

Separation of electric charge flow mechanisms in conducting polymer networks under hydrostatic pressure

A. N. Papathanassiou,^{a)} I. Sakellis, and J. Grammatikakis

Section of Solid State Physics, Department of Physics, University of Athens, Panepistimiopolis, Zografos, GR 157 84 Athens, Greece

(Received 14 September 2006; accepted 12 October 2006; published online 27 November 2006)

To distinguish between different electric charge flow mechanisms in conducting polymer networks, the authors performed ac conductivity and complex permittivity measurements in conducting polypyrrole at various hydrostatic pressure values. Pressure influences capacitive coupling of chains or conducting grains. The measurement of ac conductivity and complex permittivity in the frequency domain at different hydrostatic pressures seems to be a tool for resolving different conductivity modes in conjugated polymer networks and understanding electric signal propagation in random networks. © 2006 American Institute of Physics. [DOI: 10.1063/1.2397010]

The concept of distinguishing different modes of electric charge transport in conduction polymers experimentally is still under investigation.¹⁻⁵ Electric charge flow in conducting polymers proceeds over a frame of doped polymer chains characterized by orientation and conformation disorder. A more refined model for conducting polypyrrole is that of the granular metal characterized by inhomogeneous disorder, in which conducting grains are embedded inside an insulating matrix.⁶ Conductive grains consist actually of aligned polymer chains rich in polarons.⁷ Metallic conduction occurs within the grain, while hopping from one grain to another proceeds by phonon assisted tunneling through the insulating separation (mainly along the chains linking neighboring grains).⁷ dc conductivity involves the charge transfer along the specimen's dimensions over conduction paths consisting of long coupled polymer chains bridging the measuring electrodes, or, most likely, of polymer chains linking metallic grains (intercluster connection). Macroscopic dc conductivity involves the slowest transport process and stems from an unraveled interplay between intra- and interchain (or cluster) charge flows. ac conductivity, which provides information at time scales proportional to the frequency f of the applied field, has the advantage to trace charge flow over the percolation network that gives rise to macroscopic conductivity, as well as over shorter paths. The ac conduction modes are of the same type as those for the dc transport, i.e., intra- and interchain hoppings, but ac conductivity can trace charge flow along chains with dead ends (which do not participate to the macroscopic conductivity), provided that a capacitive (dielectric) element is considered as dead end.

The starting idea of this letter is that pressure affects the interchain (or intergrain) void space more dramatically than the length of individual polymer chain (or metallic grain) itself. Subsequently, pressure can change the transfer rate of different conduction modes and enforce the resolving power of the frequency domain experiments towards a separation between elementary conductivity modes. The combined use of pressure and ac measurements in conducting polymers has not been reported yet. Few dc conductivity measurements as a function of pressure were reported earlier, but the results

are related to the macroscopic conductivity and the interpretation regards the polymers as disordered three-dimensional semiconductors, i.e., disregarding inter- and intrachain effects.⁸ High-frequency ac conductivity measurements at ambient pressure⁵ and infrared reflectance experiments² were employed towards a better understanding of inter- and intrachain transports. The contribution of this letter in the field of unraveling different types of charge flow is the introduction of hydrostatic compression for improving the resolving power of frequency domain technique.

Details about the sample preparation were reported in a recent publication.⁹ ac conductivity measurements were performed from 10^{-2} Hz to 10 MHz by employing a Solartron SI 1260 frequency response analyzer. Isobaric conditions to 0.35 GPa were achieved in a fluid transmitting pressure vessel,¹⁰ which was immersed in a heat bath maintaining isothermal conditions. Controlled and standard measurements were performed to exclude the possibility of any parasitic resonance type signals arising from cabling.

The knowledge of the response of a conducting polymer (such as conducting polypyrrole) to an external electric harmonic field was limited to ambient pressure conditions.¹⁰⁻¹² The real part of the ac conductivity σ' exhibits a low-frequency dc plateau followed by a dispersive high-frequency region. Accordingly, the imaginary part of the permittivity $\varepsilon'' = \sigma(\omega)/\varepsilon_0\omega$, where ε_0 denotes the permittivity of free space, consists of a low-frequency dc component and a dielectric loss peak at frequencies higher than a critical one separating the dc plateau from the dispersive region in the $\sigma'(\omega)$ plot. Earlier measurements (at ambient pressure) from room temperature to 85 K identified a broad dielectric loss peak.^{12,13} Here, we performed isobaric measurements up to 0.35 GPa. Isothermal conditions were achieved from 273 K to room temperature. The increase of pressure has distinct effects on both the dc and ac regimes of the measured $\sigma'(\omega)$, respectively (Fig. 1): (i) The low-frequency dc component increase on pressure according to a second order polynomial law [Fig. 1(a)]. We shall not focus on this phenomenon, since such behavior has already been observed earlier by four-probe dc measurements and was attributed to the increase of density of electronic states upon the volume reduction on increasing pressure.^{8,14} (ii) The dispersive conductivity consists of one pressure-insensitive region around 10^5 Hz and

