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Ramified Polymerization in Dirty Medium: a New Critical Phenomenon

by

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Abstract

We simulate $d = 2$ polymer growth by allowing for a branching probability b and an impurity concentration c $(0 \leq b, c \leq 1)$. In the (b, c) space we find a critical line (locus of vanishing order parameter and diverging correlation length) which separates **infinite** from **finite** growth regimes; in particular, a **nonzero** critical value for b exists even for $c = 0$.

Key-words: Polymer; branching; steric hindrance; critical phenomena; disordered media.

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Polymerization is an extremely important phenomenon which, during the last decades, has been modeled and studied in a variety of manners. The simplest, of course, is the *random walk*. The first non trivial complexity arrives when the polymer is not allowed to cut itself, i.e. *the self-avoiding random walk* [1,2]. In this case, growth stops whenever the randomly chosen growth direction leads onto an already occupied site. More realistic models have been introduced in which the growing end tries to avoid occupied regions; in this category falls the so called *kinetic growth model* [3-5]. However, even in these models unavoidably occurs the *steric hindrance* effect [5], i.e., the growth necessarily stops because the polymerization has occured in a narrow "*cul de sac*". This effect determines the nature of polydispersion (hence of the viscoelastic properties[6]), the consequences being particularly dramatic in two dimensions, in which case the growth stops with probability one. Nevertheless, the statistical relevance of this hindrance effect has never been focused in detail, as far as we know. In the present letter, we generalize the kinetic growth model by allowing for *branching* (or *ramification*) of the polymer as well as for *impurities* (see, for instance, [7, 8] for relevant features about branching). We shall exhibit that the competition between hindrance (due to both self-avoiding growth and impurities) and branching will bring up interesting phenomena associated with a new kind of phase transition. This type of critical phenomenon should be relevant in the discussion of real ramified polymers [1,9]; the inclusion of impurities in the model can be useful in the discussion of a variety of substances (e.g., commercial polymer paints, in which the colour is obtained through addition of tinny chemically inert pigments).

Let us consider an L x L square lattice in the center of which we start, at $t = 0$, growing a polymer. The growth direction is randomly chosen among the four possible first neighbors. At $t = 1$, the growing end

avoiding manner. Successive bifurcations will of course generate a great number of growth ends. At **every** time step t, **each one** of those ends is sequentially visited (in a clock-wise-like manner following the sequence of births) and can bifurcate with probability b. For a particular growth end, bifurcation can effectively occur only if at least **two** first-neighbors are unoccupied. If only one first-neighbor is available, it necessarily grows in a linear manner. If no first-neighbor is available, that particular end stops growing. The process is continued as long as at least one end keeps growing, or until at least one end touches the contour of the L x L square lattice. The entire experiment is then repeated $N_{exp} >> 1$ times; this constitutes the ensemble over which we perform the averages (noted $< \cdots >$).

We note N the number of occupied bonds (linking first-neighboring sites), i.e., the number of connected monomers; in a real polymer, N is proportional to its total mass. If $b = 0$, then $N = t$. If $b = 1$, then $N \leq 2^t - 1$. If $0 < b < 1$, N becomes a random variable satisfying $< N > \leq [(1 + b)^t - 1] / b$; the equality holds for arbitrary t if the self-avoiding restriction is either relaxed (i.e., random walk branched polymerization) or inoperative (e.g., on a Cayley tree, or on a $d \rightarrow \infty$ d-dimensional Bravais lattice). In the thermodynamic limit ($L \rightarrow \infty$), $< N >$ can, in principle, either indefinitely grow with t (**infinite growth** regime) or stop at a certain range of t (**finite growth** regime). In practice, once the growth has stopped, a polymer will be said "infinite" if at least one of its growing ends touched the L x L contour; otherwise, it will be said "finite". We note P_∞ the fraction of polymers that are **infinite**, and $P_N(N)$ the distribution law of N, corresponding to the **finite** polymers.

