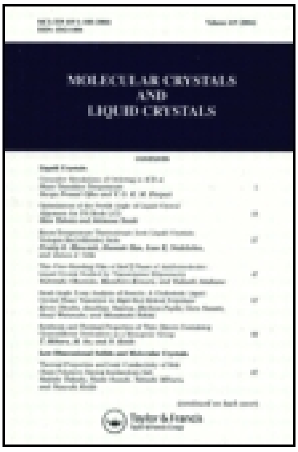

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Evidence of Room Temperature Charge-Density Wave Behavior and Glass-like States in Pressed Pellets of Lightly Doped Poly (3-methyl thiophene)

V. M. Souza [a] , L. Walmsley [a] , A. A. Correa [b] , E. C. Pereira [b] & A. L. Gobbi [c]

[a] Departamento de Física, IGCE-Universidade Estadual Paulista, C. P. 178, Rio Claro, S.P., CEP 13500-970, Brazil

[b] CMDMC-LIEC Departamento de Química, Universidade Federal de S. Carlos, CP 676, São Carlos, SP, CEP 13565-905, Brazil

[c] Laboratório Nacional de Luz Sincroton, C.P. 6192, Campinas, S.P., CEP 13084-971, Brazil

Version of record first published: 29 Oct 2010

To cite this article: V. M. Souza, L. Walmsley, A. A. Correa, E. C. Pereira & A. L. Gobbi (2002): Evidence of Room Temperature Charge-Density Wave Behavior and Glass-like States in Pressed Pellets of Lightly Doped Poly (3-methyl thiophene), Molecular Crystals and Liquid Crystals, 374:1, 119-124

To link to this article: http://dx.doi.org/10.1080/10587250210435

Mol. Cryst. Liq. Cryst., Vol. 374, pp. 119-124

1058-725X/02 $12.00 + .00

Evidence of Room Temperature Charge-Density Wave Behavior and Glass-like States in Pressed Pellets of Lightly Doped Poly (3-methyl thiophene)

V. M. SOUZA[a], L. WALMSLEY[a], A. A. CORREA[b], E. C. PEREIRA[b] and A. L. GOBBI[c]

[a]*Departamento de Física, IGCE-Universidade Estadual Paulista C. P. 178 - CEP 13500-970 - Rio Claro - S.P. - Brazil,*
[b]*CMDMC-LIEC Departamento de Química, Universidade Federal de S. Carlos, CP 676, CEP 13565-905 - São Carlos - SP - Brazil and*
[c]*Laboratório Nacional de Luz Síncroton, C.P. 6192, CEP 13084-971, Campinas - S.P. - Brazil*

We show room temperature charge-density wave (CDW) characteristics in d.c. and a.c. electric data in pressed pellets of lightly doped poly(3-methylthiophene). The possibility of a Peierls glass is discussed and metastables states are observed. D.C. and A.C. data also show a state with negative differencial resistance.

Keywords: conducting polymers; charge-density waves; metastable states; Peierls glass; negative differential resistance.

INTRODUCTION

Conjugated polymers are quasi one-dimensional systems in which dimerization takes place, leaving the system an insulator . Upon doping, charged defects are created, and for moderate doping levels, the system undergoes a metal-insulator transition [1] and conduction takes place mainly due to the overlap of the charged defects. In lightly poly(3-methylthiophene) the stable defects, the polarons, are localized and the system has a very large electrical resistivity because the only expected conduction mechanism is inter-polaron hopping. . But, as discussed by

Kivelson and Emery [2] the undoped state of a conjugated polymer is a charge-density wave (CDW) state or a Peierls insulator. Upon doping, a Peierls glass is expected, with the longe range order being replaced by short range order [2,3].

In this work we report room temperature CDW electrical behavior in lightly doped poly(3-methylthiophene). But, due to the disorder introduced by the anions, those states are metastable and the system can be driven from one metastable state to another with the application of bias, in a not well controlled way. Negative differential resistance has been observed in some of these states.

EXPERIMENTAL

The samples were electrochemically synthesized and reduced as previously described [4]. The final value of V_{oc} =0.5 V (sample A) and V_{oc} =0.35 V(sample B). After the reduction, the polymeric sample was scrapped and the resultant powder was uniaxially pressed to form a pellet (6.2 kbar). The dimensions of the sample are radius r=2mm and thickness 375μm (sample A) and 324 μm (sample B). Gold contacts (r=1.5mm and thickness 150 nm) were deposited by sputtering on both faces of the samples kept at a temperature of 300 K. D.C. measurements were performed using a Keithley 617 electrometer/source and A.C. data were collected using a Solartron 1260A Impedance Analyzer.

