

## Polyconductivity in polypyrrole: The correlated electron glass

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p-toluensulfonate doped polypyrrole (PPy), undergoes an electric-field induced reversible transition from an insulating state to a highly conductive one. The spatially average field can be as small as 200 V/cm, when the temperature of the sample is below 20 K. The applied electric field leads to a sharp jump in the value of the current to a value which is nearly five orders of magnitude higher than before. When the applied electric field is reduced to below a critical value, the system switches back to a low conductive state. The effect is reversible, symmetric in voltage, and reproducible for different samples. The switching is, we believe, an electronic glass melting transition and it is due to the disordered, highly charged granular nature of PPy.

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Polypyrrole (PPy) samples can be made using a variety of procedures each of which generates a material with different electrical behavior.<sup>1,2</sup> Differences are due to doping and structure at the nano and mesoscopic levels.<sup>3</sup> In 1998 it was observed that p-toluensulfonate (PTS) doped PPy exhibits nonlinear conductive properties at low temperatures when subjected to rather small electric fields.<sup>4</sup> In this paper, we report a drastic increase in the differential conductivity with applied electric field, reaching an apparently “infinite” slope at temperatures of about 20 K with applied average fields lower than 300 V/cm. The origin of the observed anomaly was, at the time, considered to be a puzzle. The experimental data were not extensive enough to clarify the mechanism involved. Although it was suggested that many-body effects can produce such anomalies, it was thought that field heating was the most likely explanation. Here we present the result of interesting experiments carried out in a number of samples of PPy extracted from different synthesised batches. The observations reported here were reproduced using different types of experimental configurations at temperatures down to 4 K. The results clearly show, using nonoptical techniques,<sup>5</sup> the existence of a field-induced metal insulator transition in a disordered conducting polymer. It is worth mentioning that a similar behavior has recently been reported in single walled carbon nanotubes (SWNT's) networks.<sup>6</sup> Even superconductive fluctuations have been reported in SWNT's,<sup>7</sup> this is important in the present context because the possibility of field-induced superconductivity in a highly correlated electron glass was speculatively predicted many years ago<sup>8</sup> by Mattis and Landovitz (ML). The ML theory seems to be the right explanation for the present effect as we shall see in detail below.

PTS doped PPy were obtained by anodic oxidation (0.3 mA/cm<sup>2</sup>) as previously described<sup>9</sup> (films of 0.1 mm

thickness, depending on the polymerization time: typically, 0.11 mm for 16 h electrolysis). dc transport measurements were carried out in a cold finger closed-loop refrigerator (Lake Shore DRC-91C) and by direct immersion in a helium cryostat. The electric contacts were prepared with silver or graphite paste at intervals of about 3 mm in samples of nearly 10 mm long by 4 mm wide. Typical contact resistances less than 1  $\Omega$  were produced at room temperature. Both voltage or current source (Keithley 220 or Keithley 2400) were used while the data was acquired using a Keithley 2000 voltmeter in a four-probe configuration setup. In the current-voltage characteristics, the source output was changed by a very small step size (i.e., 1 mV in experiments with voltage excursions of several volts). This was followed by a settling down time of the order of 3 sec. No time-dependent variations of the results or relaxation process were observed even after the longest experimental runs (nearly 12 h). At room temperatures with  $V < 10$  V/cm (this is the maximum applicable value with no sample degradation), the  $I$ - $V$  relationship is linear. In the very low voltage range and down to temperatures near 40 K, one can if one insists plot the resistivity as an  $\exp[(T_o/T)^{1/3}]$  law. This behavior is reminiscent of a two-dimensional Mott variable range hopping law. However, as explained in great detail in our previous paper, the hopping interpretation would be misleading.<sup>4,10</sup> In fact the resistance is very much non-Ohmic as we go down in temperature. The non-Ohmic behavior starts at very small applied electric fields of a few V/cm. These electric fields are much too small to influence the magnitude of a phonon assisted hop. An exciting effect occurs as we measure the temperature dependence at higher electric fields. The relatively smooth  $\exp(T_o/T)^{1/3}$  behavior develops a sharp insulator to metal “kneelike” structure [Fig. 1(a)] at above 20 K and a nominal field of only about 15 V/cm. The reader should note

