# Percolation transition in conducting polymer networks

J. S. Andrade, Jr.
*Departmento de Física, Universidade Federal do Ceará, 60451-970 Fortaleza, Ceará, Brazil*
*and Department of Production Technology, Showa Denko K. K., 13-9 Shiba Daimon 1-Chome, Minato-ku, Tokyo 105, Japan*

N. Ito
*Department of Applied Physics, Faculty of Engineering, The University of Tokyo, Tokyo 113, Japan*

Y. Shibusa
*Department of Production Technology, Showa Denko K. K., 13-9 Shiba Daimon 1-Chome, Minato-ku, Tokyo 105, Japan*
(Received 8 April 1996)

A percolation model for conducting polymers is proposed in terms of a random resistor network. The macroscopic conductivity at the critical polymer density is studied. Substantial deviations have been detected from the standard conducting behavior in percolating structures generated with a large difference between inter- and intrachain conductance elements. This behavior could be explained in terms of a distinctive finite-size effect and the relevance of the results discussed in context with real polymer systems. [S0163-1829(96)03230-4]

## I. INTRODUCTION

The emergence of conducting polymers as a new class of functional materials has been fully recognized, especially due to their importance in basic and applied research and many potential applications in technology.[1–3] The investigation of their metallic state formation, dimensionality, and electrical transport mechanisms responsible for the wide range variation in conductivity with doping has been the main focus of the most recent experimental and theoretical studies on this field.[4–9] For example, in the case of polyaniline, conductivity changes of 9 orders of magnitude can be observed in a very limited range of protonation.[6,9] However, the interpretation of this kind of transport data in terms of specific theoretical models is still very controversial.[10] Some fundamental representations for conducting polymer systems and its metal-to-insulator transition have been of widespread utilization in recent studies. In order to explain many unusual properties of real conducting polymer systems, the first models were based on the assumption that each chain in the polymeric matrix would be an isolated one-dimensional conductor.[11,12] This one-dimensional (1D) description, however, could not account for the metallic behavior upon doping displayed by the majority of the conducting polymers, including polyacetilene. The quasi-one-dimensional disordered system (quasi-1D-DS) representation[13] certainly is the most acclaimed model on the subject. It has been developed to overcome the serious drawback of the strict 1D model by considering the interchain coupling as a relevant charge transport mechanism through the polymer material. For instance, it was under this framework that Wang *et al.*[8] proposed this type of transport model for oriented polyaniline in its fully doped emeraldine form, consisting of bundles of well-coupled chains in which electron states are three-dimensionally extended. According to this 3D ''metallic-island'' description, the conductivity threshold could be justified in terms of a localization-to-delocalization crossover in the electronic states within conducting clusters. Alternatively, Mizoguchi *et al.*[6] used a percolation paradigm based on the pathway connectivity among long chains of conducting polymer in the bulk of the disordered system to explain the sudden drop in the transverse spin diffusion coefficient at a given range of the protonation level. It has been the theme of an ample and interesting debate whether one representation is more appropriate than the other.[14,15]

Under a microscopic point of view, the charge transfer phenomena in conducting polymer systems have been extensively discussed in terms of well-established concepts from condensed matter physics such as solitons, polarons, and bipolarons.[10,16] Macroscopic models, on the other hand, can offer a phenomenological insight on the heterogeneous essence of the conductive process.[17] There is, however, a clear gap between the micro- and macroscopic perspectives to represent the transition to a high conductivity state in such functional materials. Few studies have been dedicated to provide a consistent description for the complicated morphology of the polymeric matrix.[18–20] For example, an interesting aspect of some conducting polymers (e.g., polypirrole), is the fractal morphology they can display when electrochemically generated by means of a diffusion-limited polymerization process.[21,22] As indicated by the experimental variability of the conduction behavior for different samples and preparation procedures, the structural details and microscopic imperfections of the polymeric system may represent a key factor for the development of highly conducting materials. Baughman and Shacklette[18] proposed a resistor network model to investigate the effect of conjugation length upon the electrical transport behavior of conducting polymers. By considering both interchain and intrachain processes of charge transfer, good agreement could be observed between available experimental data and theoretical results of the conceptual model. In a subsequent study,[19] the basic features of a random network model have been adopted as a hypothetical

