Kinetics of Formation and Mean Shape of Branched Polymers

Z. Alexandrowicz
Polymer Research, Weizmann Institute of Science, Rehovot 76100, Israel
(Received 18 September 1984)

Branched polymers, the formation of which is controlled by a finite monomer supply or by termination, are studied with a Monte Carlo simulation. The radius-mass dependence of the two models (in dimension from 2 to 8) is unequal, showing that branched polymers *in toto* cannot be identified with "animals." Study of the growth of mass with time helps to interpret the result.

PACS numbers: 64.60.Fr, 61.40.Km

The shape of branched chains is described by a mean radius (R) versus mass (M) dependence,

$$R \sim M^{\nu_M}. \tag{1}$$

The critical exponent ν_M is (assumedly) determined by the dimension D alone; in view of Eq. (1) it should constitute the reciprocal fractal dimension, $\nu_M = d_f^{-1}$. Common wisdom has it that the statistical behavior of branched polymers corresponds to that of "animals," viz., to an unweighted ensemble of distinct graphs drawn from M bonds on a lattice. On this basis ν_M has been calculated[1-4] for D from 2 to $D_c = 8$ (above D_c the chain becomes ideal). It seems to me, however, that a blanket identification of branched polymers with animals is open to the following criticism. The construction of an ensemble of animals is at equilibrium with respect to the bonds' rearrangement. But such a condition is seldom, if ever, realized with actual branched polymers. The latter are generally synthesized with the help of a stepwise process: Bifunctional or polyfunctional monomers become irreversibly attached to current "growing tips" of the chain. The formation of various topological structures is kinetic; it is not clear whether these structures are weighted equally, like in the equilibrium ensemble. It seems therefore worthwhile to study the effect of definite kinetic models on the distribution of topological structures and hence on the statistics of shape. One possible kinetics is that of unlimited growth. During a given interval of time, all growing tips propagate, either linearly or with branching (corresponding respectively to the addition of a bifunctional or polyfunctional monomer), which leads to an exponential increase of M with the time. Such growth would overfill the space and exhaust the monomer supply. Hence sustained growth necessarily involves some limiting mechanism. Two simple kinetic models are studied here. In the first model S, growth is limited by a fixed rate of supply of a (homogeneously distributed) monomer. In a given interval of time *not all* but only a fixed number of tips (say one) adds a bifunctional or trifunctional monomer. This number is assumed to be randomly distributed among the current set of G tips. As a result of branching, G increases with M, forming an ever growing waiting list (with randomly ordered service!). In the absence of interactions, for $D \geq D_c$, $G \sim M$. Model S corresponds to that adopted by Redner.[5] In the second kinetic model T, growth is limited through *termination*. A growing tip may either add a bifunctional or trifunctional group, with probabilities P_1 and P_2, respectively, *or* become terminated with probability $1-(P_1+P_2)$. (The termination may be due to addition of a monofunctional monomer or to loss of a radical.) Sustained growth, for which branching precisely compensates termination,[6] requires the critical value $P_1^c + 2P_2^c = 1$. In the absence of fluctuations this value would lead to a linear growth, viz., to $G = \text{const}$. Because of fluctuation, however, G will nonetheless increase with M. In the absence of correlation between consecutive stochastic steps, G increases as $M^{1/2}$. Since $G/M \to 0$, the limitation to a fixed rate of monomer supply should be immaterial (anyhow, the algorithm described below fits that limitation). For the sake of simplicity, the formation of closed loops, through attachment of a trifunctional monomer to a pair of growing tips, is disallowed with both models.

The foregoing discussion repeatedly refers to a "time" of growth of the branched chain. This may be defined as follows. The chain starts to grow on a lattice from an origin, at $t = 0$. Nearest neighbors to the origin may join the chain; those that do constitute the shell $t = 1$. In turn, nearest neighbors to the sites constituting the shell $t = 1$ may join the chain; those that do constitute the shell $t = 2$, etc. It should be stressed that the next nearest neighbors to the origin *do not* necessarily belong to the shell $t = 2$, etc.; indeed the growing chain may bend upon itself and arrive at a next-to-nearest neighbor to the origin after an arbitrary (odd) value of t. Furthermore, in actual kinetics (like models S and T), entire iso-t shells need not be filled one after another in succession. Some branches may grow faster (in real time) than others, viz., take a larger number t of steps from origin. The time t provides a *length* variable, which enables one to study the mean radius versus length dependence, like in a linear chain,