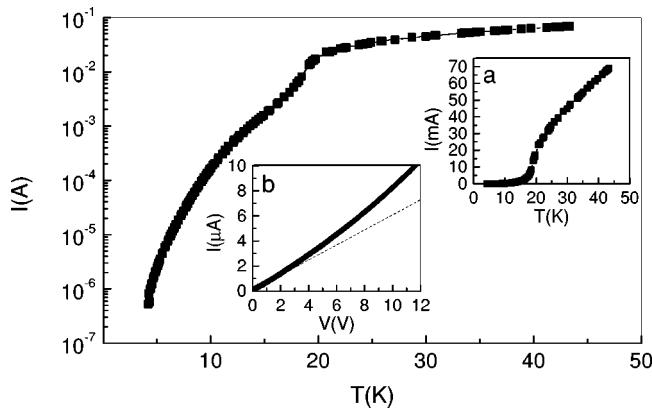


FIG. 1. Temperature dependence of the current flowing through sample S1 at constant applied voltage  $V=3$  V (15 V/cm). The curve displays a kneelike structure around 20 K, similar to a insulator-to-metal crossover. (a) The “knee” is clearly seen in a linear scale. (b) Nonlinear response is observable at very low applied electric fields below 20 K.

that this field would give rise to a negligible hot carrier energy of  $10^{-5}$  eV (0.1 K) in a 1-nm tunneling or hopping step. The behavior displayed in Fig. 1(a) is an electrical signature of “charge freezing” into an insulating Coulomb glass in a highly doped conjugated polymer. Normally, in a system having an average charge-carrier concentration as high as the one observed in PPy (of at least  $10^{20}/\text{cm}$ , see, for instance, p. 114 of Ref. 1), we would expect a metallic state. In our PPy, however, we are dealing with metallic islands separated by narrow barriers caused by topological domains and structural defects at the nanoscale.<sup>2,11</sup> The charge density can give rise to barrier regions which can be overcome by collective charging. The model will be discussed in more detail below.

A fascinating feature appears in the conductivity when the applied field is increased beyond a given threshold at low temperatures. When the applied voltage is increased by only a few mV above a critical voltage value ( $V_s$ ) (Fig. 2:  $V_s=11$  V corresponding to an electric field of 50 V/cm; using graphite paste electrical contacts), the current switches to a higher value. The resistivity decreases nearly four orders of magnitude and the current then exceeds the maximum current output allowed by the source delimiter (100 mA). The current remains high (“ON” state) as long as the voltage is held above a “critical value” ( $V_h$ ) below which it switches back down again. The response is symmetric when the field is applied in the opposite direction. During the experiment, no damage or permanent changes were detected on the sample. The overall ramp rate was established at 6 V/h. Experiments carried out at slightly different measuring speed do not reveal time dependence or relaxation phenomena.

Switching, albeit with different phenomenology, is also observed when silver paste is used to make the electrical contacts instead of graphite paste (Fig. 3). The voltage controlled  $I$ - $V$  characteristics show a sharp and fast switch to an ON state [ $V_s=26$  V (130 V/cm) for the sample shown in Fig. 3]. Here the current jumps nearly five orders of magnitude. The current quickly reaches the maximum allowed output current which is fixed at 100 mA. Reducing the applied