In addition to the "mass", it is interesting also to measure the (linear) **size** s of the polymer. This was done as follows. Once a particular experiment stops growing (either because it touched the L x L contour or because steric hindrance stopped all the growing

ends), we determined the smallest rectangle (parallel to the L x L square) and noted s_x and s_y the lengths of its two sides. We define $s \equiv \sqrt{s_x\, s_y}$ (this choice preserves the area) and note $P_s(s)$ the distribution law associated with **finite** polymers; the mean size $\xi \equiv < s >$ plays an important role, namely that of the correlation length in standard phase transitions. The fractal dimension d_f of the branched polymer is defined through $< N > \propto \xi^{d_f}$.

To the best of our knowledge, branched polymerization in the presence of impurities has never been studied. To do this, we shall extend the model we have just introduced. More precisely, let us assume that, when growth starts, a concentration $c \in [0,1]$ of site impurities has already been randomly frozen in the lattice. The growing branched polymer must now avoid, besides itself, these obstacles . The influence of impurities on the quantities of interest (e.g., P_∞ and ξ) is followed. A particularly interesting question is to see whether impurities introduce a new universality class in the problem. Indeed, it must be noticed that, in this extended model, steric hindrance will be due to **two** different sources, namely self-avoidance and impurities, which can or cannot be overcome by branching.

Let us now present our results. We have typically worked with $300 \leq L \leq 5000$ and $200 \leq N_{exp} \leq 10^6$. Some polydispersion curves $P_N(N)$ are shown in Fig.1. We verified that, in almost all points of (b, c) space, $P_N(N)$ decays **exponentially** with N (Fig. 1.a). There is, however, a (critical) line on which the decay is a **power-law** (Fig. 1.b). We can see (in Fig. 1.b) that, for $c = 0$, the critical value for b is $b_c(0) \simeq 0.055$. On the other hand, we see, in Fig. 1.a, that $< N > \simeq 1 / 0.0097 \simeq 100$ for $b = c = 0$. Consequently, on a basis of Flory-like arguments [1], one would expect $b_c \simeq 1 / < N > \simeq 0.0097$, much lower than 0.055. The reason for this discrepancy comes from the fact that Flory's arguments rely on the hypothesis that the polymer pieces that are linked are equally sized. This is not the case in our model because steric hindrance makes most polymer

pieces shorter and shorter as time goes on, consequently the corresponding < N > is smaller than 100, hence $b_c(0)$ is expected to be greater than 0.0097, which indeed is the case. We can also check that the discrepancy with Flory's arguments increases (i.e., $< N > b_c(c)$ increases) with increasing c.

In Fig. 2 we exhibit typical results for the polymer mean size ξ as a function of (b, c) as well as of the square-lattice size L. In Fig. 3 we present the order parameter $P_\infty(b, c)$ as well the phase diagram in the (b, c) space. Finally we present, in Fig. 4, a typical example of M vs R, where M is the polymer mass contained in a square box (centered at the origin of growth) with linear size R, in a L x L lattice. This log-log representation yields the fractal dimensionality d_f. From this type of construction we extracted $d_f \simeq 2 \pm 0.004$ for the points inside the infinite growth region (e.g., $(b,c) = (0.1, 0)$). On the critical line we obtained values for d_f monotonically varying from 1.83 (at $(b, c) = (0.055, 0)$) to 1.76 (at $(b, c) = (1, 0.4072)$). This slight variation is perfectly consistent with a single universality class (characterized by $d_f \simeq 1.8$). Nevertheless, to definitely exclude a non-universal behavior along the critical line, more extensive simulations should be done. The point $(b, c) = (1, 0.4072)$ corresponds to percolation (we remind that the critical value $1 - 0.4072 = 0.5928$ is the site percolation threshold [10]). Indeed, the polymer can grow only in the subset of points which are **not** occupied by the impurities. See Fig. 5 for a typical growth at this point: note the existence of regions belonging to the infinite vacant cluster that will be never occupied. To make this point obvious we have also run **trifurcating** (instead of **bifurcating**) polymers, and have obtained **full occupancy** of the infinite vacant cluster. For this case we have consistently obtained $d_f = 1.896$, which precisely recovers the value [10] associated with (site) percolation. Since this value is definitely different from $d_f \simeq 1.76$ corresponding to bifurcations, we believe we are herein exhibiting a new universality class, clearly related to the incomplete filling of the infinite vacant cluster.

