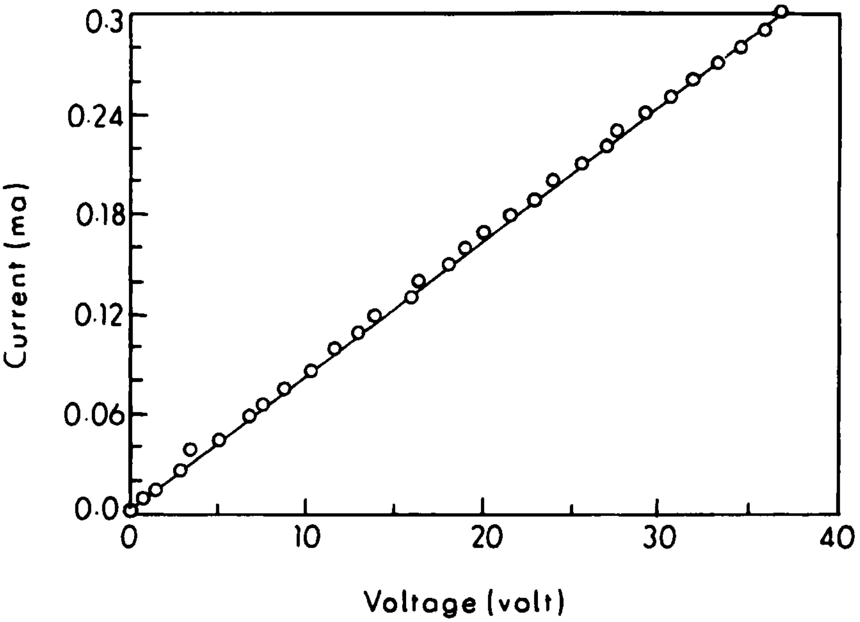

FIGURE 5 In-plane current-voltage (I-V) characteristics for polypyrrole film.

S/cm for polypyrrole and poly *N*-methyl pyrrole respectively. So, the electrical anisotropy between in-plane and transverse conductivity of these films are 10^{10}, which is usual for LB films of polyheterocyclics within fatty acid layers [7, 8, 9].

We have studied the temperature dependence of conductivity. Log σ vs 1/T plots (Fig. 6) show that the films show semiconducting behaviour and there is decrease in conductivity and increase in activation energy as we go from polypyrrole to ploy *N*-methyl pyrrole. The values of the specific conductivity and the activation energy for polypyrrole and ploy *N*-methyl pyrrole are listed in Table I. The low conductivity in poly *N*-methyl pyrrole compared to that in polypyrrole may arise from relative twisting of the pyrrole rings out of planner arrangement expected for the unsubstituted pyrrole rings [13, 14, 15, 16, 17]. This twisting occurs because of steric interaction between the methyl group on one ring and hydrogen atoms of the neighbouring rings. This reduces the overlap of the electron orbitals along the chain and leads to the decrease in the effective conjugation. The electrical conduction in doped polypyrrole system has been thought to be due to variable range hopping of charge carriers. On the basis of the concept of phonon assisted hopping between localized states, the conductivity σ is related to the temperature T by

$$\sigma \equiv \sigma_0 \exp(T/T_0)^{1/\gamma}$$

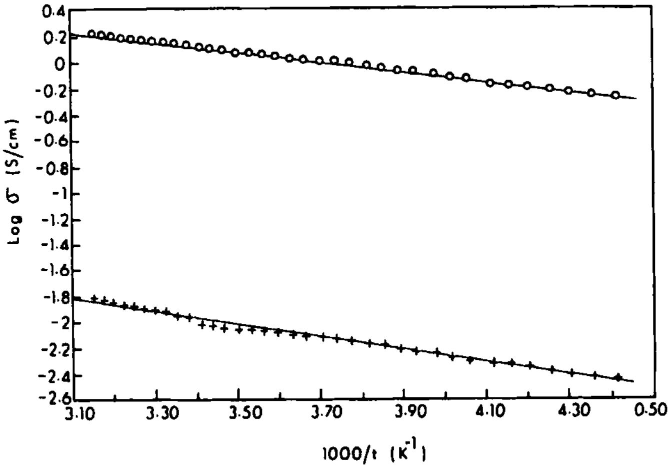

FIGURE 6 (a) Log σ vs T^{-1} plot (0) for polypyrrole (+) for poly *N*-methyl pyrrole.

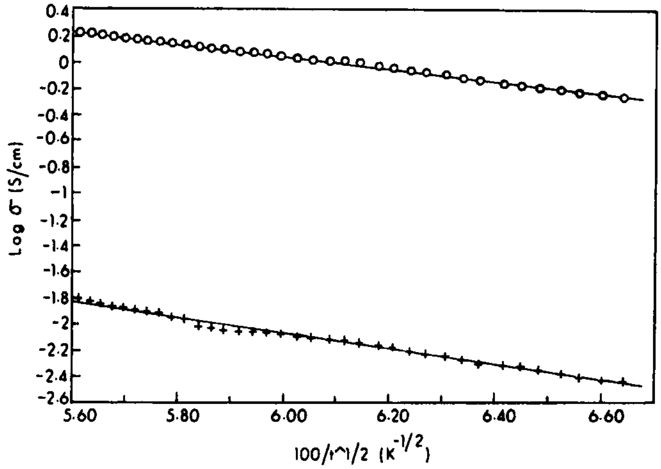

FIGURE 6 (b) Log σ vs $T^{-1/2}$ plot; (0) for polypyrrole film, (+) for poly *N*-methyl pyrrole.