 © 1996 The American Physical Society

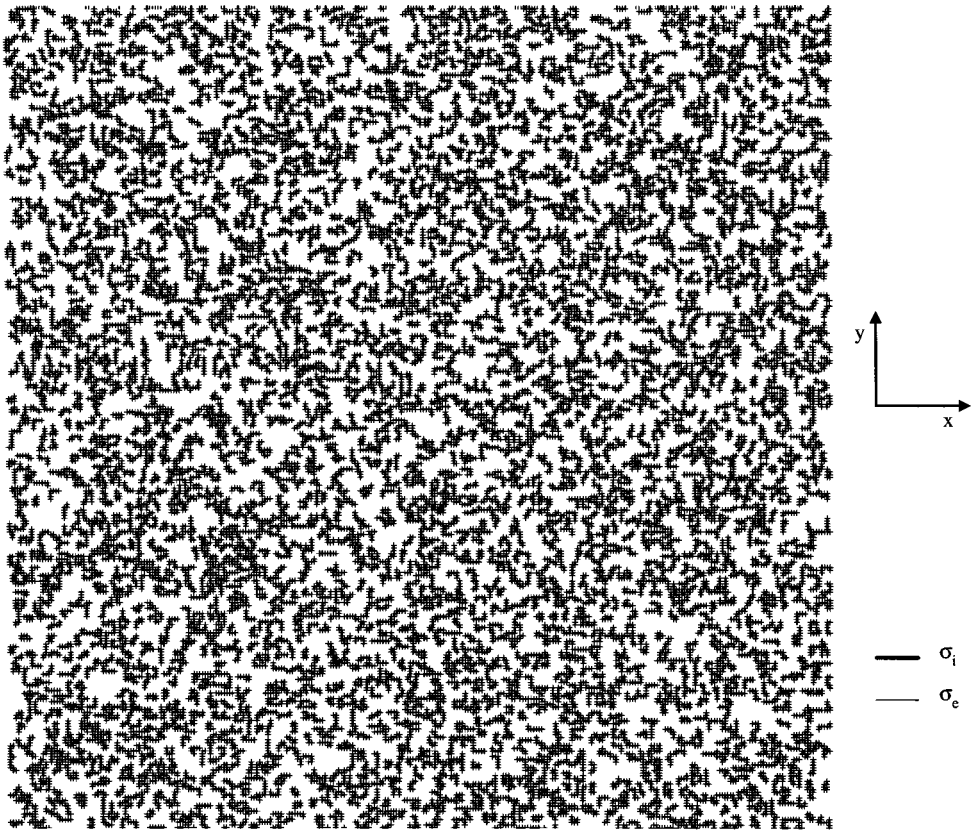


FIG. 1. Typical realization of a conducting polymer network at the percolation threshold ($l=6$). The thick lines correspond to intrachain conductances $\sigma_l$ and the thin lines to interchain conductances $\sigma_e$. Periodic boundary conditions are imposed at the $y$ direction.

framework to evaluate the influence of spatial disorder on the conducting properties of computer generated polymer clusters. The simulation results from this work clearly demonstrated the importance of including structural characteristics into the model to account for the intrinsic diversity of charge transfer mechanisms which dictate the conducting behavior of the polymer material.

In the present work, we study the effect of percolation disorder on the electrical behavior of conducting polymer networks (CPN). Basically, this representation is an extended version of the standard random resistor network (RRN) model. Instead of single bonds, the percolation elements are conducting polymer chains randomly allocated in the lattice.[19,20] The central idea is to show that the nature of the interchain connections can be a relevant factor influencing the size scaling properties of the overall maze conductivity at the critical point. Based on the results of extensive simulations, we argue that the scaling behavior of the conducting backbone of the polymer network at the threshold can be significantly affected by the temperature of the system when the ratio between polymer chain length and lattice size is sufficiently large. This fact might be relevant for the design of improved conducting polymer materials.