To conclude, let us remark that the model herein introduced presents a rich phenomenology which mimics real branched polymerization in clean or dirty medium. In particular, it gives us some insight on how impurities can affect technologically important properties such as polydispersion. Other studies of this new model would be welcome. For example, the triangular lattice enables the easy realization of higher-order branching (trifurcations, tetrafurcations, etc). Also, it seems intuitive that, for $d > 2$, $b_c(0)$ should be smaller than 0.055 because the steric hindrance effect would be less efficient. Finally, one could consider anisotropic or directional growth, anisotropic or directional branching, polymers growing (from the very begining) from both ends or from various seeds, or even growing on pre-existing nontrivial networks or in their intersticial regions.

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CAPTION FOR FIGURES

Fig. 1 - Polydispersion distribution law: (**a**) finite growth phase (semi-log representation, L = 1000 and $N_{exp} = 10^6$); (**b**) on the critical line, i.e., for $(b_c(c), c)$ (log-log representation, L = 1000 and $N_{exp} = 20000$).

Fig. 2 - Typical results for the b-dependence of the mean size ξ ($1000 \leq N_{exp} \leq 20000$)

Fig. 3 - (**a**) Typical results for the order parameter as a function of (b, c); we used L = 300 (the small tails at $P_\infty = 0$ disappear with increasing L). (**b**) Phase diagram; we used $300 \leq L \leq 5000$ (the full line is a guide to the eye); the inset schematically represents $P_\infty(b, c)$.

Fig. 4 - Log-log determination of d_f for the critical point $(b, c) = (1, 0.4072)$ (L = 5000 and $N_{exp} = 1000$).

Fig. 5 - Typical fragment of a polymer (shaded structure) grown in a 50 x 50 lattice with a particular random realization for the impurity sites (filled dots), for the critical point $(b, c) = (1, 0.4072)$. The regions A and B belong to the **infinite** cluster of vacancies **but** have not been occupied by the bifurcating polymer; region C is a **finite** cluster of vacancies (and is consequently, inaccessible to the growing polymer).