$$R \sim t^{\nu_t}. \tag{2}$$

R and t may be measured between a point on the chain

and the origin, or, indeed, between any pair of points, one of which may be taken as the "origin." In the absence of loops the definition of a length t between a pair of points is unique (in the presence of loops an average of different pathways may be used instead). The increase of M with t may be studied as well,

$$\langle M \rangle \sim t^{\gamma_t}. \tag{3}$$

From Eqs. (1)–(3) it follows that $\nu_t = \nu_M \gamma_t$. If, as here, the growth is not in iso-t shells, one should measure γ_t^{-1} from $\langle t \rangle \sim M^{1/\gamma_t}$. The description of branched chains in terms of t, ν_t, and γ_t has been first introduced by the author, in connection with a construction of percolating clusters as "critically branched chains."[7] It has been adopted in several subsequent studies of percolation and of animals.[8] (Some of these call t the "chemical" or "topological" distance.) In what follows the comparison between models S and T relies to a large extent on the measurement of the t dependence.

Samples of branched polymers corresponding to models S and T have been constructed with the help of Monte Carlo simulation. A choice is made of a definite value of P_2 (0.25 in the experiments reported below). This fixes $P_1 = 1 - P_2$ and $P_1 = 1 - 2P_2$, with models S and T, respectively. Three lotteries are made at each step. The first picks one out of a current set of growing tips. The second, with P_1 and P_2, determines whether one or two bonds grow from that tip. With model T, termination, with probability $1 - P_1 - P_2$, constitutes a third possibility. If the choice falls on the addition of two bonds to a tip, these are added one after the other in immediate succession. A third lottery determines the bond's direction in D-dimensional space. Reversal, or an overlap of two bonds growing from one tip, is excluded from the lottery. The ends of the bonds constitute the new tips. If a new tip falls into an unoccupied lattice site, the growth continues. If, however, it falls into a site which is already occupied by a preceding chain segment, violating excluded volume, the entire construction is discarded and the process restarted from the origin. Such procedure leads to "sample attrition," whereby the number of the successful chains decreases exponentially with M. To offset this difficulty, use has been made here of the standard "sample-enrichment" technique,[9] which avoids the restarting from origin. This helps to extend the maximal value attained, $M_{\max}$, by about thrice as much. Beyond that point the sample enrichment becomes unstable: Almost all trial chains fail to attain $M_{\max}$ and the very few that do are essentially replicated many times over, which leads to poor sampling. Samples of 2000–10 000 chains have been constructed, with $M_{\max}$ ranging from 150 to 2000, as D varies from 2 to 8. Here the dependence of R and $\langle t \rangle$ upon M is studied in chains which propagate to an indefinitely large M. Hence "terminal" cases, in which the number of tips falls to zero at $M' < M_{\max}$, have been excluded from the sample. (Alternatively, the exclusion has been extended to $M' = 10M_{\max}$, without any marked consequence.) The exclusion causes an incomplete sampling of fluctuations, whence g^T need not be equal to precisely $\frac{1}{2}$, even at $D \geqslant D_c$. In order to discern an inhomogeneity of the segments' density with respect to the origin, the radius-mass exponent is measured in three different ways: (i) $\nu_{M,g}$ has been determined from the average radius of gyration of M segments; (ii) $\nu_{M,0}$ has been determined from the average square distance of M segments *from the origin;* and (iii) a fractal dimension, d_f, has been determined with the help of a recently proposed technique, with which one picks a segment at random and measures the radii $R(M')$ enclosing its $M' = 1$, 2, etc., neighbors.[10] Since the chain does not grow in iso-t shells, γ_t^{-1} has been determined from $\langle t \rangle$ vs M [cf. after Eq. (3)], while ν_t is calculated from $\nu_{M,0}/\gamma_t^{-1}$. A branching exponent g, defined through $G \sim M^g$, has been determined as well.

The results are displayed in Table I; superscripts S and T denote the two models. The ideal chain, without the excluded-volume restriction (constructed in $D = 8$), is denoted by I. The following observations can be made.

(a) *Branching.*—In the absence of an effect of excluded volume, we expect that $g^S = 1$, while g^T should be approximately equal to $\frac{1}{2}$ (approximately, because of the aforementioned incomplete sampling of fluctuations). This is borne out by the results. As D decreases, excluded volume favors more linear chains, hence g decreases.