## II. MODEL

The polymer unit adopted in the simulations consists of a conjugated segment with a specified number $l$ of intrachain conductance elements $\sigma_l$ surrounded by two possible types of interchain connections $\sigma_e$: hopping $\sigma_h$ or doping $\sigma_d$ conductances. In the present realization of the model, we assume that the hopping conductances around each chain are randomly replaced by doping interchain barriers according to a fixed probability value, $p$. In this idealization, an intrachain conductance element must be viewed as a directional unit comprising either one or several monomers of the macromolecule. While the intrachain and hopping mechanisms of electrical transport in conducting polymers are reasonably well understood, the role played by doping in this system is somewhat unclear. A mechanism has been proposed by Kivelson[23] to explain the dopant part in the conduction process based on the interchain hopping between a bound charged soliton and a neutral soliton near a charged impurity. More recently, Tachibana *et al.*[24] adopted a quantum chemical approach to demonstrate that the driving force for such conduction channel is the relaxation of the nuclear geometry of the dopant in the presence of charged solitons. Since this charge transfer mechanism is induced by dopant elements present in the polymeric material, it seems reasonable to draw a connection between the occurrence of this transport barrier in the network and the doping fraction of a conducting polymer sample.

By specifying the polymer chain length and the relative proportion and values of the elementary conductances, the next step in the simulation procedure refers to the generation of a polymeric network confined to a lattice of finite dimension and regular topology. Two-dimensional square lattices have been used and periodic boundary conditions have been applied to reduce the finite-size effect in the transverse direction of the system. The polymeric units are sequentially allocated using a self-avoiding scheme so that interchain segments between different polymer units are restricted to hopping and/or doping conductances. The allocation of each