Fig. 1

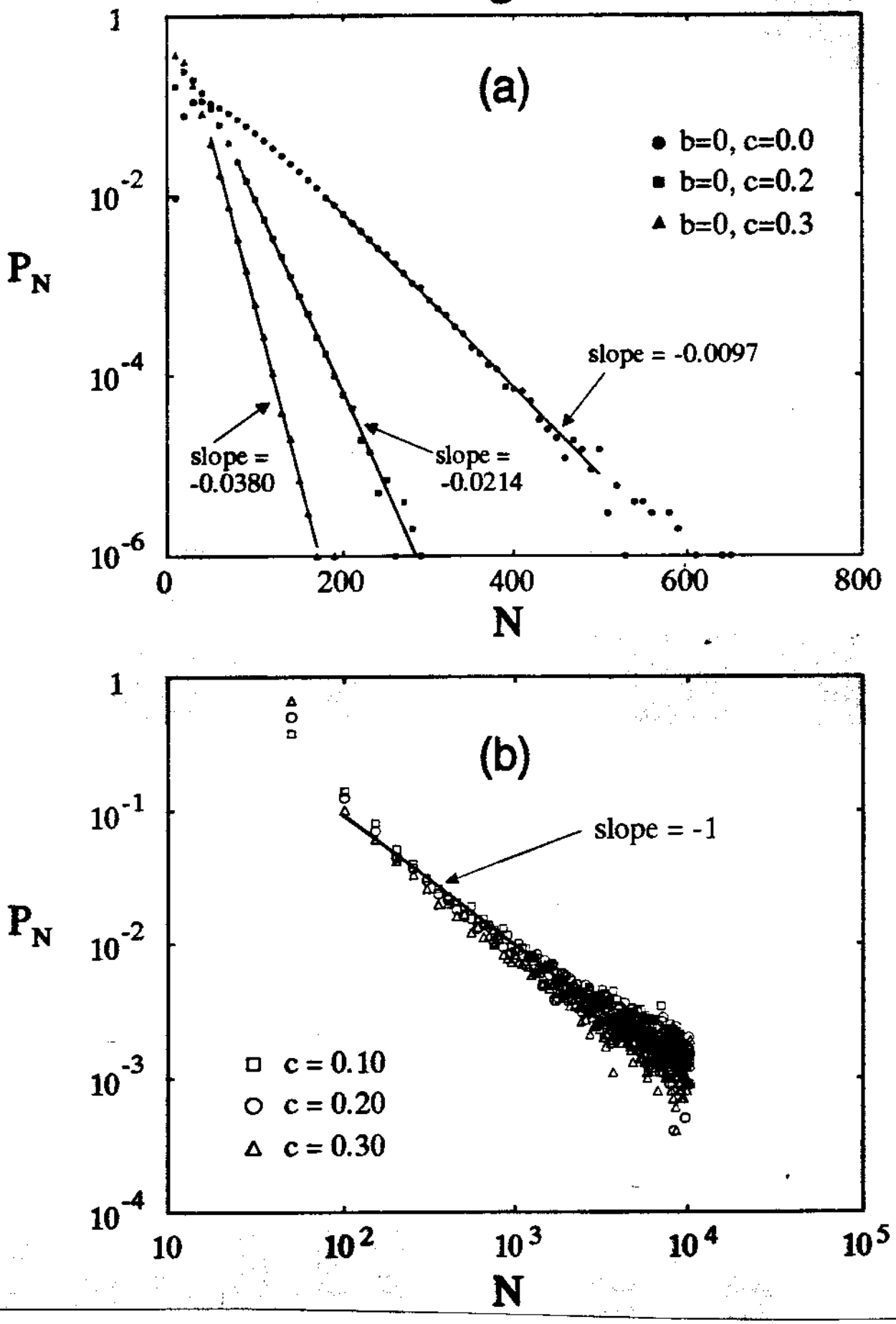

(a)
b=0, c=0.0
b=0, c=0.2
b=0, c=0.3
slope = -0.0097
slope = -0.0214
slope = -0.0380
P_N
N
1
10^-2
10^-4
10^-6
0
200
400
600
800
(b)
slope = -1
c = 0.10
c = 0.20
c = 0.30
P_N
N
1
10^-1
10^-2
10^-3
10^-4
10
10^2
10^3
10^4
10^5