(b) $\langle t \rangle$ *vs* M.—Conversely, γ_t^{-1} is minimum in the absence of excluded volume; as D decreases, γ_t^{-1} increases towards 1, corresponding to linear topology. Model T obeys very well the equation $\gamma_t^{-1} = 1 - g$, which has been derived recently for branched chains growing at criticality.[11] Very clearly, $1/\gamma_t^T > 1/\gamma_t^S$ at all D, which indicates that model T is always more nearly linear than model S. This disparity may be traced to the kinetics of formation. With model T there is no overproduction of tips ($G/M \to 0$). With model S, however, there is a vast overproduction, and growth proceeds through random access to a fast-expanding waiting list of tips. This results in the formation of a large number of relatively short branches, viz., a bulky, as opposed to linear, topology. In addition, because of repeated random access to the waiting list, monomers are more likely to join tips created at early stages of the kinetics. This should give rise to a relatively denser distribution of segments around the origin.

(c) *Radius mass.*—The bulky topology of model S is revealed by the values of the radius of gyration; thus

TABLE I. Monte Carlo results (in dimensions $D=2$ to 8 and for the ideal chain I) for exponents g, $1/\gamma_t$, $\nu_{M,0}$, and $\nu_{M,g}$, describing, respectively, the increase with mass M of the branching, of a mean time $\langle t \rangle$, of a mean radius with respect to the origin, and of the radius of gyration. The additional exponents $1/d_f$ and ν_t describe a fractal dimension (Ref. 10) and the radius-time dependence, respectively. Superscripts S and T denote present models S and T. Estimated error is 0.01–0.03, largest with g^T and with $\nu^S_{M,0}$, $\nu^S_{M,g}$, and $1/d_f^S$ at highest D and for I. It estimates statistical scatter and (more importantly) the variation of the exponents' value, depending on the portion of the log-log curve used for their determination. Values of the radius-mass exponent for animals (Refs. 2–4), ν_M^{ani}, are added for comparison.

D	g^S	g^T	$1/\gamma_t^S$	$1/\gamma_t^T$	$\nu^S_{M,0}$	$\nu^S_{M,g}$	$1/d_f^S$	$\nu^T_{M,0}$	$\nu^T_{M,g}$	$1/d_f^T$	ν_M^{ani}	ν_t^S	ν_t^T
2	0.83	0.25	0.57	0.74	0.44	0.57	0.57	0.62	0.62	0.63	0.64	0.76	0.84
3	0.91	0.34	0.46	0.66	0.32	0.42	0.42	0.47	0.47	0.50	0.50	0.70	0.71
4	0.96	0.38	0.38	0.63	0.24	0.32	0.34	0.40	0.40	0.43	0.42	0.62	0.63
5	0.97	0.41	0.33	0.60	0.20	0.26	0.30	0.35	0.35	0.38	0.36	0.61	0.58
6	0.98	0.44	0.30	0.58	0.17	0.23	0.27	0.31	0.31	0.35	0.32	0.56	0.54
7	0.99	0.46	0.26	0.54	0.14	0.19	0.24	0.29	0.29	0.32	0.28	0.53	0.54
8	0.99	0.46	0.24	0.54	0.13	0.17	0.23	0.28	0.28	0.30	0.25	0.54	0.51
I	1.0	0.46	0.20	0.52	0.10	0.13	0.22	0.26	0.26	0.28	0.25	0.50	0.50

$\nu^T_{M,g} > \nu^S_{M,g}$ at all D. Furthermore, with model S the values of $\nu^S_{M,0}$ are significantly lower than the corresponding $\nu^S_{M,g}$, which indicates that indeed, as M increases, the packing of segments around the origin becomes increasingly dense. At highest D and for I, the convergence with M is extremely slow and the very small values found for $\nu^S_{M,0}$ and $\nu^S_{M,g}$ possibly should be even smaller; indeed their ultimate convergence towards 0 cannot be ruled out. With model T, $\nu^T_{M,0} \simeq \nu^T_{M,g}$, which indicates the absence of an appreciable inhomogeneity at the origin.