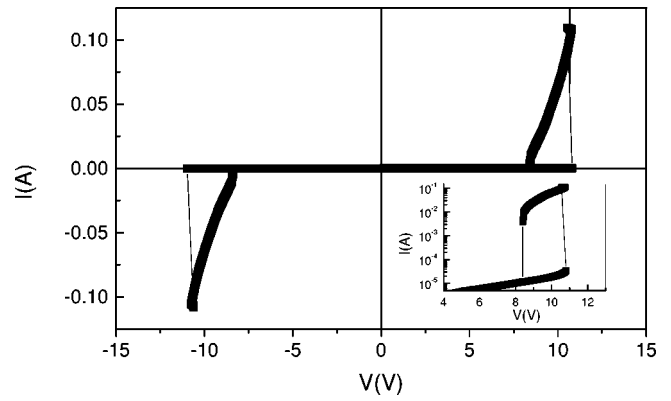


FIG. 2. Switching effect in a voltage controlled  $I$ - $V$  response (sample S2) at 4.2 K. A current jump (ON state) of around four orders of magnitude when voltage is raised up to  $V_s=11$  V (50 V/cm). Switching back to low conductive OFF state is observed when voltage is reduced below  $V_h$  (close to 8 V, see inset). The effect is symmetric for a reversing bias. The measurement was carried out in a four-probe method using graphite paste at the electrical contacts.

voltage below  $V_h=4$  V, the sample switches back to the “OFF” state but this time with a sharp transition. The switching is again symmetric for fields applied in both directions [Fig. 3(b)]. The differences observed between graphite and silver paste contacts demonstrate that the contact barrier plays a role in shaping the  $I$ - $V$  response. Graphite paste is widely used to create conductive pads on organic samples because of work function matching and silver contacts appear to produce a significant contact resistance at low temperatures.<sup>12,13</sup> Current controlled  $V$ - $I$  measurements provide us with additional information about the switching process. In Fig. 3(c), for example, the results shown display a negative differential resistance (NDR) S-shaped response [Fig. 3(c), crosses]. When voltage controlled  $I$ - $V$  measure-

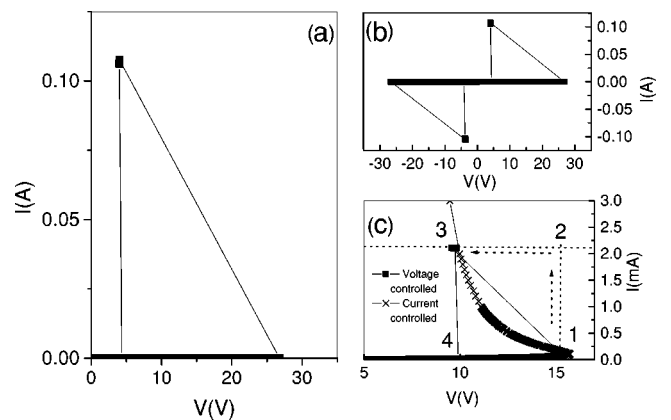


FIG. 3. (a) The switching characteristics change when silver paste contacts are used, as shown above for sample S3 at 4.2 K. (b) The effect is again reversible for applied fields in opposite direction. (c) An S-shaped negative differential resistance (NDR) is observed when the  $I$ - $V$  is measured using current control (sample S4, crosses). The measurements for the voltage controlled  $I$ - $V$  are also shown (filled squares). Switching from point 1 to point 3 is observed (see text).