Fig. 2

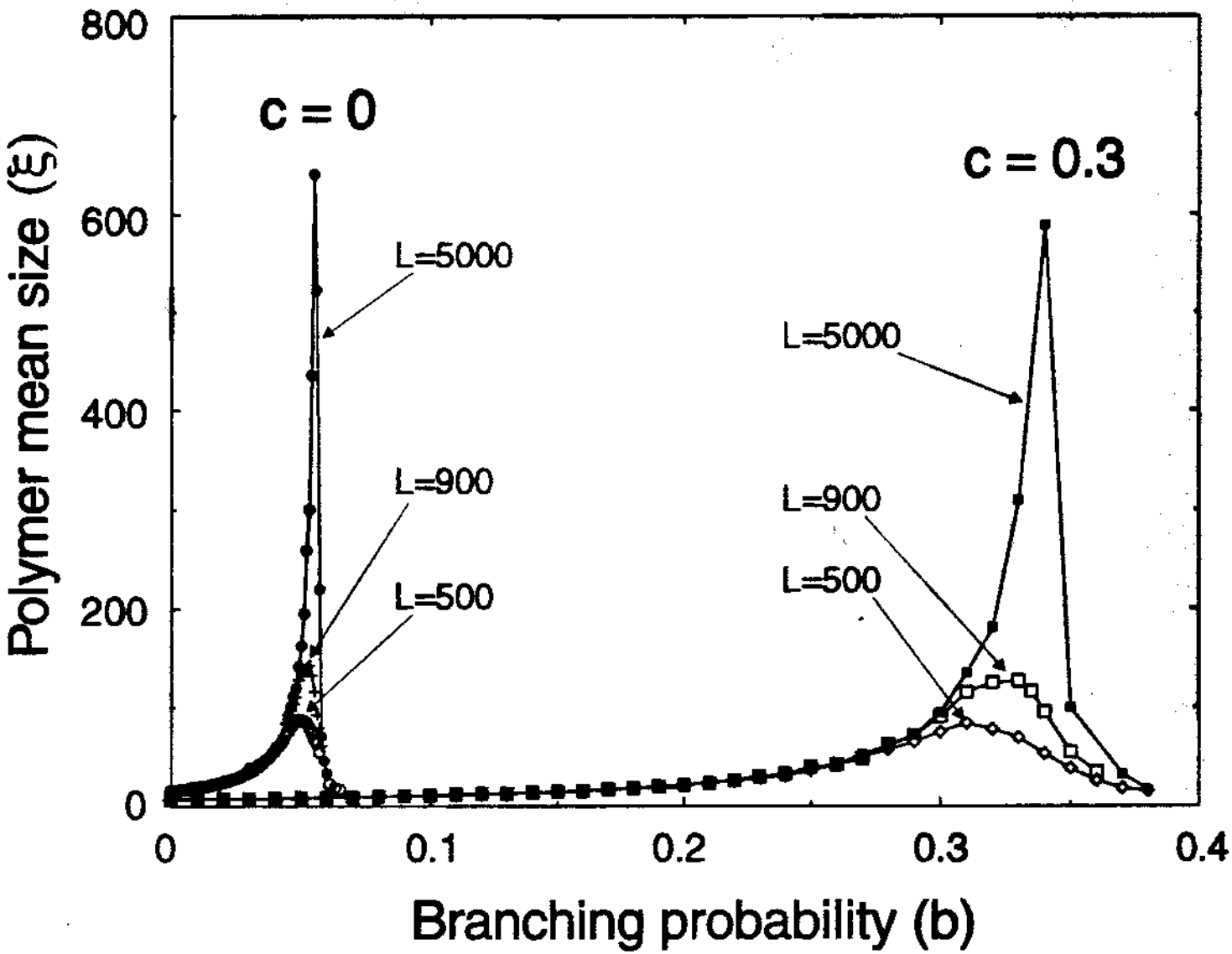
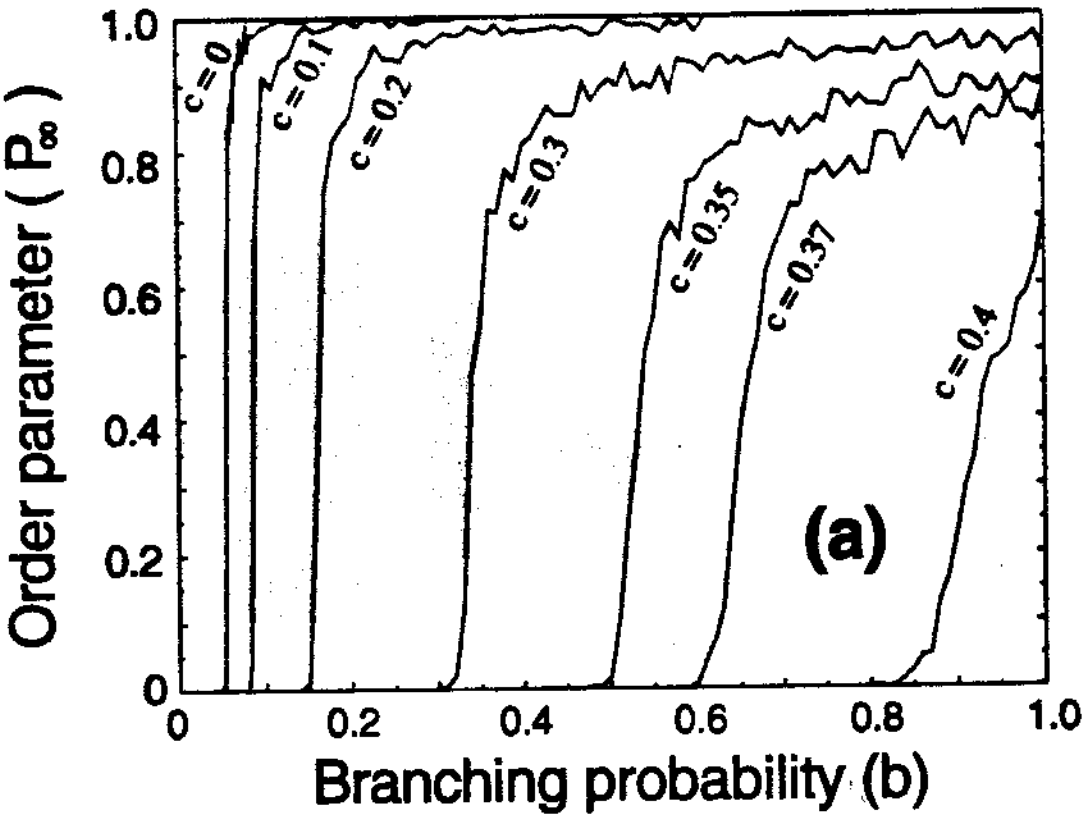

c = 0
c = 0.3
L=5000
L=900
L=500
L=5000
L=900
L=500
Polymer mean size (ξ)
Branching probability (b)
800
600
400
200
0
0
0.1
0.2
0.3
0.4