^{a)} Author to whom correspondence should be addressed; electronic mail: antpapa@phys.uoa.gr

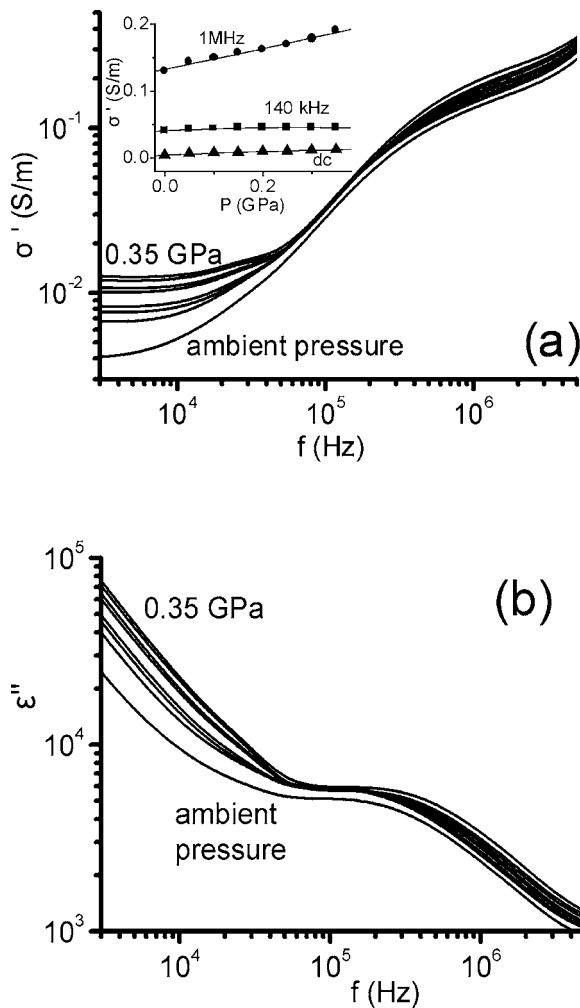


FIG. 1. (a) σ' vs frequency at $T=292$ K for various pressure values. Inset: Pressure evolution of σ' obtained from the dc low-frequency regime, at 140 kHz and 1 MHz, respectively. A second order polynomial curve was fitted to the dc data points (b) vs frequency. The curves (from bottom to top) correspond to ambient pressures of 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, and 0.35 GPa, respectively.

another one (around 10^6 Hz) where ac conductivity increases on pressure [Fig. 1(a)].

The distinction between two different ac conduction mechanisms is better visualized representing ϵ'' against frequency at various pressure values [Fig. 1(b)]. The influence of pressure on the dielectric loss [i.e., after subtracting the dc component from the measured $\sigma'(\omega)$] is depicted in Fig. 2. At ambient pressure, the loss peak does not evidence for two distinct contributions, and a stretched exponential Debye peak (or other alternatives) can be used to fit the broad dispersion. The increase of pressure permits a direct *experimental* splitting of the broad loss peak in two components: one pressure independent at 28.1 kHz (peak I) and another one (peak II) that shifts gradually from 153.9 kHz at ambient pressure to 233.5 kHz at 0.35 GPa. The increase of hydrostatic pressure on a “spaghettilike” chain network causes a primary effect of the reduction of the interchain (or intergrain) void space and secondary effects, such as slight modification of the conformational disorder and reduction of the length of each individual chain. A plausible interpretation is that the loss peak I is related to intragrain charge flow, while peak II—as more sensitive to the reduction of intergrain separation on increasing pressure—stems from interchain

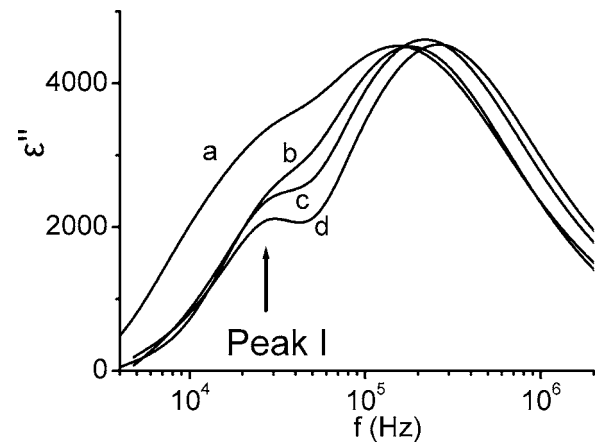


FIG. 2. Sample of loss peaks obtained after subtraction of the dc component from the measured ϵ'' vs frequency at 292 K for different pressure values: (a) ambient pressure, (b) 0.1 GPa, (c) 0.2 GPa, and (d) 0.3 GPa. The arrow indicates the position of the maximum of loss peak I.

hopping. Intrachain charge flow makes use of the entire polymer chain length, which is much longer than the interchain/cluster void space. Correspondingly, the intrachain peak is related to slower processes than the interchain/cluster one does. The phenomenon is more noticeable by increasing pressure where the shortening of interchain/cluster separation makes the high-frequency peak faster.