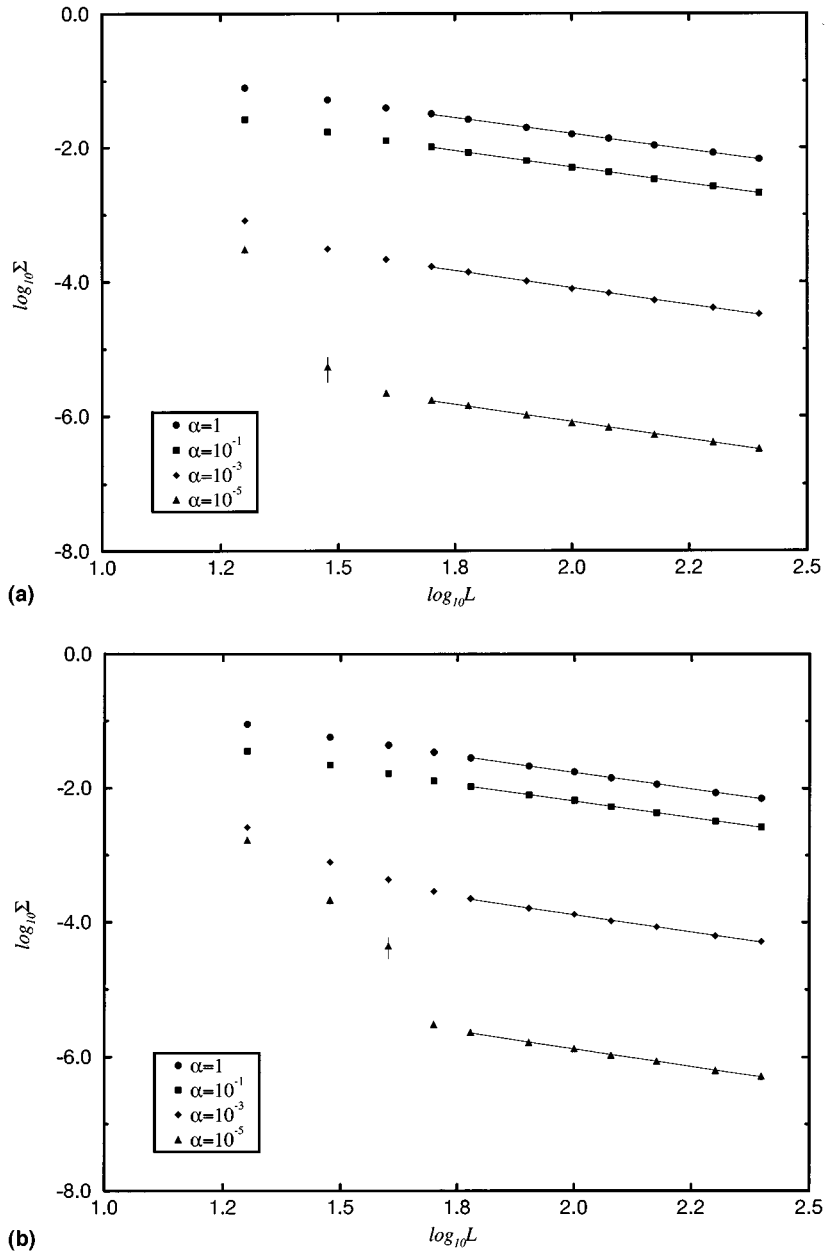


FIG. 2. Double-log plots of the conductivity $\Sigma$ as a function of the system size $L$ for (a) $l=2$, (b) $l=4$, and (c) $l=6$, and different values of $\alpha$. The solid lines are the linear best fitting for the scaling region (see Table I for the corresponding slopes).

polymer chain starts from a randomly selected and unoccupied site in the lattice. If the polymer cannot reach a specified length $l$, it is discarded. For a given realization, the generation step finishes when one of the polymer clusters percolates in the longitudinal direction, i.e., ''spans'' from one side to another through the lattice. Subsequently, an arbitrary voltage difference between these two opposite sides is applied and Kirchhoff's current law is imposed at each nodal point of the resulting configuration. Such an operation yields the following set of coupled linear algebraic equations:

$$\sum_{j\in(i)} \sigma_{ij}(V_i - V_j) = 0, \quad i = 1,2,3,\ldots,N, \tag{1}$$

where $V_i$ and $V_j$ are the electrical potentials at nodes $i$ and $j$, respectively; $N$ is the total number of internal nodes; and $(i)$ represents the set of nodes directly connected to node $i$ in the network. The effective conductivity of the network is then calculated by solving the system of coupled linear algebraic equations making use of a subroutine for LU decomposition of real sparse matrices. In a previous study,[19] explicit relationships have been adopted to describe the temperature dependence of the elementary bond conductances, according to their specification during the allocation step. In lightly doped polymers at low or moderate temperatures, the electrical transport is dominated by hopping. In such conditions, the associated conductance value for this mechanism can be many orders of magnitude smaller than intrachain and doping values. Here we simply assume that equal values can be assigned for the intrachain and doping conductances ($\sigma_l = \sigma_d$), whereas the conductance magnitude due to hopping contacts can be systematically changed according to the parameter ratio $\alpha = \sigma_h / \sigma_d$. Since hopping is a thermally activated process, a change in this variable should thus be analogous to a modification in the temperature of the conducting polymer system.

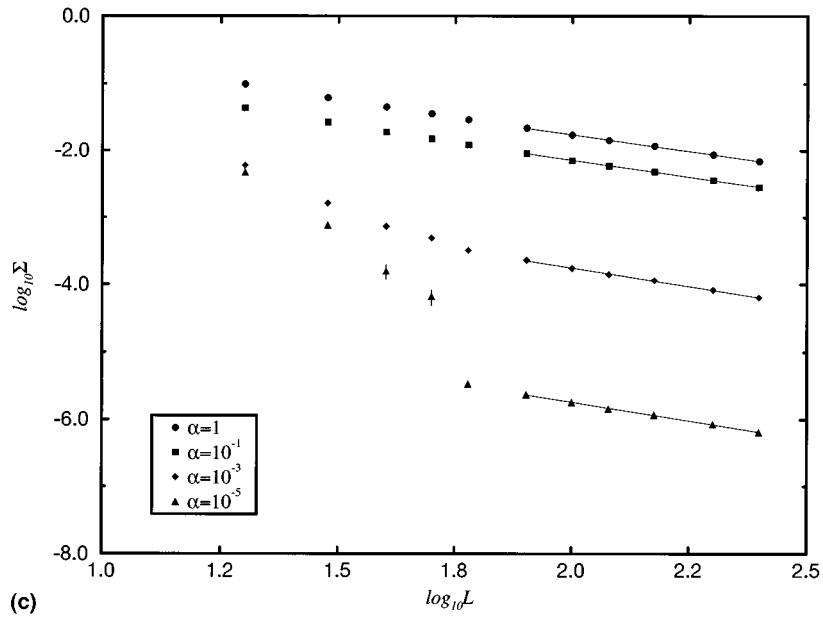


FIG. 2. (*Continued*).