Figure 1 shows the room temperature Vx I data for sample A (squares) and sample B (circles). The solid lines show the very good fitting obtained using the expression characteristic of quantum tunneling depinning of a charge-density wave [5], $I= G_{cdw}V\exp(-V_0/V) + G_M V$

where G_{cdw} is the CDW conductance, G_M is the metallic conductance

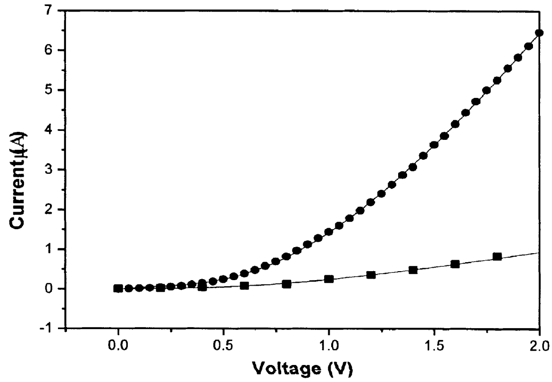

FIGURE 1 - VxI data for sample A (squares) and B (circles). Full lines is the fitting using $I=G_{cdw}V\exp(-V_0/V)+G_MV$

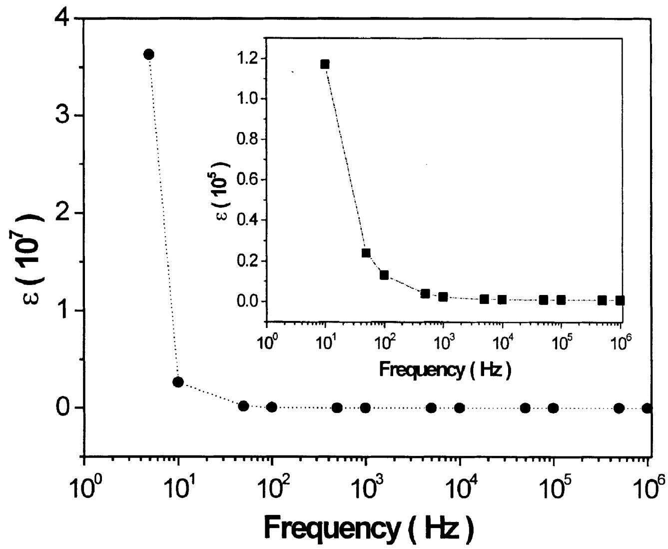

FIGURE 2 Room temperature dielectric constants for sample A (squares) and sample B (circles).

and V_0 is the Zener voltage. We obtained G_{cdw}=8.99x10^{-7} mho for sample A and 7.66 x 10^{-6} mho for sample B, G_M=6.02 x10^{-8} mho for sample A and 3.34 x 10^{-7} mho for sample B. V_0 are 1.28 V for sample A and 1.95 V for sample B. The smaller value of CDW conductance for sample A compared with sample B may be due to the increase of pinning centers with high doping level.

Figure 2 shows the dielectric constant *versus* frequency for sample A (inset) and sample B. The huge values observed at low frequencies are a signature of CDW behavior [6]. Due to the doping anions, this CDW state is in fact a metastable state and the system can be driven from this state to another metastable state with application of bias. Figure 3 shows the room temperature V-I curve for sample A in another state in which the sample was unintentionally left, probably due to the application of bias. This state is characterized by a very high threshold field, characterist of low screening. An increase of five orders of magnitude is suddenly observed at this threshold and although showing oscillations, a negative current-voltage characteristic is observed. This behavior was not observed when the voltage was decreased. Decreasing the voltage we observed steps in the V-I curve and no oscillations, with the values of current showing high stability even in the picoamperes range. The irreversible behavior of the V-I curve suggests that polarizations effects are important as observed in conventional CDW systems in the low screening case (low temperatures) [7]. Negative differential conductivity was observed in the CDW system $K_{0.30}MoO_3$ at temperatures below 40K by S. Martin et al [8]. The authors discuss their data in terms of rigid charge-density wave motion.

CONCLUSIONS

We have shown that the non linear behavior observed in pressed pellets of lightly doped P3MT can be explained in terms of quantum tunneling deppining of a CDW. We note that, being a Peirls glass, metastable states are observed, and, due to the lack of screening one of those states can have a high threshold field, which we would like to call E_0^* to make an assossiation with the high threshold fields observed in the conditions of low screening in the conventional CDW systems[7]. The negative differential resistance for this low screening state has some similarities with previous reported experiments on $K_{0.30}MoO_3$ [8] .

ACKNOWLEDGMENTS

This work was partially supported by brazilian agencies FAPESP, CEPID/FAPESP, CNPq and PADCT3/CNPq.

REFERENCES

1- J. Chen, T.-C. Chung, F. Moraes and A.J. Heeger, Solid Ste Commun. **53**, 757 (1985).

2- S. A. Kivelson and V. J. Emery, Synth. Met. **65**, 249 (1994).

3- S. A. Kivelson and V. J. Emery, Synth. Met. **80**, 151 (1996).

4-A.A. Correa, L. Walmsley, L.O.S. Bulhões, W.A. Ortiz, A.J.A. de Oliveira and E.C. Pereira. Synth. Met. 121 (1-3) 1836 (2001).

5-J. Bardeen, Phys. Rev. B **39**, 3528 (1989), and references threin.

6- G. Grüner, Reviews of Modern Physics **60**, 1129 (1988).

7- G. Mihály, T. Chen and G. Grüner, Phys. Rev. B **38**, 12740 (1988).
8- S. Martin, R.M. Fleming and L.F. Schneemeyer, Phys. Rev. B **38**, 5733 (1988).