(d) *A fractal dimension* (cf. Ref. 10).—d_f is measured over M' neighbors to a segment, without reference to the actual stepwise growth of M. This effaces the singular role of the origin in model S. Thus the values of $1/d_f^S$ are comparable with $\nu^S_{M,g}$, or higher than that. (d_f^{-1} listed in Table I have been measured with respect to segments picked at random; d_f^{-1} measured with respect to the origin, though expected to be smaller, turn out to be equal to within experimental accuracy.) The values of $1/d_f^T$ for model T are approximately equal, as they should be, to $\nu^T_{M,0}$ and $\nu^T_{M,g}$. (Still $1/d_f^T$ seem to be slightly but consistently higher.[12]) Altogether, the radius-mass exponents for model T are similar (possibly a little smaller at low D) to ν_M^{ani} calculated for lattice animals.[2-4]

(e) *Radius time.*—The values of ν_t support the expectation that for I, $\nu_t = 0.5$, like in a linear chain. The convergence of ν_t and of the other results towards their limiting values at I suggests that $D_c \simeq 8$ for model T and higher than that for model S. As D decreases ν_t for both models increase equally and only at $D=2$, $\nu_t^T > \nu_t^S$.

(f) *Other results.*—Redner's[5] ν_m for model S agree approximately with the present $1/d_f^S$, both having been measured in a manner which obliterates the singularity of the origin. γ_t for animals at $D=2$, 3, and 4 (measured as percolating clusters at $p \ll p_c$)[8e] agree very well with the present results for model T.

In conclusion: First, it appears that the kinetics of formation indeed affects the distribution of topological structures and consequently the mean shape of branched polymers (cf. a similar recent finding for gelation[13]). The applicability of animal exponents should be therefore limited to certain branched polymers only, notably to those not synthesized in an irreversibly stepwise fasion and also *perhaps* to those that are so synthesized but, like model T, grow without overproduction of tips. Second, models S and T represent two extremes, of a great overproduction of equally accessible tips and of a complete compensation of growth by termination. Actual kinetics presumably exhibits intermediate types of behavior. Finally, the present interpretation of simulation results relies on the measurement of g, of γ_t, and of the singularity of the origin, in addition to a mere determination of ν_M; "time" emerges as an important linear descriptor of the topology of branched chains.

[1]T. C. Lubenski and J. Issacson, Phys. Rev. Lett. **41**, 829 (1978), and Phys. Rev. A **20**, 2130 (1979).

[2]G. Parisi and N. Sourlas, Phys. Rev. Lett. **46**, 871 (1981).

[3]D. Dhar, Phys. Rev. Lett. **51**, 853 (1983).

[4]B. Derrida and L. De Seze, J. Phys. (Paris) **43**, 475 (1982).

[5]S. Redner, J. Phys. A **12**, L239 (1979).

[6]P. Flory, *Principles of Polymer Chemistry* (Cornell Univ., Ithaca, 1953), Chap. IX, Sect. 1.

[7]Z. Alxandrowicz, Phys. Lett. **80A**, 284 (1980).

[8a]R. Pike and H. E. Stanley, J. Phys. A **14**, L169 (1981).

[8b]J. Chalupa and F. G. Krausz, Phys. Lett. **102A**, 115 (1984).

[8c]S. Havlin and R. Nossal, J. Phys. A **17**, L427 (1984).

[8d]P. Grassberger, Math. Biosci. **63**, 157 (1983).

[8e]S. Havlin, Z. V. Djordjevic, I. Majid, H. E. Stanley, and G. H. Weiss, Phys. Rev. Lett. **53**, 178 (1984).

[9]F. T. Wall and J. J. Erpenback, J. Chem. Phys. **30**, 634 (1959).

[10]Y. Termonia and Z. Alexandrowicz, Phys. Rev. Lett. **14**, 1265 (1983).

[11]Z. Alexandrowicz, Phys. Lett. (to be published).

[12]Possibly $1/d_f$ is larger than ν_M because, with the former, $R(M')$ is measured without reference to the stepwise growth of M and hence gives a differently weighted radius-mass dependence. Another possibility is that in most cases (especially at high D and for I) the radius-mass exponents at low mass are overestimated because of correction to scaling. However, when M' becomes of the order of M itself, d_f is overestimated once again (Ref. 10).

[13]J. Herrmann, D. P. Landau, and D. Stauffer, Phys. Rev. Lett. **49**, 412 (1982).