## III. RESULTS AND DISCUSSION

Figure 1 shows a pictorial representation of our physical system for a typical network realization of dimension $300\times300$ just above the percolation threshold. Simulations have been carried out with a number of realizations ranging from 8000 to 200 for several lattice dimensions going from $20\times20$ to $250\times250$ nodal points, respectively. Once the spanning cluster is identified, the network conductivity is calculated for different values of the conductance ratio $\alpha$. For simplicity, we restricted our simulations to the case in which hopping and doping conductances are equally distributed ($p=1/2$), but randomly assigned around each polymer unit present in the lattice. Figure 2(a) shows the logarithmic dependence of the network conductivity $\Sigma$ on the system size for polymer chains composed of two elementary units ($l=2$) and four different values of $\alpha$. At $\alpha=1$, the scaling relationship

$$\Sigma\sim L^{-\zeta}, \tag{2}$$

seems to apply for the whole range of system size $L$. At very low values of the conductance ratio (e.g., $\alpha=10^{-5}$), however, interesting changes can be observed in the conductivity variation with system size and polymer chain length. The presence of a sharp finite-size crossover indicates the minimum lattice size where a percolating path consisting only of high conductances $\sigma_l$ and $\sigma_d$ could not be detected in any realization. Obviously, at low values of $\alpha$, even an insignificant number of such anomalous configurations tends to produce a dramatic increase in the average conductivity values of small lattice sizes. At this point, it is instructive to follow the ''link-nodes-blobs'' model,[25] where one can conceive the structure of the conducting backbone in terms of two distinct groups of bonds. Namely, the ''blobs'' are the multiply connected parts of the backbone which contain most of the conducting bonds of the system. The ''red'' bonds, on the other hand, constitute the set of single connections between consecutive blobs in the backbone and, as a consequence, must carry the total current passing through the percolating cluster. The occurrence of these exceptionally high conducting realizations could then be explained solely in terms of the average number of ''singly connected'' bonds available as interchain bridges in the conducting backbones of systems with different lattice sizes and polymer chain lengths. For example, a small lattice filled with large polymer chains will have a very small number of interchain conductances which can be qualified as ''singly connected.'' According to the doping probability employed in the simulations, $p=1/2$, an average of only half of the interchain bonds in the system will be assigned as hopping elements. Since there are few ''singly connected'' bonds in small lattices, the possibility of realizations with a very high conductivity increases. Likewise, the simulations performed with distinct polymer chain lengths showed entirely similar behavior [Figs. 2(b) and 2(c)], except for differences in the location of the crossover point which tends to move towards large lattice sizes as the polymer chain length increases. From these simulation results, it seems clear that this finite-size effect can be readily avoided if we calculate the critical exponents disregarding the conductivity data from small lattice sizes.

We use the same range of lattice sizes to fit the data corresponding to a given polymer chain length at different values of the parameter $\alpha$. Expectedly, the critical exponent obtained for $l=2$ and $\alpha=1$, $\zeta=0.97\pm0.01$, is very close to the value predicted by standard Monte Carlo simulations with two-dimensional percolating networks, $\zeta=0.9745$.[26] However, the resulting exponent values shown in Table I clearly demonstrate that the deviations from the standard percolation value of $\zeta$ become significant as the length of the

TABLE I. Values of $\zeta$ corresponding to the linear best fitting for the scaling regions shown in Fig. 2.