Fig. 3


Order parameter (P_∞)
Branching probability (b)
c=0
c=0.1
c=0.2
c=0.3
c=0.35
c=0.37
c=0.4
(a)

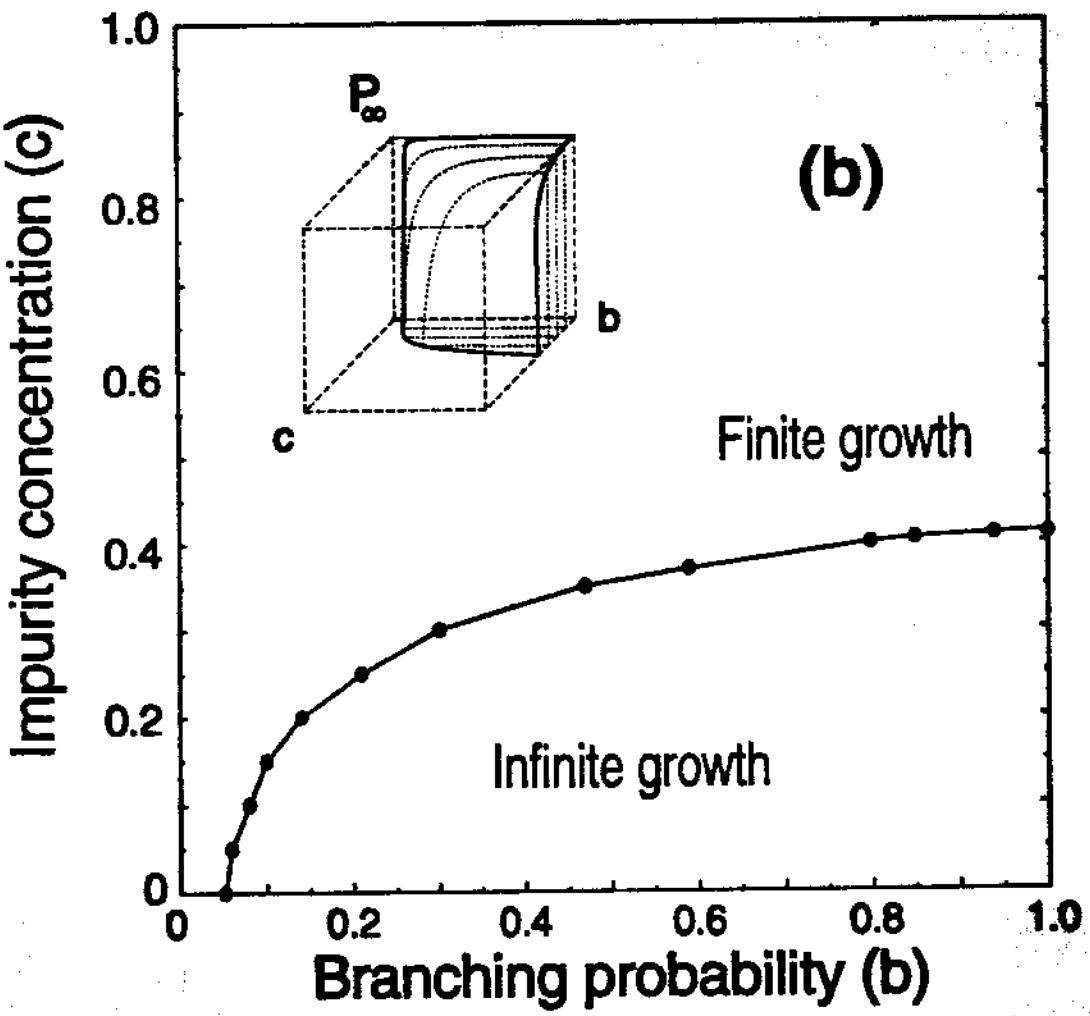

Impurity concentration (c)
Branching probability (b)
P_∞
b
c
(b)
Finite growth
Infinite growth