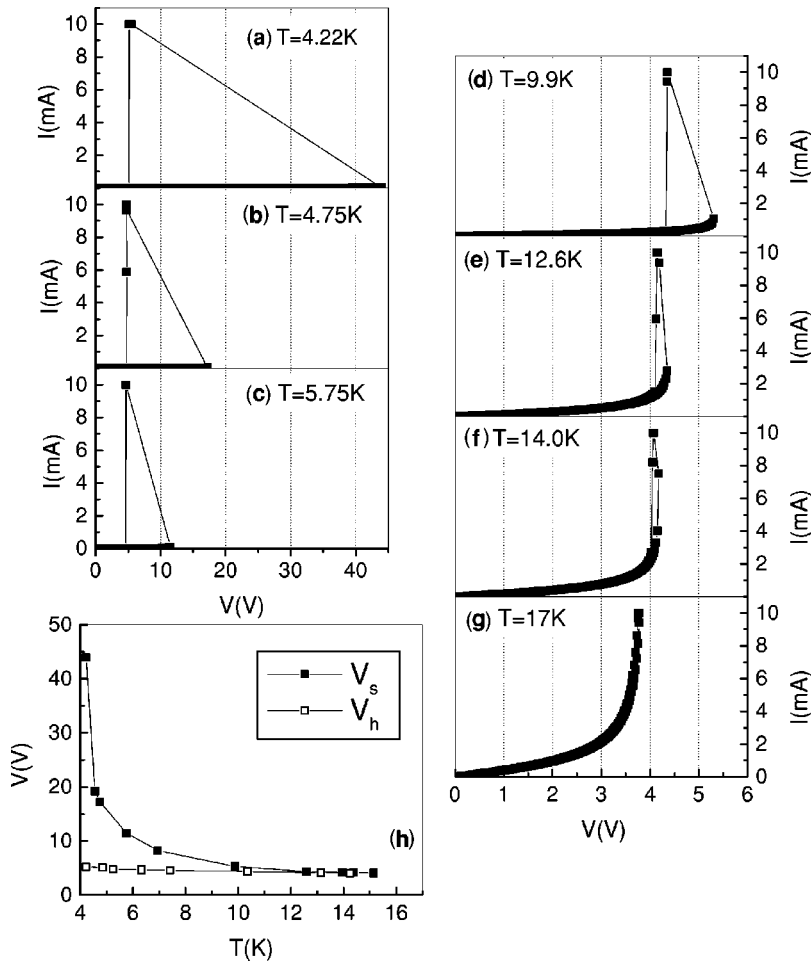


FIG. 4. The switching effect in sample S5 for a different temperatures. The switching disappears at around 17 K (g). The switching voltage depends strongly on temperature (h) and becomes nearly equal to holding voltages close to 20 K.

ment are performed [Fig. 3(c), filled squares], the system becomes unstable at point 1. This is where the switching occurs. The system jumps from point 1 to point 3, the maximum current value fixed by the delimiter.

The switching strongly depends on temperature. We can define a critical temperature  $T_c \sim 20$  K (Fig. 4) above which no switching phenomena is detected within our experimental conditions. This temperature coincides precisely with the crossover temperature shown in Fig. 1, and with the expected Coulomb glass transition temperatures reported by other authors in  $\text{PF}_6\text{-PPy}$  systems (see, for instance, p. 110 of Ref. 1).

As pointed out in our previous work,<sup>4</sup> we are dealing with a metallic grain island morphology. The metallic grains are separated by tunnel barriers which can self-destruct and reform again. The barriers are, we argue, caused by variations in charge densities and therefore Coulomb interactions. These barriers self-destruct as soon as enough charge is transferred into them. The fact that such extremely small values of “average fields” of order 1 V/cm influence the magnitude of the conductivity is itself very strong evidence for the metal-island model. The only way such a voltage can have an effect is that it actually drops across high resistance barrier regions. This then enhances the local field and produce field heating which can be of order or larger than kT.

The formation of electronic glass phases in disordered system is well documented and discussed also in a number of

theoretical papers.<sup>14</sup> In the Mott-CFO (Cohen, Fritzsche, and Ovshinsky)<sup>15</sup> model picture, the tails in the energy bands overlap in the forbidden gap. Charge is transferred from occupied to empty states. The system tries to screen the Coulomb interactions and in this way creates a new charging organization which minimizes the free energy. This new organization implies a single-particle energy gap. Depending on the dielectric properties and the dopant density, such systems can be metallic or form insulating electron glasses.<sup>16</sup> In a conjugated polymer, the coulombic self-localisation of the “electron” can also be assisted by the structural relaxation or the conventional polaron deformation. The discovery made in this work is that the barrier regions are due to electronic freezing of charge into a Coulombic glass. The freezing occurs in regions in which the densities are below the metallic threshold and which can therefore be made to melt by strong polarization fields or by adding space charge. The electronic energy gap appears to be due to many-body correlations, and is therefore self-consistent. Mattis<sup>17</sup> and later Srinivasan<sup>18</sup> argued that the magnitude of a Coulomb gap  $E_g$  should depend linearly on the number of excitations “ $n$ ”:

$$E_g = E_{g0}(1 - \alpha n_T - \beta n_F); \alpha + \beta = 2, \quad (1)$$

where  $E_{g0}$  is the zero-temperature Coulomb gap.  $\alpha$  and  $\beta$  are the relative weight of the excitations generated thermally  $n_T$  or electrically  $n_F$  by Zener tunneling:

$$n_T = \left(1 + \exp\left[\frac{e_g}{2t}\right]\right)^{-1},$$

$$n_F = \Gamma I_0 (1 - n_T) \exp\left(-\frac{e_g^{3/2}}{u}\right) \left[1 + \exp\left(-\frac{e_g^{3/2}}{u}\right)\right]^{-1}, \quad (2)$$

$$t = \frac{T}{T_c}; e_g = \frac{E_g}{E_{g0}}; 4KT_c = E_{g0},$$

where  $\Gamma$  is the recombination time,  $I_0$  the generation rate, and  $(1 - n_T)$  the suppression of backflow term. The dimensionless “ $u$ ” is related to the field across the barrier  $F_b$  by the usual WKB factors  $F_b = 81.54 \times 10^7 (E_{g0})^{3/2} u$ . Mattis and Landovitz<sup>8</sup> (ML) force the current injected from the metal contacts to tunnel through a correlation barrier of height  $(E_g/2)$  when entering the sample. The injected charge then thermalizes into unoccupied states. This gives the system an injection region and a bulk region which of course can be different for different materials and contacts. The coupled set of Eqs. (1) and (2) describe a self-consistent system in which the solution involves  $n_T$ ,  $n_F$ , and  $E_g$ . An incremental change in either  $n_T$  or  $n_F$  leads to a reduction of the gap  $E_g$ . This self-consistently modifies the  $n_T$  and  $n_F$  values. For a sufficiently high values of  $n_F$ , the gap vanishes and the system switches to a highly conductive metallic ON state. In the same way, it is possible to define a critical temperature  $T_c$  [Eq. (2)] at which the thermal excitations  $n_T$  are big enough to close the gap.

Several modifications are needed in order to apply this model to our observations. First we note that we are dealing here with extremely high charging levels and that one would in principle expect the metallic state to survive down to very low temperatures as it does in other highly doped conjugated polymers. The freezing-in has to do here with the granular nature of PPy. The insulating glassy state develops in the boundary regions between the grains where the average doping level is lower for chemical-topological reasons. It follows that the breaking down of the gap may be more complex than in a homogeneous system, with the field-induced tunneling playing a more prominent role than the thermal processes. The tunneling process triggers a much larger polarization change, so  $\beta$  may be larger than  $\alpha$ , and the field across the tunneling  $F_b$  would be much larger than the average field  $F$ . On the other hand, as the field is reduced or the temperature is lowered, the wave function localizing processes (disorder and many-body backscattering) get enhanced and there is a point at which the system thermalizes back down in the ground-state configuration which we call freezing. In the metallic state, the average energy of the carrier has to be above the mean-field mobility edge  $E_c$ . So we write a familiar mobility scaling law:

$$\mu = \mu_0 \left\{ \vartheta \left( \frac{\langle E \rangle - E_c}{E_c} \right) \right\}^\gamma + \mu_{ins}, \quad (3)$$

where  $\vartheta$  is the theta function and the exponent  $\gamma \leq 1$ .  $\langle E \rangle = \{kT/2 + eFl_{in} + E_b\}$  represents the sum of thermal, field heating, and band energy, respectively, in an inelastic length scale of  $l_{in} = \mu F \Gamma$ . As soon as the particle energy falls below