| $l$ / $\alpha$ | 1 | $10^{-1}$ | $10^{-3}$ | $10^{-5}$ |
|---|---|---|---|---|
| 2 | $0.97\pm0.01$ | $0.98\pm0.01$ | $1.02\pm0.02$ | $1.02\pm0.02$ |
| 4 | $0.97\pm0.01$ | $0.98\pm0.01$ | $1.04\pm0.02$ | $1.05\pm0.02$ |
| 6 | $0.99\pm0.01$ | $1.00\pm0.01$ | $1.09\pm0.02$ | $1.10\pm0.02$ |

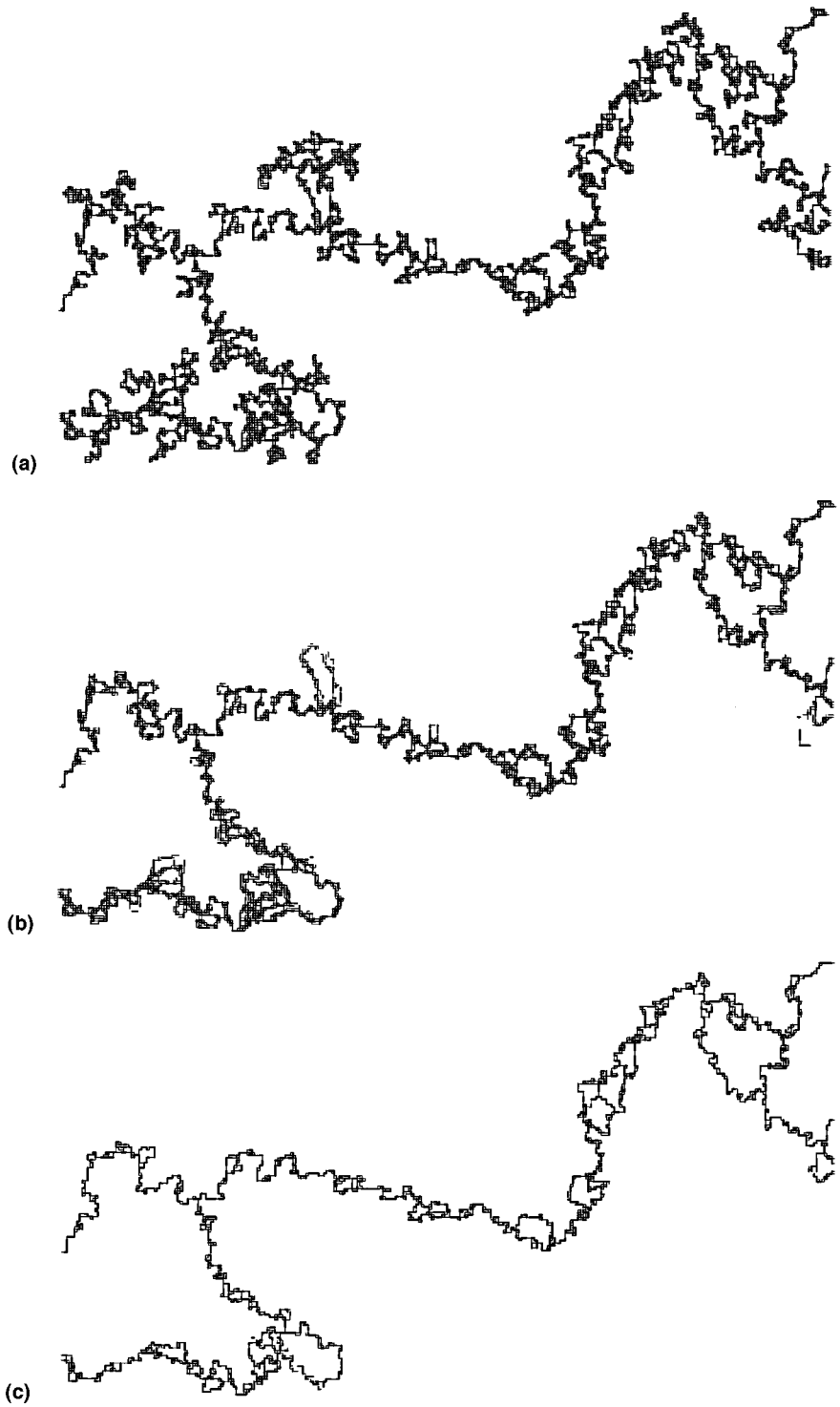


FIG. 3. Plot of the conducting backbone extracted from the network in Fig. 1 is shown in (a). Networks carrying 99% of the total bond current through this configuration are shown in (b) for $\alpha=1$, and in (c) for $\alpha=10^{-5}$.