Fig. 4

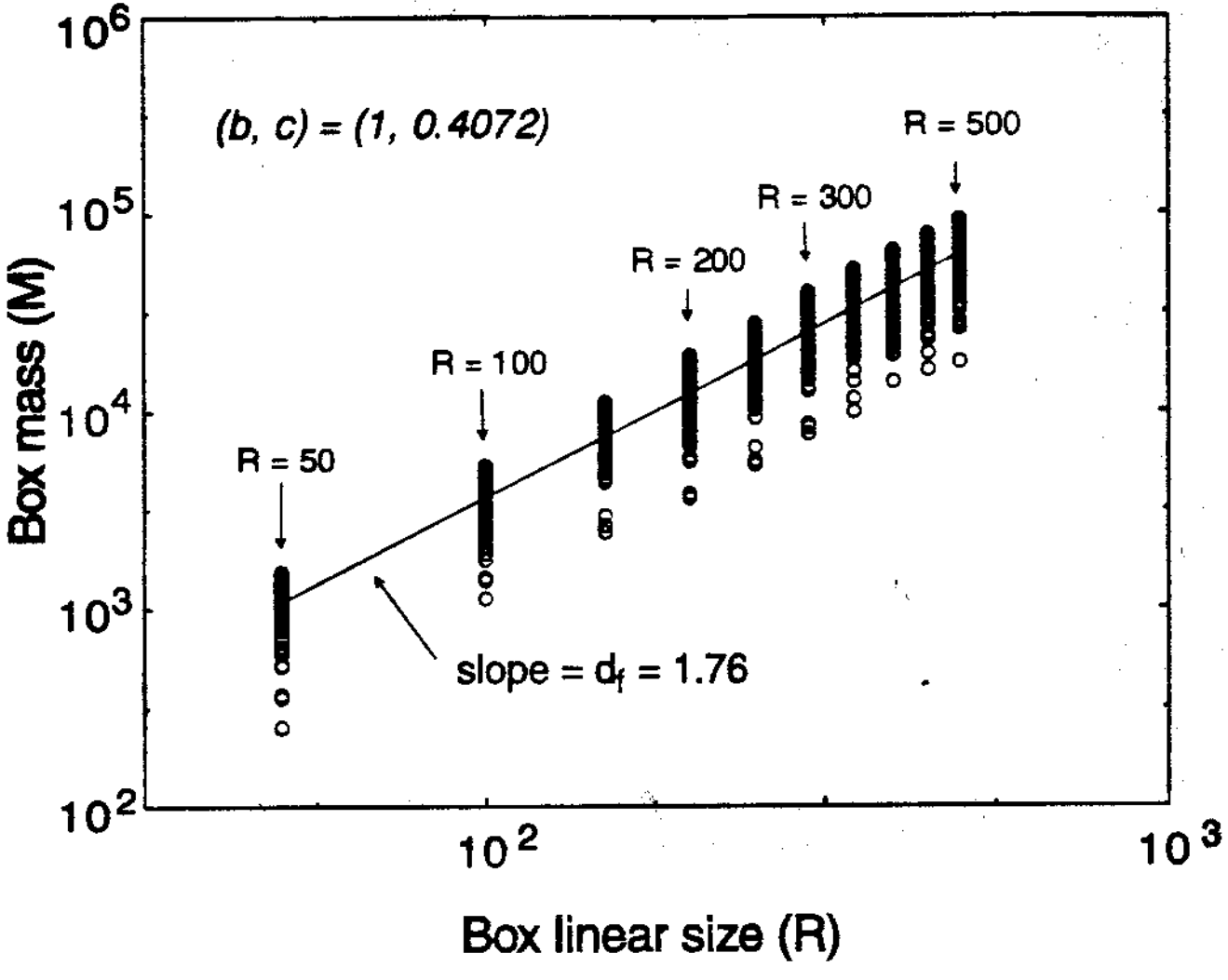
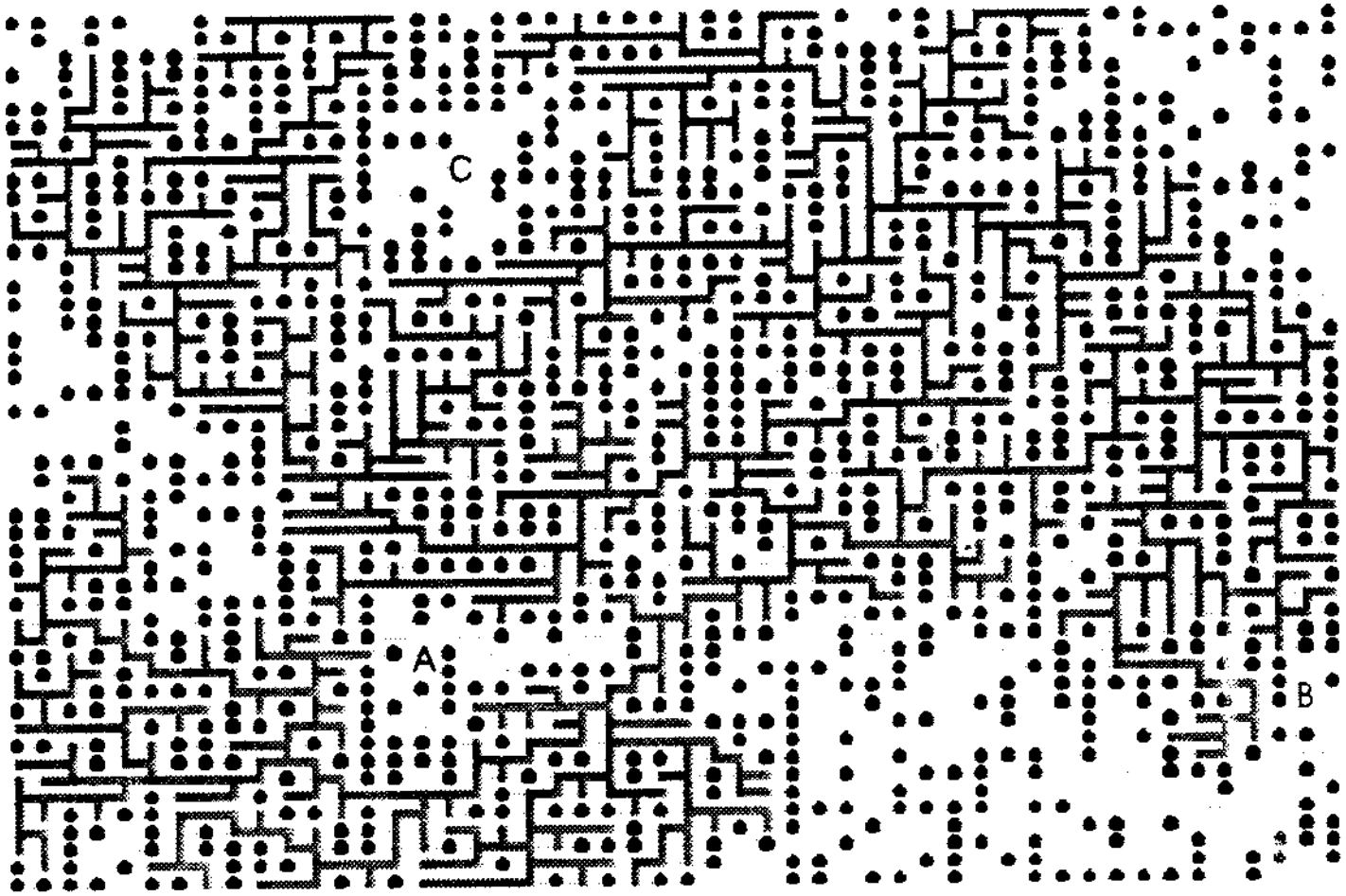

(b, c) = (1, 0.4072)
R = 50
R = 100
R = 200
R = 300
R = 500
slope = d_f = 1.76
Box mass (M)
Box linear size (R)
10^6
10^5
10^4
10^3
10^2
10^2
10^3

Fig. 5



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