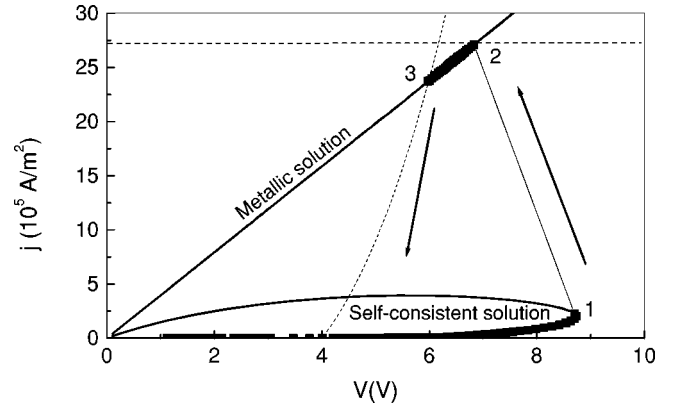


FIG. 5. Modified ML modelization of switching. The parameters are selected to be close to the ones expected for the PPy:  $b = -4$ ,  $E_{g0} = 10$  meV,  $l_b = 2$  nm and  $l_m = 90$  nm,  $N_b = 10^4$ ,  $T/T_c = 0.145$ ,  $\sigma = 3.65 \times 10^2$  S/m. The closed-loop solid line represents the self-consistent solution. The metallic solution is also shown. The horizontal dashed line represents the current delimiter value. The filled squares represent the expected system behavior. The critical freezing-in is plotted for  $\gamma = 1$  and  $V_h = 4$  V (dashed line between 3 and 4).

the “correlated electron” mobility edge  $E_c$ , we recover the glass mobility characterized by the value of the excitation densities  $\mu_{ins} = \mu'(n_T + n_F)$  where  $\mu'$  is the effective one-body band mobility. In the present simplistic approach, switch back is limited by the condition  $eF \cdot \mu F \Gamma > (E_c - E_b - kT/2)$ . More accurate first-principle modeling of the correlated localization process is beyond the scope of this paper and will be discussed in a future communication. In the present application to PTS-PPy, we will take Mattis’s first theory together with Eq. (3) and with  $\alpha = \beta$ . We include the inhomogeneous field island model consistent with the ideas of Ref. 17. The current and voltage were calculated as

$$J = N_c e \mu' F (n_T + n_F),$$

$$V = N_d (l_b F_b + l_m F_m) = N_d (l_b + l_m) F, \quad (4)$$

$$b = \ln(\Gamma I_0).$$

Here,  $l_m$  is an average length of the metallic island,  $l_b$  a typical barrier width,  $N_d$  the number of such segments,  $N_c$  the absolute carrier density. The field in the metallic island at steady conditions is  $F_m = (n_T + n_F) F_b$ . The quantity  $b$  is a measure of the steady-state concentration of purely field ionized charges and used by Mattis as a parameter. The current  $J$  is plotted in Fig. 5 for  $b = -4$ ,  $E_{g0} = 10^{-2}$  eV,  $l_b = 2$  nm and  $l_m = 90$  nm,  $N_d = 10^4$ ,  $T/T_c = 0.145$ ,  $\sigma = N_c e \mu = 3.65 \times 10^2$  S/m. These values are selected in order to reproduce qualitatively the behavior of the system, but they are indeed close to those expected in PPy. The self-consistent solution, as well as the metallic trivial solution ( $E_g = 0$ ), are plotted as solid lines. The filled squares represent the behavior of the expected system and it is consistent with our experimental results. The horizontal dashed line shows the maximum current allowed by the delimiter. As we increase the voltage the field starts to excite carriers across the gap and polarizes the

barrier region which decreases the Coulomb gap. This eventually leads to a sharp upturn at “1” and an instability into the current limited metallic state at “2.” The nature of the transition back into the localized glass can be well parametrized by the critical exponent  $\gamma$ . In Fig. 5 the dashed line “3–4” corresponds to  $\gamma=1$ . For one-body scattering localization  $\gamma=1$ . For many-body assisted scattering  $\gamma<1$ . The smaller  $\gamma$ , the sharper the transition. The curvature in the ON state shown in Fig. 2 could be understood as the result of a progressive reduction of the  $\gamma$  parameter as we lower the voltage, thus indicating a change of the mobility scaling from a one-body-like law into a collectivelike one. The holding voltage  $V_h(T)$  takes on the appearance of a critical quantity entering a mobility order parameter of the type  $\xi\sim[1-(V/V_h)^2]^\gamma$ .