In the analysis of the pressure evolution of a loss peak in disordered media, our experiments provide a definite answer to the open question¹² about the origin of the loss peaks observed in conducting polymers: the present results prove that the behavior of the position of the loss-peak maximum f_{\max} is opposite to that of rotating permanent dipole (i.e., increase of the relaxation time $\tau \equiv 1/f_{\max}$ upon pressure). The relaxation time defined by Mott and Davis¹⁵ is

$$\tau = \nu^{-1} \exp(2\alpha R) \exp(E/kT), \quad (1)$$

where ν is a typical phonon frequency value, α is the inverse localization length of the wave function, and R is a hopping distance. E coincides to the heat obtained from the phonon bath of the matrix to achieve hopping relaxation. Taking the (natural) logarithm of Eq. (1) and differentiating with respect to pressure, we get

$$\left(\frac{\partial \ln f_{\max}}{\partial P} \right)_T = \left(\frac{\partial \ln \nu_{\max}}{\partial P} \right)_T - 2\alpha \left(\frac{\partial R}{\partial P} \right)_T - \frac{1}{kT} \left(\frac{\partial E}{\partial P} \right)_T. \quad (2)$$

The first term of the right-hand side of Eq. (2) equals $\gamma\chi_T$, where γ is the Grüneisen constant and χ_T is the isothermal compressibility.¹⁶ Polarons are hosted within the benzole ring, which practically does not “feel” pressure changes; it is reasonable to assume α as pressure independent.⁸ The dimensions of the sample reduce isotropically on increasing pressure; hence, $(\partial \ln R / \partial P)_T = -\chi_T/3$. The thermodynamic quantity of the activation volume ν^{act} can be approximated at room temperature as $\nu^{\text{act}} \equiv (\partial E / \partial P)_T$.¹⁶ The physical content of the activation volume for protonic motion was given initially by Fontanella *et al.*,¹⁷ as the volume change material induced when the transferring charge undergoes a transition from a “ground” state to an “excited” one. Equation (2) can therefore modify to a formula describing polaron motion in disordered environment:

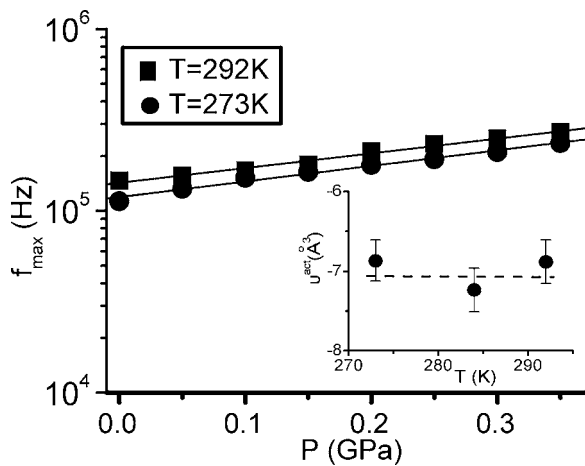


FIG. 3. Frequency f_{\max} of loss peak II vs pressure. Straight lines are best linear fits to the data points. The activation volume values at different temperatures obtained by using Eq. (3) are shown in the inset. The horizontal dash line was drawn to indicate that, within the experimental errors, v^{act} is practically constant.

$$v^{\text{act}} = -kT \left\{ \left(\frac{\partial \ln f_{\max}}{\partial P} \right)_T - \left(\gamma + \frac{2}{3} \alpha R_0 \exp(-\chi_T P) \chi_T \right) \right\}. \quad (3)$$

To analyze the data depicted in Fig. 3 we recall that αR_0 is of the order of unity, while $\chi_T = 0.08 \text{ GPa}^{-1}$.¹⁸ Note that the compressibility term results in a correction less than 10% to the direct evaluation of v^{act} from the slope of the $\ln f_{\max}(P)$ data. The use of Eq. (3) to analyze the $f_{\max}(P)$ data yields values of the activation volume, e.g., $v^{\text{act}} = (-6.9 \pm 0.3 \text{ \AA}^3)$ at 292 K. The presence of a polaron in a polymer chain (ground state) induces a volume distortion. Interchain hopping occurs by the passage of the polaron through the interseparating void space (excited state). At this instance, the volume distortion is less than that induced when the polaron is located at the chain (ground state), and the resulting v^{act} has negative sign, indicating the inward relaxation of the polymer network on the excited state of interchain hopping.