TABLE I Specific conductivity and activation energy of the Polymers in LB films

Polymer in the LB film	*In-plane Conductivity* $S\ cm^{-1}$	*Activation Energy (eV)*
Polypyrrole	1.5	0.08
Poly *N*-methyl pyrrole	0.012	0.214

where γ depends on the dimension of hopping. γ is 2,3,4 for one, two and three dimensional hopping respectively. In the LB film γ is likely to be 2 or 3. We have plotted Log σ vs $1/T^{\gamma}$ where $\gamma = 2, 3$ to examine if one or two dimensional hopping is the conduction mechanism in the LB films. In Figure 6 standard semiconduction plots of log σ vs $1/T$ is presented. This plot and also the plots for log vs $1/T^{1/2}$ and log σ vs $1/T^{1/3}$ exhibit good linearity. In fact the standard error coefficient for the three plots are .003 and .009 for $1/T$ 0.004 and 0.01 for $1/T^{1/2}$ and 0.006 and 0.015 for $1/T^{1/3}$ for polypyrrole and poly *N*-methyl pyrrole respectively. So it seems that for $T^{-1/2}$ and T^{-1} plots, the fit is better than that of $T^{-1/3}$ plots. These results suggest that one dimensional variable range hopping (VRH) model is applicable for charge transport in our LB films. However, the proportionality of log vs $1/T^{1/2}$ also corresponds to other possible transport models such as three dimensional hopping in Coulomb gap [18] and charging energy limited tunneling between highly conducting grains of variable sizes [19]. A linear log σ vs $1/T$ dependence may indicate the applicability of standard band model for semi conduction in LB films with the slopes giving activation energy. The measured value of activation energy for polypyrrole is 0.08 eV and for poly N-methylpyrrole it is 0.214 eV.

It is to be pointed out that a linear log σ vs $1/T$dependence also arises from nearest neighbour hopping of charge carriers in weakly conducting materials. However, it has generally been established that the conduction mechanism in polypyrrole system is VRH. It then becomes likely from log σ vs $T^{1/2}$ plots that in these LB assemblies one dimensional VRH is the mechanism of charge conduction.

Acknowledgements

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References

[1] T. Skotheim, *A handbook of conducting polymers*, Vol I & II, (Dekker, New york, 1988).
[2] D. Bloor, A. P. Monkman, G. C. Stevens, K. M. Chenng and S. Pugh, *Mol. Cryst. Liq. cryst.*, **187**, 231 (1990).
[3] K. M. Chenng, D. Bloor and G. C. Stevens, *Polymer*, **29**, 1709 (1988).
[4] A. F. Diaz and K. K. Kanazawa, *Extended linear chain compounds*, Ed. J .S. Miller, (Plenum, New york, 1983), **3**, p. 417.
[5] G. Tourillon and F. Garnder, *J. Electroanalyt. Chem.*, **135**, 173 (1982).
[6] M. Saton, K. Kaneto and K. Yashino, *J. Appl Phys.*, **23**, L-875 (1984).
[7] D. Sarkar, A. Paul and T. N. Misra, *Thin Solid Film*, 227 105 (1993).
[8] A. Paul, D. Sarkar and T. N. Misra, *Solid State Communication*, **89**(4), pp. 363–367.
[9] A. Paul, D. Sarkar and T. N. Misra, *J. Of. Physics D.*, (in press).
[10] J. R. Reynold, P. A. Poropatic and R. L. Toyooka, *Macromolecules*, **20**(5), 958 (1987).
[11] B. Mallik, A. Ghosh and T. N. Misra, *Bull. Chem. Soc. Jpn.*, **52**, 2091 (1979).
[12] A. O. Patil, A. J. Heeger and F. Wuld, *Chem. Rev.*, **88**, 183 (1988).
[13] K. K. Kanazawa, A. F. Diaz, M. T. Krounbi and G. B. Street, *Synth. Metals*, **4**, 119 (1981).
[14] J. R. Reynolds, P. A. Poropatic and R. L. Toyoka, *Macromolecules*, **20**, 958 (1987).
[15] G. B. Street, S. E. Lindsey, A. I. Nazzat and K. J. Wynne, *Mol. Cryst. Liq. Cryst.*, **118**, 137 (1985).
[16] G. R. Mitchell, F. J. Davis and M. S. Kiani, *J. Polymer*, **23**, 157 (1990).
[17] A. I. Nizzal, G. B. Street and K. J. Wynne, *Mol. Cryst.Liq. Cryst.*, **125**, 303 (1985).
[18] P. Sheng and J. Klafter, *Phys. Rev. B.*; **27**, 2583 (1983).
[19] A. L. Efros and B. J. Shkolvskii, *J. Phys. C.*, **8**, L 49 (1975).