polymer chain $l$ increases from 2 to 6 and the conductance ratio $\alpha$ is systematically reduced from 1 to $10^{-5}$. For instance, a deviation of almost 13% between the calculated exponent $\zeta$ assuming $l=6$ and $\alpha=10^{-5}$, $\zeta=1.10\pm0.02$, and the classical percolation value can no longer be justified in terms of typical finite-size effects. The objective here is to demonstrate that, at intermediate values of the ratio $l/L$, a decrease in the parameter $\alpha$ tends to increase the conductivity exponent towards the fractal dimension of the ''minimal self-avoiding walk'' (Ref. 26) through the conducting backbone. At low values of the conductance ratio, the hopping mechanism is dominant due to the high resistance of these interchain barriers. At low values of $\alpha$, those paths through the ''blobs'' having a relatively large number of hopping connections will contribute very little to the electrical transport. If the ratio $l/L$ is substantially large, the contribution of the low conductance paths will be virtually eliminated in some blobs because relatively long and highly conductive polymer chains can now ''percolate'' through them. As already mentioned, this finite-size effect breaks down the fractal morphology of the electrical system at low length scales and can somehow be compared to the ''minimal self-avoiding walk'' process in a typical percolating lattice. A convincing evidence for this behavior can be visualized if we

recursively plot only the conducting bonds of the original spanning cluster.[27] Figure 3(a) shows the conducting backbone extracted from the critical percolating network represented in Fig. 1. In Figs. 3(b) and 3(c), the set of bonds carrying 99% of the total current in the original structure are displayed for $\alpha$ values equal to 1 and $10^{-5}$, respectively. These pictures have been reconstructed after calculating the potential drop at each node and current at each bond of the lattice. Subsequently, without considering position and direction, all bond currents have been rearranged in descending order of their numerical values and summed up to the total current flowing through the network. Finally, the bonds carrying the largest currents are sequentially replotted, up to the point in which the desired percentage of the total current is already present in the system. Compared with Fig. 3(b), the tenuous aspect of the conducting pathway in the 99% network shown in Fig. 3(c) is a clear indicative that the relevant structures for transport are rather different for distinct $\alpha$ values. Under these circumstances, by decreasing the temperature (i.e., lowering the parameter $\alpha$) in systems with large polymer chains (more precisely, at intermediate values of the ratio $l/L$) one should then expect the critical conductivity exponent to increase approaching the maximum limit of $\zeta_{\max}=D_{\min}\approx 1.13$, where $D_{\min}$ is the fractal dimension for the ''minimal self-avoiding walk'' in a two-dimensional percolating network. This is in good agreement with the results of our simulations. Furthermore, the values shown in Table I could also indicate that the exponent $\zeta$ might not vary continuously with the parameter $\alpha$. Instead, by increasing $\alpha$, the occurrence of a crossover from the limiting value $\zeta_{\max}$ ($\alpha\rightarrow 0$) to the standard value of $\zeta=0.9745$ should be the most likely behavior. This possibility has to be further investigated.

## IV. SUMMARY

From the simulation results with the CPN model, we could demonstrate that the size scaling properties of conducting polymer systems might be fairly susceptible not only to their morphological and topological features but also to the physical conditions under which experiments have been performed (e.g., temperature). Moreover, the last factor appears to be associated with a distinctive finite-size effect in systems close to criticality generated with intermediate values of $l/L$ and at low values of the conductance ratio, $\alpha$. We expect this behavior to be observed in real conducting polymer systems. Sufficiently large chains or conjugation lengths can ''percolate'' through metallic islands in the granular three-dimensional material, breaking the possible self-similar hierarchy at low length scales.