In this letter we propose ac conductivity measurements at various pressure values as a tool to discriminate mixing conductivity modes in conducting polymer networks. The microstructural features of polymer systems indicate that an increase of hydrostatic pressure affects mainly the interchain (or, most likely, the intergrain) space and, subsequently, the interchain (or intercluster) hopping. Intrachain (or intragrain) conductivity effects are much weaker since, within the inhomogeneous structure of the polymer, it is more energetically favorable to achieve conformational rearrangement as the sample volume is suppressed than reducing the length of

individual chain (and the intrachain length, respectively). The experimental results have revealed pressure-insensitive and pressure-dependent ac conductivity regimes. In the complex permittivity formalism, a broad loss peak which is recorded at ambient pressure splits into two components: one is constant and the other depends on pressure. To a rough approximation, the first loss mechanism could probably be related to intrachain/cluster charge flow and the latter with interchain/cluster hopping over the void space separating neighboring chains/grains. The quantity of the activation volume related to polaron motion indicates an inward distortion characterizing interchain/cluster hopping. Other explanations could probably be more proper to explain the response of polymer networks under pressure, but this is a matter of future investigation.

The present research was financed from the Operational Program for Education and Initial Vocational Training ‘EPEAEK-2’ within the frame of project ‘Pythagoras: Support of University Research Groups’ by 75% from EU Fund and 25% from National Resources.

- ¹A. B. Kaiser, Adv. Mater. (Weinheim, Ger.) **13**, 927 (2001); Rep. Prog. Phys. **64**, 1 (2001).
- ²K. Lee and A. J. Heeger, Phys. Rev. B **68**, 035201 (2003); K. Lee, S. Cho, S. Heum Park, A. J. Heeger, C.-W. Lee, and S.-H. Lee, Nature (London) **441**, 65 (2006).
- ³V. N. Prigodin and A. J. Epstein, Synth. Met. **125**, 43 (2002).
- ⁴V. N. Prigodin, A. N. Samukhin, and A. J. Epstein, Synth. Met. **141**, 155 (2004).
- ⁵J. A. Reedijk, H. C. F. Martens, H. B. Brom, and M. A. J. Michels, Phys. Rev. Lett. **83**, 3904 (1999).
- ⁶R. S. Kohlman, A. Zibold, D. B. Tanner, T. Ishiguro, Y. G. Min, A. G. McDiarmid, and A. J. Epstein, Phys. Rev. Lett. **78**, 3915 (1997).
- ⁷A. J. Epstein, W.-P. Lee, and V. N. Prigodin, Synth. Met. **117**, 9 (2001).
- ⁸D. S. Maddison and T. L. Tansley, J. Appl. Phys. **71**, 1831 (1992).
- ⁹A. N. Papathanassiou, J. Grammatikakis, I. Sakellis, S. Sakkopoulos, E. Vitoratos, and E. Dalas, Appl. Phys. Lett. **87**, 154107 (2005).
- ¹⁰A. N. Papathanassiou and J. Grammatikakis, Phys. Rev. B **53**, 16247 (1996).
- ¹¹E. Singh, A. K. Narula, R. P. Tandon, A. Mansingh, and S. Chandra, J. Appl. Phys. **80**, 985 (1996).
- ¹²S. Capaccioli, M. Luccher, and G. Ruggeri, J. Phys.: Condens. Matter **19**, 5595 (1998).
- ¹³A. N. Papathanassiou, J. Grammatikakis, I. Sakellis, S. Sakkopoulos, E. Vitoratos, and E. Dalas, J. Appl. Phys. **96**, 3883 (2004).
- ¹⁴A. Lundin, B. Lundberg, W. Sauerer, P. Nandery, and D. Naegle, Synth. Met. **39**, 233 (1990).
- ¹⁵N. E. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials* (Clarendon, Oxford, 1979), Chap. 2.15, pp. 59–62.
- ¹⁶P. A. Varotsos and K. D. Alexopoulos, in *Thermodynamics of Point Defects and Their Relation with Bulk Properties*, edited by S. Amelinckx, R. Gevers, and J. Nihoul (North-Holland, Amsterdam, 1985).
- ¹⁷J. J. Fontanella, C. A. Edmondson, M. C. Wintersgill, Y. Wu, and S. G. Greenbaum, Macromolecules **29**, 4944 (1996).
- ¹⁸P. Ferraris, A. W. Webb, D. C. Weber, W. B. Fox, E. R. Carpenter, Jr., and P. Brant, Solid State Commun. **40**, 1007 (1981).