We reported the observation of a truly Coulomb correlated electron glass in a conjugated polymer. We used a

slightly modified version of Mattis’s theory<sup>17</sup> for our system. We have presented in the form of an “ansatz” a method by which one could extend the ML theory to also describe the return into the glassy phase. Finally and importantly, we cannot at this time completely exclude the possibility of superconducting fluctuations surviving in the metallic domains. This exciting possibility needs to be investigated in experiments that are in progress.

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<sup>1</sup>R. S. Kohlman and A. J. Epstein, *Handbook of Conducting Polymers*, 2nd edition, edited by Skotheim, Elsenbaumer, Reynolds (Marcel Dekker Inc., New York, 1998), Vol. 1, p. 85.

<sup>2</sup>G. B. Street, in *Handbook of Conducting Polymers*, 1st edition, edited by T. H. Skotheim (Marcel Dekker Inc., New York, 1996), Vol. 1, p. 267.

<sup>3</sup>C. Zhihua and C. R. Martin, *J. Am. Chem. Soc.* **111**, 4138 (1989).

<sup>4</sup>J. M. Ribó, M. C. Anglada, J. M. Hernández, X. Zhang, N. Ferrer-Anglada, A. Chaibi, and B. Movaghar, *Synth. Met.* **97**, 229 (1998).

<sup>5</sup>V. Vescoli, L. Degiorgi, W. Henderson, G. Grüner, K. P. Starkey, and L. K. Montgomery, *Science* **281**, 1181 (1998).

<sup>6</sup>S. H. Jhang, G. T. Kim, S. W. Lee, Y. W. Park, and P. Bernier, *Synth. Met.* **121**, 1243 (2001).

<sup>7</sup>Z. K. Tang, L. Zhang, N. Wang, X. X. Zhang, G. H. Wen, G. D. Li, J. N. Wang, C. T. Chan, and Ping Sheng, *Science* **292**, 2462 (2001); M. Kociak, A. Y. Kasumov, S. Guéron, B. Reulet, I. I. Khodos, Y. B. Gorbатов, V. T. Volkov, L. Vaccarini, and H. Bouchiat, *Phys. Rev. Lett.* **86**, 2416 (2001).

<sup>8</sup>D. C. Mattis and L. F. Landovitz, *J. Non-Cryst. Solids* **2**, 454 (1970).

<sup>9</sup>J. M. Ribó, A. Dicko, M. A. Valles, J. Claret, P. Dallemer, N. Ferrer-Anglada, R. Bonnett, and D. Bloor, *Polymer* **34**, 1047 (1993).

<sup>10</sup>M. C. Anglada, N. Ferrer-Anglada, J. M. Ribó, and M. Movaghar, *Synth. Met.* **78**, 169 (1996).

<sup>11</sup>A. Chaibi, N. Ferrer-Anglada, J. A. Gorri, L. L. Fajari, and M. C. Anglada, *Appl. Magn. Reson.* **12**, 575 (1997).

<sup>12</sup>J. Kanicki, in *Handbook of Conducting Polymers*, 1st edition, edited by T. H. Skotheim (Marcel Dekker Inc., New York, 1996), Vol. 1, p. 558.

<sup>13</sup>E. van der Donck and J. Kanicki, *Eur. Polym. J.* **16**, 677 (1980).

<sup>14</sup>M. Grunewald, B. Pohlmann, L. Schweitzer, and D. Wuertz, *J. Phys.: Condens. Matter* **15**, 1153 (1982); J. Davies, P. A. Lee, and T. M. Rice, *Phys. Rev. Lett.* **49**, 758 (1982).

<sup>15</sup>M. H. Cohen, H. Fritzsche, and S. R. Ovshinsky, *Phys. Rev. Lett.* **22**, 1065 (1969).

<sup>16</sup>C. O. Yoon, M. Renghu, D. Moses, and A. J. Heeger, *Phys. Rev. B* **49**, 10 851 (1994).

<sup>17</sup>C. Mattis, *Phys. Rev. Lett.* **22**, 936 (1969).

<sup>18</sup>G. Srinivasan, *Phys. Rev. B* **4**, 2581 (1971).