We conclude by emphasizing the necessity for a detailed structural description of the electrical transport in conducting polymers. The modeling technique introduced here is flexible to bring together a variety of conduction mechanisms and correlate them spacially, according to specific features of the material and physical conditions. In other words, this model allows for structural and phenomenological aspects of the system to be simultaneously represented. Hopefully, the modeling approach developed in this study will enable us to provide more useful information on the topological aspect of the electrical transport in conducting polymers.


[1] H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang, and A. J. Heeger, J. Chem. Soc. Chem. Commun. 578 (1977).

[2] Y. W. Park, A. J. Heeger, M. A. Druy, and A. G. MacDiarmid, J. Chem. Phys. **73**, 946 (1980).

[3] C. O. Yoon, J. S. Yoo, Y. W. Park, K. Akagi, and H. Shirakawa, Synth. Met. **55-57**, 4848 (1993).

[4] F. Zuo, M. Angelopolous, A. G. MacDiarmid, and A. J. Epstein, Phys. Rev. B **36**, 3475 (1987).

[5] T. A. Ezquerra, J. Rühe, and G. Wegner, Chem. Phys. Lett. **144**, 194 (1988).

[6] K. Mizoguchi, M. Nechtschein, J.-P. Travers, and C. Menardo, Phys. Rev. Lett. **63**, 66 (1989).

[7] Z. H. Wang, A. Ray, A. G. MacDiarmid, and A. J. Epstein, Phys. Rev. B **43**, 4373 (1991).

[8] Z. H. Wang, E. M. Scherr, A. G. MacDiarmid, and A. J. Epstein, Phys. Rev. B **45**, 4190 (1992).

[9] P. K. Kahol, N. J. Pinto, E. J. Berndtsson, and B. J. McCormick, J. Phys. Condens. Matter **6**, 5631 (1994).

[10] Y. Lu, *Solitons and Polarons in Conducting Polymers* (World Scientific, Singapore, 1988).

[11] W. P. Su, J. R. Shriefer, and A. J. Heeger, Phys. Rev. B **22**, 2099 (1980).

[12] G. M. Ginder and A. J. Epstein, Phys. Rev. B **41**, 10 674 (1990).

[13] S. A. Kivelson and A. J. Heeger, Phys. Rev. Lett. **55**, 308 (1985).

[14] A. J. Epstein, A. G. MacDiarmid, and J. P. Pouget, Phys. Rev. Lett. **65**, 664 (1990).

[15] K. Mizoguchi, M. Nechtschein, and J.-P. Travers, Phys. Rev. Lett **65**, 665 (1990).

[16] L. Zuppiroli, S. Paschen, and M. N. Bussac, Synth. Met. **69**, 621 (1995).

[17] A. B. Kaiser, Phys. Rev. B **40**, 2806 (1989).

[18] R. H. Baughman and L. W. Shacklette, J. Chem. Phys. **90**, 7492 (1989).

[19] J. S. Andrade Jr., Y. Shibusa, Y. Arai, and A. F. Siqueira, Synth. Met. **68**, 167 (1995).

[20] J. S. Andrade Jr., D. A. Street, Y. Shibusa, and N. Ito, Fractals (to be published).

[21] J. H. Kaufman, C. K. Baker, A. I. Nazzal, M. Flickner, O. R. Melroy, and A. Kapitulnik, Phys. Rev. Lett. **56**, 1932 (1986).

[22] J. H. Kaufman, A. I. Nazzal, M. Flickner, O. R. Melroy, and A. Kapitulnik, Phys. Rev. B **35**, 1881 (1987)

[23] S. Kivelson, Phys. Rev. Lett. **46**, 1344 (1981).

[24] A. Tachibana, S. Ishikawa, and T. Yamabe, in *New Functionality Materials, Synthetic Process and Control of Functionality Materials*, edited by T. Tsuruta, M. Doyama, and M. Seno (Elsevier, Amsterdam, 1993), Vol. C, p. 75.

[25] H. E. Stanley, J. Phys. A **10**, L211 (1977).

[26] D. Stauffer and A. Aharony, *Introduction to Percolation Theory* (Taylor & Francis, London, 1992).

[27] R. F. Angulo and E. Medina, J. Stat. Phys. **75**, 135 (1994).